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**VOLATILIZATION OF MERCURY FROM SOILS IN RESPONSE
TO SIMULATED PRECIPITATION**

A Thesis

Presented to

The Faculty of Graduate Studies

of

The University of Guelph

by

XIAOXI SONG

In partial fulfillment of requirements

for the degree of

Master of Science

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ABSTRACT

VOLATILIZATION OF MERCURY FROM SOILS IN RESPONSE TO SIMULATED PRECIPITATION

Xiaoxi Song
University of Guelph, 2004

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Dr. Bill Van Heyst

Increases in mercury volatilization from naturally enriched soils due to precipitation events have been observed in the field, leading to the need for further research on the exact mechanisms responsible for the increase in the observed fluxes.

In this research, the effects of precipitation on fluxes were simulated in a controlled laboratory experiment using a dynamic flux chamber system coupled with a Tekran[®] 2537A Mercury Vapour Analyzer. The experimental results indicate a sharp and rapid spike in the mercury flux, during and immediately following the precipitation event, which is a result of the physical displacement of the Hg-containing interstitial soil air by infiltrating rain water. The enhanced mercury emission flux after a precipitation event is dependent on both the quantity of infiltrating rain and the soil moisture content prior to the rain event, pointing to the mobilization of Hg (II) from soil particle to soil solution phase as the probable controlling process. The critical soil moisture range for surface soil moisture before a precipitation event is between 13% and 15%, above which enhanced mercury emissions do not occur.

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TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION	1
CHAPTER 2. BACKGROUND LITERATURE	3
2.1 MERCURY IN THE ENVIRONMENT	3
2.1.1 BIOGEOCHEMICAL CYCLE OF MERCURY	3
2.1.2 SOURCES OF ATMOSPHERIC MERCURY	7
2.1.2.1 ANTHROPOGENIC SOURCES AND NATURAL SOURCES.....	7
2.1.2.2 MERCURY EMISSIONS FROM THE SOILS	10
2.2 METHODOLOGY OF MERCURY EMISSION MEASUREMENT	13
2.2.1 MICROMETEOROLOGICAL APPROACHES (MM)	13
2.2.2 DYNAMIC FLUX CHAMBER METHODS (DFC).....	16
2.2.3 COMPARISONS BETWEEN MM AND DFC METHODS	17
2.2.4 TOTAL GASEOUS MERCURY ANALYZERS	19
2.3 CHAMBER DESIGNS AND THEIR INFLUENCES ON MERCURY FLUX.....	21
2.3.1 CHAMBER FLUSHING RATE	21
2.3.2 CHAMBER DIMENSION	24
2.3.3 FLUX CHAMBER MATERIALS	24
2.3.4 AIR TRANSPORT CONDITION INSIDE THE CHAMBER	25
2.4 FACTORS INFLUENCING THE MERCURY VOLATILIZATION RATE FROM SOILS	27
2.4.1 SOIL CHARACTERISTICS	28
2.4.1.1 SOIL TEXTURES.....	28
2.4.1.2 SOIL MERCURY CONCENTRATION	29
2.4.1.3 SOIL ACIDITY	31
2.4.1.4 SOIL MOISTURE.....	32
2.4.2 METEOROLOGICAL CONDITIONS	35
2.4.2.1 AIR AND SOIL TEMPERATURES.....	35
2.4.2.2 RELATIVE HUMIDITY.....	36
2.4.2.3 WIND SPEED	37
2.4.3 OTHER INFLUENCING FACTORS	38
2.4.3.1 SOLAR RADIATION.....	38
2.4.3.2 PRECIPITATION EFFECT	39
2.5 RESEARCH OBJECTIVES	41
CHAPTER 3. EXPERIMENTAL APPARATUS AND METHODOLOGY	43
3.1 EXPERIMENTAL APPARATUS	43
3.1.1 LABORATORY DYNAMIC FLUX CHAMBER SYSTEM	45
3.1.1.1 DYNAMIC FLUX CHAMBER.....	46
3.1.1.2 INTERIOR PRECIPITATION GENERATOR.....	48
3.1.1.3 SOIL SUBSTRATE	50
3.1.1.4 PUMPS AND SAMPLING PATHS	52
3.1.2 PARAMETER MEASURING SYSTEM.....	55
3.1.3 DATA ACQUISITION SYSTEM	57
3.2 RESEARCH METHODOLOGY	58
3.2.1 SYSTEM VALIDATION	59
3.2.1.1 AIR-TRANSPORT CONDITION TEST.....	59
3.2.1.2 CHAMBER AND PRECIPITATION GENERATOR SEAL TEST	60
3.2.1.3 DFC SYSTEM SEAL TEST	61
3.2.1.4 RAIN RATE TEST	61
3.2.1.5 SOIL PROPERTY TESTS.....	62

3.2.2 EXPERIMENTAL METHODOLOGY	66
CHAPTER 4. EXPERIMENTAL RESULTS AND DATA ANALYSIS.....	73
4.1 RAW DATA PROCESSING.....	73
4.2 RAW EXPERIMENTAL RESULTS.....	74
4.2.1 DISCOVERY OF THE LIGHT EFFECT.....	75
4.2.2 SINGLE RAIN EVENTS	76
4.2.3 DOUBLE RAIN EVENT	80
4.2.4 TRIPLE RAIN EVENTS APPLIED AT DIFFERENT SOIL MOISTURES	81
4.2.4.1 TRIPLE RAIN EVENT WITH 1-DAY AND 5-DAY DELAY	81
4.2.4.2 DISCOVERY FROM A 3L RAIN EVENT	82
4.2.4.3 TRIPLE RAIN EVENT WITH 8-DAY AND 5-DAY DELAY	84
4.3 WATER VAPOUR FLUX AND Hg FLUX	96
4.3.1 SINGLE RAIN EVENTS	96
4.3.2 DOUBLE RAIN EVENT	97
4.3.3 TRIPLE RAIN EVENTS AT DIFFERENT SOIL MOISTURE.....	97
4.4 SOIL MOISTURE AND Hg FLUX	105
4.4.1 SINGLE RAIN EVENTS	105
4.4.2 DOUBLE RAIN EVENT	105
4.4.3 TRIPLE RAIN EVENTS AT DIFFERENT SOIL MOISTURES	106
4.4.4 TRANSITIONAL SOIL MOISTURE AND PRECIPITATION ENHANCEMENT FACTOR	111
CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS.....	115
5.1 CONCLUSIONS.....	115
5.2 RECOMMENDATIONS	116
REFERENCES	118
APPENDIX A: INSTRUMENT CALIBRATION	123
A.1 SYSTEM CLEANING AND CHAMBER BLANK TEST	123
A.2 CALIBRATION OF THE TEKRA [®] N MERCURY ANALYZER.....	124
A.3 CALIBRATION OF TDR SOIL MOISTURE PROBES	125
APPENDIX B: SAMPLE CALCULATIONS.....	128
B.1 SATURATED HYDRAULIC CONDUCTIVITY	128
B.2 WATER VAPOUR FLUX, ESTIMATION BASED ON RAIN VOLUME	128
B.3 NORMALIZATION OF MERCURY FLUX, WATER VAPOUR FLUX, RH.....	131
B.3.1 MERCURY FLUX	132
B.3.2 RELATIVE HUMIDITY AND WATER VAPOUR FLUX	133
B.4 CALCULATION CHECK FOR PHYSICAL DISPLACEMENT	134
APPENDIX C: ERROR ANALYSIS	139
C.1 DIRECT MEASUREMENT ERRORS.....	139
C.1.1 RELATIVE HUMIDITY AND AIR TEMPERATURE	139
C.1.2 SOIL TEMPERATURE.....	140
C.1.3 SOIL MOISTURE	140
C.1.4 FLUSHING FLOW RATE	140
C.1.5 Hg CONCENTRATION	140
C.2 PROPAGATION OF ERRORS INTO OTHER RESULTS.....	141
C.2.1 Hg FLUX	141
C.2.2 WATER VAPOUR FLUX.....	142
APPENDIX D. SOURCE CODES.....	144
D.1 MAIN PROGRAM FOR NI-DAQ CARD	144
D.2 INTERRUPT SERVICE ROUTINE PROGRAM FOR NI-DAQ CARD	151
D.3 DATA COLLECTION AND AVERAGING PROGRAM FOR CR23X DATALOGGER	177

LIST OF FIGURES

FIGURE 2-1: SCHEMATIC DIAGRAM OF THE BIOGEOCHEMICAL CYCLE OF MERCURY	6
FIGURE 2-2: PIE CHART OF CANADIAN MERCURY EMISSIONS IN 2000	8
FIGURE 2-3: A GENERAL CONCEPTUAL SCHEME OF MERCURY EMISSION PROCESSES IN SOIL..	12
FIGURE 2-4: SCHEMATIC OF A DYNAMIC FLUX CHAMBER (DFC)	16
FIGURE 2-5: MERCURY FLUX CHANGES IN RESPONSE OF FLUSHING FLOW RATE OF THE CHAMBER OVER NATURALLY ENRICH SOILS	22
FIGURE 2-6: TGM Hg FLUXES FROM BACKGROUND AND MINERALIZED GEOLOGY SITES ACROSS CANADA VERSUS TGM CONCENTRATION	30
FIGURE 2-7: SOIL MATRIX WITH DIFFERENT SOIL MOISTURE	33
FIGURE 3-1: DIAGRAM OF THE EXPERIMENTAL APPARATUS	44
FIGURE 3-2: DIAGRAM OF THE DYNAMIC FLUX CHAMBER SYSTEM	45
FIGURE 3-3: DIAGRAM OF THE LABORATORY DYNAMIC FLUX CHAMBER	46
FIGURE 3-4: PICTURE OF THE DYNAMIC FLUX CHAMBER	47
FIGURE 3-5: THE CHAMBER TRANSITION ZONE.....	48
FIGURE 3-6: THE DIAGRAM OF THE PRECIPITATION GENERATOR	49
FIGURE 3-7: THE PICTURE OF THE PRECIPITATION GENERATOR	50
FIGURE 3-8: PICTURE OF THE SOIL SUBSTRATE	52
FIGURE 3-9: SCHEME OF VALVE SWITCHING BETWEEN SAMPLING PERIODS	54
FIGURE 3-10: DIAGRAM OF THE ELECTRICAL CONNECTIONS OF THE DATA ACQUISITION SYSTEM AND THE PARAMETER MEASURING SYSTEM	58
FIGURE 3-11: THE SMOKE TEST FOR THE AIR-TRANSPORT CONDITIONS IN THE CHAMBER	60
FIGURE 3-12: SOIL PERMEAMETER USED IN SATURATED HYDRAULIC CONDUCTIVITY AND FIELD CAPACITY TESTS	63
FIGURE 3-13: EXPERIMENTAL SET-UP FOR SOIL SATURATION PROCESS	64
FIGURE 3-14: EXPERIMENTAL SET-UP FOR FALLING-HEAD TEST	65
FIGURE 3-15: CHRONOLOGY OF EXPERIMENTAL PROCEDURES	72
FIGURE 4-1Z: LIGHT EFFECTS ON Hg EMISSION FLUX IN THE FIRST TRIAL OF SINGLE RAIN EVENT	89
FIGURE 4-2: Hg FLUX AND OTHER PARAMETERS FOR THE FIRST SINGLE RAIN EVENT, NORMALIZED TO 20°C	90
FIGURE 4-3: Hg FLUX AND OTHER PARAMETERS FOR THE SECOND SINGLE RAIN EVENT, NORMALIZED TO 20°C	91
FIGURE 4-4: Hg FLUX AND OTHER PARAMETERS FOR THE DOUBLE RAIN EVENT, NORMALIZED TO 20°C	92
FIGURE 4-5: Hg FLUX AND OTHER PARAMETERS FOR THE TRIPLE RAIN EVENT WITH A 1-DAY AND 5-DAY INTERVAL, NORMALIZED TO 20°C	93
FIGURE 4-6: Hg FLUX AND OTHER PARAMETERS FOR THE 3L RAIN EVENT, NORMALIZED TO 20°C	94
FIGURE 4-7: Hg FLUX AND OTHER PARAMETERS FOR THE TRIPLE RAIN EVENT WITH 8-DAY AND 5-DAY INTERVAL, NORMALIZED TO 20°C	95
FIGURE 4-8: Hg FLUXES AND WATER VAPOUR FLUX FOR THE FIRST SINGLE RAIN EVENT, NORMALIZED TO 20°C	99
FIGURE 4-9: Hg FLUXES AND WATER VAPOUR FLUX FOR THE SECOND SINGLE RAIN EVENT, NORMALIZED TO 20°C	99

FIGURE 4-10: CORRELATION BETWEEN MERCURY FLUX AND WATER VAPOUR FLUX FOR THE FIRST SINGLE RAIN EVENT	100
FIGURE 4-11: CORRELATION BETWEEN MERCURY FLUX AND WATER VAPOUR FLUX FOR THE SECOND SINGLE RAIN EVENT	100
FIGURE 4-12: HG FLUX AND WATER VAPOUR FLUX FOR THE DOUBLE RAIN EVENT, NORMALIZED TO 20°C.....	101
FIGURE 4-13: CORRELATION BETWEEN THE HG FLUX AND WATER VAPOUR FLUX FOR THE DOUBLE RAIN EVENT	101
FIGURE 4-14: HG FLUX AND WATER VAPOUR FLUX FOR THE TRIPLE RAIN EVENT WITH A 1-DAY AND 5-DAY DELAY	102
FIGURE 4-15: CORRELATION BETWEEN HG FLUX AND WATER VAPOUR FLUX FOR THE TRIPLE RAIN EVENT WITH A 1-DAY AND 5-DAY DELAY	102
FIGURE 4-16: HG FLUX AND WATER VAPOUR FLUX FOR THE TRIPLE RAIN EVENT WITH AN 8-DAY AND 5-DAY DELAY	103
FIGURE 4-17: CORRELATION BETWEEN HG FLUX AND WATER VAPOUR FLUX FOR THE TRIPLE RAIN EVENT WITH AN 8-DAY AND 5-DAY DELAY	103
FIGURE 4-18: HG FLUX AND WATER VAPOUR FLUX FOR THE 3L RAIN EVENT.....	104
FIGURE 4-19: CORRELATION BETWEEN HG FLUX AND WATER VAPOUR FLUX FOR THE 3L RAIN EVENT.....	104
FIGURE 4-20: CORRELATION BETWEEN HG FLUXES AND SURFACE SOIL MOISTURE FOR THE SINGLE RAIN EVENTS.....	107
FIGURE 4-21: CORRELATION BETWEEN THE HG FLUX AND SURFACE SOIL MOISTURE FOR THE DOUBLE RAIN EVENT	108
FIGURE 4-22: CORRELATION BETWEEN HG FLUX AND SURFACE SOIL MOISTURE FOR THE TRIPLE RAIN EVENT WITH A 1-DAY AND 5-DAY DELAY	109
FIGURE 4-23: CORRELATION BETWEEN HG FLUX AND SURFACE SOIL MOISTURE FOR THE TRIPLE RAIN EVENT WITH AN 8-DAY AND 5-DAY DELAY	110
FIGURE 4-24: SURFACE SOIL MOISTURE AND HG FLUX BEFORE AND AFTER THE FIRST SINGLE RAIN EVENT.....	112
FIGURE 4-25: PRECIPITATION ENHANCEMENT FACTOR VERSUS SURFACE SOIL MOISTURE BEFORE A RAIN EVENT FOR 6 EXPERIMENTS.....	114
FIGURE A-1: CALIBRATION CURVE OF THE TEKRA [®] MERCURY ANALYZER.....	125
FIGURE A-2: CALIBRATION CURVE OF THE TDR SOIL MOISTURE PROBES	126
FIGURE B-1: ORIGINAL AND NORMALIZED HG FLUX AND OTHER PARAMETERS FOR THE FIRST SINGLE RAIN EVENT	135

LIST OF TABLES

TABLE 3-1: SOIL PROPERTIES OF THE CLYDE FORKS SOIL	51
TABLE 3-2: SPECIFICATIONS FOR TEKRA [®] 2537A	56
TABLE 4-1: SUMMARY OF SOIL MOISTURES AND MERCURY FLUXES BEFORE AND AFTER A PRECIPITATION EVENT IN THE SIX EXPERIMENTS	113
TABLE B-1: RESULTS OF THE FALLING HEAD EXPERIMENT	128
TABLE B-2: A SET OF RAW DATA FROM THE FIRST SINGLE RAIN EVENT	131
TABLE B-3: HG FLUX IN THE PEAK FROM THE FIRST SINGLE RAIN EVENT	136
TABLE B-4: PARTITION COEFFICIENTS AND ENTHALPIES OF PHASE CHANGE FOR MERCURY SPECIES	137

NOMENCLATURE

a	cross-sectional area of buret or other standpipe in falling head method, m^2
a'	cross-sectional area of soil sample in falling head method, m^2
A	footprint area of the flux chamber, m^2
A'	pre-exponential factor in Arrhenius equation, $\text{ng}\cdot\text{m}^{-2}\text{s}^{-1}$
C_{inlet}, C_{outlet}	mercury concentration at inlet and outlet of the chamber, $\text{ng}\cdot\text{m}^{-3}$
C_S, C_L, C_G	mercury concentration in soil particle, soil solution and soil air phases, $\text{g/kg}, \text{g/m}^3, \text{g/m}^3$
CF	unit correction factor
D	absolute error
d	zero plane displacement height, m
e, e_s	water vapour pressure and saturation water vapour pressure, Pa
E_a	activation energy in Arrhenius equation, cal/mol
E_r	relative error
f	precipitation enhancement factor, $\text{ng}\cdot\text{m}^{-2}\text{s}^{-1}$
f_{OC}	fraction of organic carbon in the soil, m^3/m^3
FC_s	mercury flux from the chamber substrate, $\text{ng}\cdot\text{m}^{-2}\text{s}^{-1}$
F_{Hg}	mercury flux, $\text{ng}\cdot\text{m}^{-2}\text{s}^{-1}$
F_{wv}	water vapour flux, $\text{g}\cdot\text{m}^{-2}\text{s}^{-1}$
h_1, h_2	hydraulic head across sample at the beginning and end of test, m
$[Hg]$	mercury concentration, $\text{ng}\cdot\text{m}^{-3}$
$\Delta [Hg]$	mercury concentration difference between two sampling locations, $\text{ng}\cdot\text{m}^{-3}$

ΔH_v	enthalpy of phase change, kJ/mol
k	saturated hydraulic conductivity, m/s
K_{Hg}	eddy diffusivity of Hg, m ² /s
K_D	adsorbed-liquid partition coefficient, m ³ /kg
K_H	Henry's law constant
K_{OC}	organic carbon distribution coefficient, m ³ /kg
L	soil sample length, m
M	mass, kg
MW	molecular weight, g/mol
Q	flow rate of air-stream, L/min
R	gas constant, J·mol ⁻¹ ·K ⁻¹
t	elapsed time of falling head test, s
T	temperature, K
u_*	friction velocity, m/s
$\bar{u}()$	mean wind velocity, m/s
u', w'	instantaneous fluctuation velocity components in the mean streamwise and vertical direction, m/s
z, z_u, z_l	vertical height, and heights of the upper and lower sampling locations in flux gradient method, m

GREEK SYMBOLS

$\rho_{wv,out}, \rho_{wv,in}$	water vapour density at the inlet and outlet of the chamber, kg/m ³
$\bar{\rho}_b$	soil bulk density, kg/m ³
ρ_p	soil particle density, kg/m ³
$\psi_{h,u}, \psi_{h,l}$	adiabatic correction functions for the upper and lower sampling

	locations
ψ_m	empirical correction function for momentum
ϕ	porosity, m ³ /m ³

ACRONYMS

CVAFS	cold-vapour atomic fluorescence spectrophotometry
DFC	dynamic flux chamber
ER	eddy correlation
MBR	modified Bowen ratio
MM	micrometeorological method
NI-DAQ	National Instrument data acquisition card
RE	rain event
RH	relative humidity
SC	source mercury concentration
SM	soil moisture
SToRMS	Nevada Study and Tests of the Release of Mercury from Soil
TDR	time domain reflectometry
TGM	total gaseous mercury

CHAPTER 1. INTRODUCTION

Mercury, considered as a global pollutant (Environment Canada, 2004a), has been studied by researchers for over twenty-five years (Hogg, 1978). Mercury enriched soils are a major source to the global atmospheric mercury budget. Important influencing environmental factors of mercury emissions from soils, such as temperature, solar radiation, and wind speed have been quantified in order to estimate the contribution of mercury enriched soils to the global atmospheric mercury budget (Carpi and Lindberg, 1998; Poissant and Casimir, 1998). In recent field studies, increases in mercury volatilization from soils in response to precipitation events have been observed (Lindberg *et al.*, 1999 and Poissant *et al.*, 1999), pointing to precipitation as one of the important factors affecting mercury soil emissions and requiring further quantification. The major suspected controlling processes are surface gaseous mercury displacement by infiltrating rain water and aqueous divalent mercury redox reactions (Zhang and Lindberg, 1999). However, there is no concrete evidence that these are the controlling processes due to the convolution of the field flux data with other environmental parameters.

To further investigate the precipitation effects on mercury emissions, a laboratory dynamic flux chamber (DFC) system coupled with a precipitation generator and a gaseous mercury analyzer (Tekran[®] 2537A) was designed. Using this DFC system, a series of laboratory experiments under controlled conditions were conducted to isolate and study the precipitation effects on mercury emissions from soils to better understand the underlying mechanisms. Experimental data was analyzed to explain the underlying mechanisms in terms of the hypothesized controlling processes of (1) the displacement of Hg-containing interstitial soil air by infiltrating water, and (2)

enhanced aqueous redox reactions due to the increase in soil moisture from precipitation. Several conclusions in terms of underlying mechanisms have been drawn based on the observation and analysis of experimental data, followed by some recommendations on future work.

The following four chapters make up the main body of the thesis. Chapter 2 presents a review of the current scope and theory of mercury emissions which forms the basis of this research as well as the objectives of this present work. Chapter 3 gives a detailed introduction of experimental set-up and methodology. Chapter 4 reports the experimental results and the analysis of these results to explain the hypothesized controlling mechanisms. Chapter 5 summarizes the main conclusions and contributions of this research as well as the recommendations for future work.

CHAPTER 2. BACKGROUND LITERATURE

2.1 Mercury in the environment

Mercury, due to its toxic and highly bio-accumulative properties, is listed as a “toxic substance” under the Canadian Environmental Protection Act (Environment Canada, 2004a). As the only heavy metal in a liquid state at the room temperature, mercury can easily volatilize into the air and be carried throughout the atmosphere. Mercury can be converted to methylmercury, known as a highly toxic and bio-accumulative substance that affects both human and wildlife. The bioaccumulation of methylmercury in natural ecosystems has become a great environmental concern (Environment Canada, 2004a). Mercury can be emitted from both natural and anthropogenic sources, and migrate between various media in the environment. A detailed description about mercury biogeochemical cycle and major sources is presented in this section.

2.1.1 Biogeochemical cycle of mercury

Mercury is a naturally occurring element and has 3 possible oxidation states: Hg (0), Hg (I), and Hg (II). Hg (I) is unstable and can be easily transformed into either Hg (0) or Hg (II). Therefore in the atmospheric environment, mercury exists predominantly in the elemental form (oxidation state 0) and in the divalent or reactive form (+2 oxidation state) (Environment Canada, 2004a).

A conceptual biogeochemical cycling model of environmental mercury is illustrated in Figure 2-1 (Gustin and Lindberg, 2000). In the environment, mercury can migrate

between atmospheric, biologic, lithologic (i.e. geologically enriched sources, such as soils and volcanoes), anthropogenic and aquatic components. In order to assess the global mercury budget and describe the biogeochemical cycle of mercury, the mercury sources and the fluxes between different compartments in the environment need to be quantified and characterized on a global scale.

Mercury is the only metal existing in liquid form under ambient temperature and pressure (Schroeder and Munthe, 1998). With a relatively high vapour pressure, elemental mercury can easily vaporize from soil and water surfaces into the atmosphere. In the atmosphere, approximately 98% of mercury is in the elemental form of Hg (0) (Environment Canada, 2004a). Relatively inert to chemical attack by other air constituents and contaminants, elemental mercury vapour has an atmospheric residence time between 0.5 and 2 years (Slemr *et al.*, 1985) and is considered as “a global pollutant”. Therefore, the atmosphere is the primary pathway of elemental mercury transport between different environmental compartments (Gustin and Lindberg, 2000). Another form of mercury in the atmosphere is Hg (II) in compounds such as HgCl₂. Also mercury can be bound to atmospheric particles as particulate mercury Hg (p) predominantly in the form of HgO, which is the oxidation product of Hg (0), O₃, NO₃ and other oxidants (Schroeder and Munthe, 1998). Removal from atmosphere occurs primarily through wet scavenging and wet deposition of Hg (II) in precipitation or “dry” deposition of Hg (p) or Hg (0) (Poissant and Pilote, 1998).

As previously mentioned, mercury can be scavenged from the atmosphere into aquatic systems by wet or dry deposition. In aquatic systems, elemental mercury and divalent mercury can be dietabilized by microbes and transform into methyl and

dimethylmercury, which is highly toxic, mobile and bioaccumulative (Mason and Fitzgerald, 1991). The major inter-conversion process is $\text{Hg}(0) \leftrightarrow \text{Hg}(\text{II})_{\text{ing}} \leftrightarrow \text{MeHg}$ (Sang and Lourie, 1997), where $\text{Hg}(\text{II})_{\text{ing}}$ stands for inorganic mercury forms such as HgS and HgO .

As a matter of fact, in most chemical forms, mercury is a neurotoxin causing damage to the brain and central nervous system, while methylmercury is the most toxic form among all the chemical forms (Environment Canada, 2004). The bioaccumulation of methylmercury in natural ecosystems is an environmental concern due to its increasing level of harm on higher organisms in the food chain. Methylmercury is able to migrate through membranes and bio-accumulate in living tissue (Environment Canada, 2004b). Elevated methylmercury levels in the human body can cause health problems and even death with consumption of significant quantities of fish or other mercury-contaminated food. The most infamous case of mercury poisoning happened in Minimata, Japan, in 1952 (Bunce, 1994). Methylmercury has been listed on United States Environmental Protection Agency (USEPA)'s Integrated Risk Information System (IRIS) as "Class C" or "Possible Human Carcinogen" substance (Schroeder and Munthe, 1998). Besides migration of mercury from water to the food chain, the main pathway of mercury removal from water is the evaporation to the atmosphere in the form of $\text{Hg}(0)$ and MeHg (Gustin and Lindberg, 2000).

Soils are a main sink receiving mercury from the atmosphere and water through different pathways, such as dry and wet depositions. In the meantime, soils are a major natural mercury source in the lithologic component (Gustin and Lindberg *et al.*,

Figure 2-1: Schematic diagram of the biogeochemical cycle of mercury (adjusted from Gustin and Lindberg, 2000)

Note: Hg^0 and Hg^{2+} refer to $\text{Hg} (0)$ and $\text{Hg} (\text{II})$ in the text, respectively.

2000). Mercury can also be bound to organic materials forming methylmercury and dimethylmercury. Through chemical and biological processes, these compounds can be transformed into elemental mercury, which will eventually be emitted into the atmosphere. However, the underlying mechanisms controlling the formation of elemental mercury are poorly understood (Lindberg *et al.*, 1995). A more detailed description of mercury soil emission is given in Section 2.1.2.2.

2.1.2 Sources of atmospheric mercury

As shown in Figure 2-1, mercury emissions can originate from anthropogenic sources, such as industries, which are considered as point sources (Gustin and Lindberg, 2000). Also, area sources, especially natural sources of mercury are not negligible. Due to the current limited understanding of the underlying mechanisms (Lindberg *et al.*, 1995) and the potential of re-emission of previously deposited anthropogenic mercury, mercury emissions from natural sources require more investigation and research. An introduction of mercury emissions from anthropogenic and natural sources is presented in this section, followed by a more detailed description of mercury soil emissions.

2.1.2.1 Anthropogenic sources and natural sources

Anthropogenic sources refer to a variety of industrial and combustion processes contributing to global mercury releases. A pie chart of Canadian mercury emissions from

anthropogenic sources in 2000 is shown in Figure 2-2 (Environment Canada, 2004a). The largest sources in Canada include electricity generation and metal smelting, which are equally the largest sources of mercury into the atmosphere, each accounting for 25% of Canadian emissions (Environment Canada, 2004a; Sang and Lourie, 1997; Pacyna and Pacyna, 2002). The "other" category includes emissions from residential wood and fuel combustion, commercial fuel combustion, marine transportation, crematoriums, fluorescent tube breakage, dental amalgams, sewage sludge application to land, and landfill gas (Environment Canada, 2004a).

Canadian Atmospheric Mercury Emissions in 2000

Figure 2-2: Pie chart of Canadian mercury emissions in 2000 (adapted from Environment Canada, 2004a)

Mercury from anthropogenic sources is mainly in forms of Hg (0), Hg (p) and in organic forms of Hg (II), such as methylmercury (Environment Canada, 2004a). Organic forms of mercury are short-lived compared to inorganic mercury such as HgS, but highly toxic to human body. Long-time exposure to mercury can damage the human central nervous

system and cause quarrelsome behaviour, headache and depression, and muscle tremors (Bunce, 1994).

Since industrialization, the amount of mercury found in the environment has increased by a factor of 2 to 4, predominately due to human activities (Environment Canada, 2004b; Sang and Lourie, 1997). Canadian anthropogenic mercury emissions for the year 1990 were estimated to be 38.8 tonnes (Pacyna and Pacyna, 2002). To eliminate anthropogenic sources, reduction strategies on mercury were enforced by the Canadian government. The chloralkali industry was the largest anthropogenic source of mercury until the 1980s in Canada (Environment Canada, 2004a). Now the number of chloralkali factories has reduced from 15 in 1970's to 1 in 2000 (Environment Canada, 2004a). Between 1990 and 1995, Canadian anthropogenic mercury emissions dropped to 11 tonnes primarily as a result of process improvements in the base metal mining industry (Environment Canada, 2004b). From 1995 to 2000, Canadian anthropogenic mercury emissions dropped to a total of just over 8 tonnes (Environment Canada, 2004a). In a word, Canada's continued implementation of mercury management options has made considerable progress on mercury emissions from anthropogenic sources.

Natural sources of mercury emissions include volcanoes, soils, under sea vents and mercury-rich geological zones, as well as fresh waters and oceans, plants, forest fires, sea salt spray and meteoric dust (Kemp, 2001). Mercury from natural sources has a long lifetime greater than 10^4 years, and is released mainly in the form of Hg (0) vapour (Gustin and Lindberg, 2000). Also, mercury adsorbed on particulate matter/aerosols

may originate from some types of natural sources or processes (e.g. volcanoes, soil erosion) (Environment Canada, 2004ab). Although Hg (0) is thought to be the main form of mercury vapour, dimethylmercury (DMM), and volatile inorganic Hg compounds (e.g. volatile oxides, sulphides and halides) can also vaporize into the atmosphere (Schroeder and Munthe, 1998).

Different from anthropogenic sources, natural sources often cover large areas, and some are heterogeneous in mercury distribution and are often located in rugged and remote terrains (Gustin and Lindberg, 2000). Therefore, natural sources are usually more difficult to constrain than anthropogenic ones. What's more, mercury originated from anthropogenic sources can deposit on various surfaces, and be re-emitted back to the atmosphere, which makes the mercury global budget more difficult to model (Dastoor and Larocque, 2004). Therefore, differentiating between natural and recycled anthropogenic emissions is one challenge for researchers attempting to describe and quantify the global mercury budget.

2.1.2.2 Mercury emissions from the soils

As shown in Figure 2-1, the biogeochemical cycle of mercury involves all the compartments of the Earth system, including water bodies, soils, atmosphere, etc. Among all the natural sources, soil evasion is the dominant pathway for mercury volatilization into the atmosphere (Schlüter *et al.*, 1995).

Soils are highly complex natural systems where mercury emissions potentially being controlled by different physical, chemical and biological processes in the soil compartment. In comparison with biological processes, physical and chemical processes have faster and more significant effects on mercury volatilization (Allard and Arsenie, 1991; Zhang and Lindberg, 1999). These physical and chemical processes mainly involve (1) physical distribution of different mercury species between different soil phases, and (2) production of gaseous mercury through redox reactions in soils (Zhang and Lindberg, 1999).

As shown in Figure 2-3, soils exhibit three phases, including soil air, soil solution and soil solid particles, which behave as a dynamic and heterogeneous system. Both mercury physical distribution and redox reactions happen in all the three soil phases, making mercury emission a multiphase process.

The dominant species of mercury are Hg (0) and Hg (II). Among three different soil phases, Hg (0) vapour predominantly exists in soil air, the level of which is an important parameter in mercury emission process. Hg (0) also can be adsorbed on or desorbed from soil solid particles surfaces (McKay *et al.*, 1995). In soil solutions, elemental mercury can be dissolved by natural surface waters (Amyot *et al.*, 1997). As for Hg (II) from natural sources, it predominantly exists in inorganic forms of HgS, HgO or HgCl₂, and can also be dissolved in soil solutions or adsorbed by inorganic components on soil particles. Hg (II) is also partly adsorbed by organic compounds in soil particle phase, existing in organic form of methylmercury or dimethylmercury. The adsorption and

desorption of Hg (II) has a crucial impact on mercury emissions (Zhang and Lindberg, 1999).

Figure 2-3: A general conceptual scheme of mercury emission processes in soil (adapted from Zhang and Lindberg, 2000)

The contribution of mercury emission from naturally enriched soil is hard to estimate because the underlying mechanism of controlling processes and influencing factors of mercury soil emission are not well understood (Schlüter, 2000). Additionally, the recent in-situ measurements of mercury emissions from naturally enriched substrate are one to five orders of magnitude higher than values applied in global models (Zhang and Lindberg, 1999). Since the importance of naturally enriched landscapes are more recognized than in the past, more investigations have been conducted in regards to these aspects to reassess our knowledge of biogeochemical cycle of mercury.

2.2 Methodology of mercury emission measurement

In order to estimate emissions from naturally enriched soil substrates, the methods applied to measure mercury fluxes need to be firstly assessed. Based on reliable methodologies, the factors controlling emissions need to be characterized and a database of emissions from representative areas needs to be developed. Eventually the emission models can be developed on local, regional and global scales (Gustin and Lindberg, 2000). The mercury flux measurement generally refers to the measurement of total gaseous mercury, which is mainly in the form of Hg (0). The methods commonly applied to assess the in-situ flux of total gaseous mercury to the atmosphere are dynamic flux chambers (DFC) and micrometeorological (MM) methods. In addition, laboratory gas exchange chambers, which are the laboratory applications of DFCs, have been used to develop a minimum estimation of the mercury fluxes and characterize influencing factors under controlled conditions (Gustin and Lindberg, 2000; Lindberg, *et al.*, 1999). Basic principles of micrometeorological approaches and DFC methods are introduced in this section, followed by some comparisons of these two methods. The gaseous mercury flux measurement technology applied in both methods is also briefly introduced at the end of this section.

2.2.1 Micrometeorological approaches (MM)

Micrometeorological methods used to measure mercury emissions from soils are still

relatively new technologies (Kim and Lindberg, 1995; Poissant *et al.*, 1999). Micrometeorological approaches (MM) are usually applied to quantify emissions of trace gases from environmental surfaces. The common MM methods include the eddy correlation (ER) method, the flux gradient method and the modified Bowen ratio (MBR) method. A brief introduction of these methods is presented in this section.

The eddy correlation method is one of the most desirable methods with a direct measurement of the flux. However, a fast response measurement ($>1\text{Hz}$, Hensen *et al.*, 1997) is required for this method. Unfortunately no fast response measurement is currently available for Hg and thus other methods need to be employed.

The flux gradient method is based on Monin-Obukhov similarity theory and requires the simultaneous measurement of the mercury concentration gradient between 2 heights. The flux is related to the gradient by:

$$F_{Hg} = -K_{Hg} \frac{\partial[Hg]}{\partial z} \quad (2.1)$$

where F_{Hg} is the flux of mercury, K_{Hg} is the eddy diffusivity, $[Hg]$ is the mercury concentration, z is the vertical height, and $\frac{\partial[Hg]}{\partial z}$ is the mercury concentration gradient (Edwards *et al.*, 2001). Typically, the equation is recast as:

$$F_{Hg} = \frac{-\kappa u_* \Delta[Hg]}{\ln\left(\frac{z_u - d}{z_l - d}\right) - \psi_{h,u} + \psi_{h,l}} \quad (2.2)$$

where κ is the von Karman's constant (0.4), u_* is the friction velocity, $\Delta[Hg]$ is the

mercury concentration difference between two sampling locations. z_u and z_l are the heights of the upper and lower sampling locations. d is the zero plane displacement height, and $\psi_{h,u}$ and $\psi_{h,l}$ are the adiabatic correction functions for the upper and lower sampling locations, respectively. Except for the friction velocity, all the remaining parameters can be either measured directly or determined indirectly by empirical relationships. The friction velocity can be estimated by log law:

$$\bar{u}(z) = \frac{u_*}{\kappa} \ln \left(\frac{z - d}{z_0} - \psi_m \right) \quad (2.3)$$

where $\bar{u}(z)$ is the mean wind velocity at the height of z , z_0 is the surface roughness, and ψ_m is an empirical correction function for momentum. Also the friction velocity can be determined by using sonic anemometers from the relationship:

$$u_* = \sqrt{-\overline{u'w'}} \quad (2.4)$$

where u' and w' are the instantaneous fluctuation velocity components in the mean streamwise direction and the vertical direction. However, sonic anemometers do not work well during precipitation and dew events.

The Modified Bowen ratio technique is based on the assumption that all passive scalars are transferred analogously in the atmospheric surface layer. Thus the turbulent transfer coefficients are equivalent for the different passive scalars. Since gaseous mercury cannot be measured over the desired time scale, the fluxes of heat, water vapour, and/or CO₂ are measured instead to infer the turbulent transfer coefficient for gaseous mercury.

2.2.2 Dynamic flux chamber methods (DFC)

DFCs are a popular method to measure air-surface exchange rates of total gaseous mercury and to isolate and characterize environmental and geochemical processes controlling emissions (Kemp, 2001). Compared to various principles of different MM methods, the DFC methods are all based on one simple principle. In a dynamic flux chamber method, an open-bottom chamber is placed on the soil substrate, and an air-stream is pulled through the chamber. The total gaseous mercury (TGM) concentrations in the inlet stream and outlet stream are measured, and the difference between them represents the total gaseous mercury flux from the substrate inside the chamber. Figure 2-4 presents a schematic diagram of a DFC.

Figure 2-4: Schematic of a dynamic flux chamber (DFC)

The mass balance equation in the DFC system is given as:

$$FC_s = (C_{outlet} - C_{inlet}) \times Q / A \quad (2.5)$$

where FC_s is mercury flux from the DFC, C_{inlet} is the concentration in the inlet stream, C_{outlet} is the concentration in the outlet stream, Q is the flow rate of air-stream, and A is the footprint area of the chamber.

The dynamic flux chamber methods can be used for in-situ measurement, which is called field flux chambers. In addition, dynamic flux chambers have also been designed as

laboratory flushing chambers. Laboratory flushing chambers are used to estimate a minimum mercury flux and isolate influencing parameters under controlled conditions for characterization (Gustin and Lindberg, 2000; Lindberg, *et al.*, 1999; Gustin, *et al.*, 1999).

Currently, no specific method for measuring mercury fluxes has been endorsed by the mercury research community (Gustin and Lindberg, 2000). Without a standardized design, the flux chambers have been designed in various shapes, sizes, and materials (Edwards, *et al.*, 2001; Gao, *et al.*, 1997; Gillis and Miller, 2000). A detailed introduction of different chamber designs and their influences on mercury flux are given in Section 2.3.

2.2.3 Comparisons between MM and DFC methods

Both MM methods and DFC methods have been applied in field studies. The Nevada Study and Tests of the Release of Mercury from Soil (SToRMS) campaign was carried out to intercompare terrestrial mercury fluxes using different methodologies and to assess the limitation and applicability of each of these methods of in-situ mercury flux measurement (Poissant, *et al.*, 1999). Experimental results showed that the mercury fluxes measured by MM methods were typically three times greater than those measured by DFC methods. Although this discrepancy between the values measured by MM and DFC methods was probably due to the site heterogeneity, the result still possibly indicated that the enclosed module of the DFC obstructed mercury emission from the soil and led to smaller mercury fluxes. For example, the secure seal of the chamber isolates

the emitting surfaces from most environmental parameter changes that influence mercury soil emissions. As a result, the mass transfer of the elemental mercury across the air-soil surface interface was affected and controlled by the chamber (Kemp, 2001). On the other hand, MM experimental set-up does not disturb the soil surface, and thus the results were deemed to be more representative of the real fluxes at this point. Additionally, MM methods are more flexible for heterogeneous sites with much bigger footprints up to 200m of fetch to represent large areas (Kemp, 2001). Compared to the footprints of MM methods, the footprint of DFC is limited to the area covered by the chamber. For heterogeneous sites, more measurements have to be taken by moving the chamber to different representative locations to obtain the same spatial averaging as obtained from MM methods (Kemp, 2001).

Despite these advantages, MM methods are a relatively new technology, the theories of which are more complicated than the DFC methods and vary from one single method to another. The need for measuring more parameters in MM methods necessitates more instruments than in DFC methods. One representative example of MM methods is the flux gradient method. In addition to instruments needed in both MM and DFC methods (e.g. mercury analyzer), the flux gradient method requires additional instruments to quantify atmospheric turbulence. Sonic and/or cup anemometers are needed to measure fluctuations in wind speed and direction to determine the turbulent transfer coefficient K , and hygrometers are also required to measure latent heat fluxes (Kemp, 2001). The data analysis of MM methods is complex and considerable programming expertise is needed.

In terms of instrumentation and the theory of methodology, the DFC methods are much simpler and easier than MM methods.

One of the unique advantages of DFC methods is that the flux chamber can be applied in laboratory studies, while MM methods are specifically designed for field measurements. In the application of laboratory dynamic flux chamber methods, chamber conditions can be regulated to mimic environmental conditions in the field as closely as possible by improving sample handling and chamber experimental designs (Gustin *et al.*, 1999). Therefore, the DFC methods are more promising for isolating influencing parameters and understanding specific effects under controlled operating conditions. Since DFC methods are based on an enclosed module, the mercury fluxes measured by DFC methods are more or less affected by the covered chamber. Studies of the chamber design effects on mercury flux measurements and corresponding improved chamber designs have been done in the recent decade (Gao *et al.*, 1997; Gillis and Miller, 2000; Kemp, 2001). The chamber structure, operating condition related factors and chamber design improvements done in the past are discussed in Section 2.3.

2.2.4 Total gaseous mercury analyzers

In both MM and DFC methods, a method to measure the total gaseous mercury (TGM) concentrations is needed. In the late 1970's, the TGM fluxes were measured by a two-stage gold trap analysis technique (Fitzgerald and Gill, 1979) using cold-vapour atomic fluorescence spectrophotometry (CVAFS), which had a low detection limit of TGM on

an order of subnanogram with good accuracy. This technique had been successfully applied on a laboratory basis and was promising for field measurement.

Using this state-of-the-science technique, Tekran Inc. invented an automated dual channel, single amalgamation, CVAFS analyzer with high time resolution (Tekran[®] 2537A gaseous mercury vapour analyzer, Tekran Inc., Toronto, Canada) (Tekran, 1996).

The Tekran[®] mercury analyzer has two cartridges with a programmable sampling period (usually 5 minutes) for each cartridge. When one cartridge is adsorbing mercury during one sampling period, the other is thermally desorbing mercury and analyzing total gaseous mercury. Once desorbed in the cartridge, mercury is carried by the carrier gas and analyzed using CVAFS. Highly pure Argon gas is selected as carrier gas, which is non-detectable in the mercury vapour (Tekran, 1996). The detection limit is on the order of $0.3 \text{ ngHg}\cdot\text{m}^{-3}$ (Tekran, 1996), which offers a high resolution in mercury flux measurement in DFC methods. After one sampling period the functions of the two cartridges are switched, allowing for the continuous sampling of airstreams. With a 5-minute sampling resolution for each cartridge, one sampling event using two cartridges can be finished in 10 minutes. This allows a nearly real-time measurement of mercury fluxes suitable for the tracking of fairly rapid changes in mercury fluxes in response to influencing factors. In addition, the auto-calibration system and compatible PC serial port contribute to accurate measurement and data transmission.

2.3 Chamber designs and their influences on mercury flux

As illustrated by the results from the study of Nevada STORMS campaign, mercury volatilization can be affected by the chamber design and operating conditions (Gao et al., 1997; Gillis and Miller, 2000; Kemp, 2001). A good flux chamber design depends on a proper chamber structure with good transport conditions, which allow chamber conditions to closely match real field conditions. Factors of DFC design, which influence the flux of mercury, are explained in the following section.

2.3.1 Chamber flushing rate

The chamber flushing rate is a significant chamber-operating parameter affecting mercury emission fluxes. In the STORMS experiments, chamber flushing rate effects on the mercury fluxes measured by DFCs were studied by doing parallel experiments using three different field flux chambers (Poissant et al., 1999). Hg flux increases in response to environmental changes were not observed when a low chamber flushing rate (5 L/min) was applied, while the mercury fluxes increased quickly in response to environmental variations when a higher chamber flushing rate (15 L/min) was supplied (Wallschläger et al., 1999). Low flow rates might suppress the natural air-surface exchange process by building up mercury concentration inside the chamber. On the other hand, very high flow rates might create a negative pressure in the chamber resulting in artificially high mercury fluxes. Therefore, more investigations are required to find the optimal flow rate that does not suppress or enhance mercury emission fluxes.

Figure 2-5: Mercury flux changes in response of flushing flow rate of the chamber over naturally enrich soils (reproduced from Lindberg et al., 2002)

In light of this need, more experiments on chamber flushing rate effects were done by Lindberg *et al.* (2002) under controlled conditions by using flux chambers. Different types of flux chambers with different materials and dimensions and different soil samples from naturally enriched sites, mercury contaminated sites and background soils were applied in the experiments. As shown in Figure 2-5, the general trend is an increase in the mercury flux with increasing flushing rates. At lower flushing flow rates, the mercury flux increased faster in response to the increasing flow rates. When the flow rate was greater than 25 L/min, the rate of change in mercury flux became smaller compared to the mercury flux increase at lower flushing flow rates. The mercury flux became stable at higher flushing flow rates (>40L/min), which indicated a maximum mercury flux at significantly high flow rates.

Shown in Figure 2-5, mercury concentrations inside the chamber (C_i) at different flow rates were always higher than the mercury concentration at the outlet of the chamber ($C_o=3.8\text{ng/m}^3$), while the discrepancy between the concentration at the outlet and inside the chamber decreased with the increasing flow rates. These results indicate that the accumulation of mercury inside the chamber was due to the high chamber resistance caused by low air exchange rates generated by low chamber flow rates and the enclosed module of the DFCs.

The flushing flow rate effect is inherent with DFC methods, but independent of the chamber designs and soil properties (Lindberg *et al.*, 2002). Under very low flushing rates, DFCs behave similarly to a closed flux chamber with the mercury emission controlled by molecular diffusion instead of convective conduction (Lindberg *et al.*, 2002). With increasing flushing flow rates, however, mass transfer induced by flushing flow can enhance Hg air/soil exchange, which is similar to the process occurring naturally with typical mid-day turbulence levels. As a result convective mass transfer also occurs and is controlled by flushing flow rates. On one hand, the application of flux chambers demands laminar flow inside the chamber, which does not have any vertical component. On the other hand, turbulence is assumed to be the major driving forces of air-surface exchange of gases (Wallschläger *et al.*, 1999). In DFC measurement, a high flushing rate will ensure that DFC reaches steady state quickly, so an optimum flushing rate is very important for DFC method. The optimum flushing rate should be the rate that can provide an internal aerodynamic condition most representing the average external environmental conditions while minimizing the extra suppression of mercury emission

potential from the enclosed module of DFCs. The proper flushing rate range proposed for a common size DFC is $\sim 15\text{-}40\text{ lmin}^{-1}$ (Zhang *et al.*, 2002). However, most of the DFCs used for mercury flux studies did not have a flushing rate in this range (Poissant *et al.*, 1999).

2.3.2 Chamber Dimension

In order to simulate gaseous mercury emissions from soils measured by DFC, various DFC model development and corresponding experiments have been carried out (Zhang, *et al.*, 2002, Lindberg *et al.*, 2002). Based on the simulation and experimental results, some conclusions of chamber dimension effects were drawn. A smaller chamber dimension has the same effect as a high flushing rate, expediting the interior transport in reaching a steady state, by increasing the turnovers of air in the chamber (Lindberg *et al.*, 2002). However, in the field studies, a small footprint of flux chamber might require more on site experiments at different locations to ensure site homogeneity in the field study (Kemp, 2001). Therefore an optimum dimension needs to be determined to get a good balance among the various factors.

2.3.3 Flux chamber materials

Flux chamber material is very important for mercury measurement in DFC methods. Materials with low tendency to adsorb mercury are preferred for accurate measurement of mercury fluxes. Transparent materials are preferred over opaque ones, such as stainless

steel, since solar radiation can penetrate the chamber especially in studies on solar radiation effect on mercury emissions (Kemp, 2001). The typical materials used to make chamber covers include Plexiglas (polymethyl methacrylate), quartz glass, and polycarbonate plastic. Kemp (2001) developed a series of field flux chambers to measure in-situ mercury emissions at the University of Guelph. The chambers applied included a Plexiglas Teflon[®]-lined flux chamber, quartz glass and polycarbonate plastic flux chamber (Kemp, 2001). Plexiglas Teflon[®]-lined flux chambers are widely used in many Hg flux studies, due to the reasonable price of Plexiglas and the low mercury absorption of Teflon[®] material. Quartz glass shows premium transparency among many kinds of materials, but is extremely expensive. The polycarbonate plastic flux chamber is the most cost effective chamber type with the lowest price and is also being applied by some research groups for mercury flux studies (Kemp, 2001).

2.3.4 Air transport condition inside the chamber

As concluded from the flushing flow rate and chamber dimension effects on mercury fluxes, an optimum air-transport chamber condition will minimize the negative effects inherent in the DFC methods. In most of the DFC designs, the flux chamber is a one-inlet and one-outlet rectangular box skirted into the soil, which may produce stagnant regions and heterogeneity of airflow inside the chamber. To mimic the real field condition as closely as possible, stagnant regions inside the chamber should be avoided to prevent chamber short circuit.

In order to minimize stagnant areas, Gillis and Miller (2000) developed a flux chamber with some inlet structure changes. Different from the typical one-inlet and one-outlet chamber design, this flux chamber had nine inlet holes, 2.5 cm in diameter, evenly spread on the inlet wall of the chamber. The airflow through the inlet holes was split evenly into smaller airstreams, thus a negative pressure within the chamber was prevented (Gillis and Miller, 2000).

In Kemp (2001)'s DFC design, two Teflon[®] fans were installed on the top of the chamber. In doing so, the air was well mixed inside the chamber and channelling was avoided as well (Kemp, 2001). However, the mass transfer promoted by the fans created a vertical velocity component in the chamber air, which might disturb the processes controlling the air/soil exchange of mercury.

Another chamber design to eliminate the stagnant areas and ensure homogeneity of airflow is to add flow baffles at the inlet and outlet of the chamber (Gao et al., 1997). The chamber consisted of an inlet transition zone, a square main body and an outlet transition zone. Six equally spaced air channels were set both in the inlet and outlet zones. The airflow was conducted and spread uniformly across the soil surface to produce a simple horizontal and uniform air stream through the flux chamber. Compared to the nine-hole-inlet design, the airflow baffles work better in creating homogeneity in the air stream. However, in the real field, mercury evaporation is partially driven by the turbulent mass transfer above the soil surface (Wallschläger et al., 1999). The principle of this baffle chamber design was based on a laminar flow mechanism (Gao et al., 1997).

Therefore, further studies on new chamber structure designs are needed to create optimum air-transport conditions inside the chamber.

2.4 Factors influencing the mercury volatilization rate from soils

Based on reliable methods of mercury emission measurement, important factors in controlling mercury emissions should be characterized to better the understanding of the underlying mechanisms. In naturally enriched soils, mercury is mainly in the form of HgS, HgCl₂, and HgO, and partly in organic forms, such as methylmercury and dimethylmercury (Zhang and Lindberg, 1999). The major controlling processes include: (1) the transformation from Hg (II) to Hg (0) in soils through chemical and biological processes and (2) the mass transfer of mercury between the three soil phases and the soil-air interface. The mercury volatilization rate is directly dependent on the factors governing the transport of mercury vapour in the soil and the release of mercury vapours from the soil to the atmosphere. In addition, factors controlling the reaction kinetics of processes producing Hg (0) and Hg (II) are also important especially for natural mercury sources (Schlüter, 2000). Influencing factors can be sorted into three groups as: soil characteristics, micrometeorological conditions, and other meteorological conditions, which can affect mercury volatilization directly or indirectly.

2.4.1 Soil characteristics

2.4.1.1 Soil textures

Different types of soils will have different physical characteristics, such as interstitial pore space, shape of the soil particles, and porosity of the soil (Schlüter, 2000). All of these soil parameters will affect the transition of elemental mercury vapour through soil textures. Fursov (1990) found that a migration rate of elemental mercury vapour through fine-grained sands was $1 \text{ cm} \cdot \text{min}^{-1}$ and through loams was $0.25 \text{ cm} \cdot \text{min}^{-1}$. This result indicated that a greater porosity and interstitial pore space would induce a higher mercury migration rate. Therefore the mercury emission over sand should be faster and greater than over clay, considering larger porosity and interstitial spaces in sand than in clay.

Different types of soils contain different constituents such as organic matter and metal oxides, which might induce or hinder the transformation of Hg (II) to Hg (0). As a class B metal in the Pearson classification, mercury has high affinity for soft bases, such as S (e.g. S^{2-} , HS^- , organic S), I, P, and N. Therefore mercury tends to coordinate with NH_3 , CN^- , and S donors, more than H_2O , OH^- , and O donors (Zhang and Lindberg, 1999). Organic matter, some types of clay minerals, and Fe-, Mn-, and Al-oxides have high sorption capacities for inorganic Hg (II) and methylmercury (Schlüter, 2000), which are the main forms of soil mercury.

Biologically, there are more organic matters and bacteria existing in loams than in sands, bonding mercury to soil particles. This also explains a faster migration of Hg in sandy soils than in loams and clays.

However, no quantified analysis in terms of soil texture effects has been concluded to date. Further investigations on the difference of Hg evaporation among different soil textures are needed for a better understanding.

2.4.1.2 Soil mercury concentration

Substrate mercury concentration has been demonstrated as a dominant parameter controlling Hg fluxes from naturally enriched substrates (Schroeder *et al.*, 2004, manuscript in preparation). Based on Hg fluxes collected from various locations across Canada, the correlation of substrate Hg concentration and Hg flux from background and mineralized geology soils is reproduced in Figure 2-6 (Schroeder *et al.*, 2004, manuscript in preparation). Additionally, laboratory experiments in the dark under controlled conditions also demonstrated a strong correlation ($r^2 = 0.997$) between mercury flux and soil mercury concentration (Gustin *et al.*, 2000). Similar correlation between mercury flux and substrate mercury concentration was also found by other research groups (Rasmussen *et al.*, 1998).

Figure 2-6: TGM Hg fluxes from background and mineralized geology sites across Canada versus TGM concentration (adjusted from Schroeder et al., 2004; Data analysis and plotting for this figure were done by Goretty Dias)

Due to the concentration difference along the soil/air interface, a high gaseous mercury concentration in the soil air will produce a high mercury evaporation flux. This relationship between soil mercury concentration and mercury emission flux can also be explained by the movement of the redox reaction balance towards the production of Hg (0) when the soil Hg (II) concentration is high. The strong correlation between mercury fluxes and substrate mercury concentration indicated that soil mercury concentration might be a practical parameter to scale up in-situ Hg fluxes for regional emission estimations (Gustin *et al.*, 2000).

2.4.1.3 Soil acidity

In the mid 1970's mercury evaporation rate from various soil substrates was found to increase with increasing soil pH (Schlüter, 2000). In terms of the processes of gaseous mercury translocation among different soil phases, this phenomenon can be explained by the pH-dependant adsorption of Hg (II) in the soil (Zhang and Lindberg, 1999). Due to the greater covalency of the HgOH^+ , the stability of the bonds between the bridging hydroxyl groups and the oxide surface is minimized to release mercury (Rogers and McFarlane, 1979). With a high affinity for the S-containing functional groups of the organic substances, mercury can be strongly adsorbed by soil organic matter. The content of dissolved organic matters bound to Hg (II) was also found to decrease with increasing soil pH (Schlüter, 2000). Therefore, the decreasing organic matter in the soil led to increasing mercury fluxes caused indirectly by the increasing soil pH.

Another explanation of the correlation between soil pH and soil mercury flux is based on divalent mercury redox reaction theory. With a considerable concentration of Fe (III) in the soil, one of the possible redox reactions is (Zhang and Lindberg, 1999):

- *Fe (III)-organic acid complex + light $\rightarrow$ Fe (II) + organic free radicals*
- *organic free radicals + Hg (II) $\rightarrow$ Hg (0) + CO_2 + products*

Based on the chemical reaction equilibrium theory, a higher concentration of the Fe (III)-organic acid complex results in a smaller pH and a higher gaseous mercury concentration to produce a high mercury emission flux. However, because of the complexity of the soil organic content, the above reactions represent only one potential scenario. More studies are needed to find out the actual pH-dependant reactions controlling this process.

2.4.1.4 Soil moisture

Soil moisture is a significant parameter controlling mercury volatilization, but needs more understanding of the underlying controlling mechanism. In the mid 1970's, a few investigations and experiments were done in terms of soil moisture effect on mercury volatilization (Landa, 1978a, 1979; Fang 1981; Sensi and Schnitzer 1977). It was concluded that water content influences the formation process of volatile mercury as well as the release of the volatile mercury from the soil into the air, causing a combined effect on volatilization of mercury (Schlüter, 2000).

A field dynamic flux chamber was developed by Carpi and Lindberg (1998) to qualify soil mercury flux over background soil, including the studies on the soil moisture. The field test results showed that soil moisture did affect mercury emission. A laboratory flux chamber was also used in a water infiltration experiment to study the soil moisture effect (Gillis and Miller, 2000). The experiment results showed increasing emissions with increasing soil moisture peaking at approximately field capacity and decreasing slightly until saturation.

Two underlying mechanisms were proposed based on the analysis of soil moisture influence on the volume of the three different soil phases (Zhang and Lindberg, 1999). In the soil column, the proportion of the volume of soil air and soil solution changes with changing soil moisture, while the volume of soil particle is not affected by soil moisture. Shown in Figure 2-7 (a), when the soil is fairly dry, there is only a thin water film covering the surface of the soil particles. Therefore, the volume of the soil air is relatively

Figure 2-7: Soil matrix with different soil moisture

Figure 2-8: Hypothesized controlling processes in mercury volatilization from soils
(adapted from Zhang and Lindberg, 1999)

large in comparison to the soil solution. Since elemental mercury predominantly exists in the soil air phase (McKay et al., 1995), there is a considerable amount of elemental mercury contained in the interstitial soil air in the dry soil. With increasing soil moisture, the volume of soil solution increases, leading to decrease in the proportion of soil air, as shown in Figure 2-7 (b). The interstitial soil air occupied by Hg (0) is displaced by

water, causing a temporary increase in the mercury emission, which is called physical displacement of soil air by incoming water (indicated in Figure 2-8).

From a chemical reaction point of view, Hg (II) is predominantly bonded on soil particles and direct desorption of Hg (II) (indicated in Figure 2-8) can barely happen (Zhang and Lindberg, 1999) in a fairly dry soil. When the soil is getting moist, however, the volume of soil air decreases with the increasing volume of soil solution. The thicker water films around soil particles serves as a medium to enhance the mobility of Hg (II) from soil particles into soil solution (the dissolution of Hg (II) in soil solution) and consequently promote the aqueous redox reaction of reactive Hg (II), which produces more gaseous mercury (indicated in Figure 2-8) (Gillis and Miller, 2000).

The potential aqueous redox reactions of Hg (II) are proposed by Zhang and Lindberg (1999) as shown below:

Unfortunately, it is still unclear what the actual controlling processes in the soil exactly are. As such, no concrete conclusion can be drawn in terms of the soil moisture effect.

and more research is needed to fill in this knowledge gap. More description of rain-related soil moisture effects is presented in Section 2.4.3.2.

2.4.2 Meteorological conditions

Mercury emissions are greatly influenced by meteorological condition changes, which can affect the controlling processes of mercury volatilization both directly and indirectly. Dominant meteorological parameters include soil and air temperature, relative humidity, and wind speed. The effects of these factors on mercury volatilization are discussed in the following sections.

2.4.2.1 Air and soil temperatures

Among all the meteorological parameters, temperature effects have been most widely reported and quantitatively studied (Kemp, 2001; Gustin *et al.*, 1997). Mercury volatilization was found to increase with temperature from both background and uncontaminated soils (Schlüter, 2000; Gustin *et al.*, 1997; Kemp, 2001). Based on the experimental data, the temperature over the soil surface showed a strong positive correlation ($r = 0.87$) with Hg flux by using the Arrhenius equation.

$$F_{Hg} = A' e^{\frac{E_a}{RT}}$$

where F_{Hg} is the flux of Hg, A' is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is temperature in Kelvin (Poissant and Casimir, 1998). Similar correlations between soil and air temperature and mercury flux were concluded by using

laboratory flux chamber (Gillis and Miller, 2000), field flux chamber (Carpi and Lindberg, 1998) and MM methods (Kemp, 2001; Lindberg et al., 1999).

This strong correlation between mercury emissions and soil and air temperatures can be explained by two mechanisms. The increasing thermal motion caused by the rising temperature lead to an increasing vapour pressure of Hg (0) and a decreasing sorption by soil. The soil air rises with the increasing temperature, thus contributing to mercury emission from the soil (Schlüter, 2000). Another proposed mechanism could be explained by the mercury redox reaction, in that higher temperatures provide more energy to promote the production of elemental mercury, possibly even sunlight-induced (Zhang and Lindberg, 1999).

2.4.2.2 Relative humidity

Based on data from Poissant and Casimir (1998), the mercury emission fluxes increased with decreasing relative humidity, showing a negative correlation between relative humidity and mercury emission flux ($r = -0.8$). Poissant (1997) investigated the relationship between water vapour and mercury fluxes. The positive correlation between water vapour fluxes and the mercury fluxes supported the earlier negative correlation between relative humidity and mercury soil flux (Poissant and Casimir, 1998; Poissant, 1997). The air moisture effects on mercury emission might not only be due to the physical transfer mechanism, but also caused by chemical reaction in the air. Elemental mercury could react with ozone in the air, expressed as (Poissant, 1997):

The water content in the air could influence the chemical reaction balance and contribute to the changes of gaseous mercury fluxes.

2.4.2.3 Wind speed

As mentioned earlier, two major methodologies of mercury flux measurement, MM and DFC methods were applied and compared to each other in field study during Nevada STORMS campaign (Poissant *et al.*, 1999). MM method results were three magnitudes greater than mercury flux measured by DFCs. The reason causing this result was possibly due to the DFCs' closed structure obstructing the air turbulence above the soil surface, while the MM methods were non-intrusive and did not affect the soil surface (Poissant *et al.*, 1999). This discrepancy in measurement methods points to the importance of wind effects on mercury volatilization.

Compared to temperature and solar radiation, wind speed only shows a moderate positive correlation with Hg flux ($r = 0.62$) (Poissant and Casimir, 1998). This correlation became negligible when the soil and air temperatures were higher than 40°C (Gustin *et al.*, 1997). The probable explanation of wind effect on mercury volatilization is that the turbulent airflow produced by the wind passing over the soil surface introduced an enhanced mass transfer at the soil surface. Therefore, wind speed has a greater effect on mercury transport from soil into the atmosphere than within the soil.

2.4.3 Other influencing factors

In addition to the meteorological factors, there are some other influencing factors that can either directly or indirectly affect mercury volatilization fluxes. The understanding of these factors is unclear due to the complex underlying mechanisms controlling mercury emission. An introduction of the state of the research on these parameters and discussions on corresponding conclusions are presented in this section.

2.4.3.1 Solar Radiation

Solar radiation was found to have a strong positive effect on mercury soil emission (Wallschläger *et al.*, 1999). Results from Poissant and Casimir's field experiments (1998) showed a high correlation between net radiation and mercury evaporation rate ($r = 0.96$). A laboratory-controlled experiment was carried out to study the solar radiation effect by using simulated sunlight. The experimental results supported the previous field-observed light enhancement of mercury emission fluxes by showing an obvious positive correlation (Gustin *et al.*, 1999). This relationship between solar radiation and mercury emissions can also be explained by both temperature effect and chemical reaction theories (Gustin *et al.*, 1999).

Mercury fluxes have shown strong correlation with both air and soil temperatures, which are strongly dependent on incident solar radiation (Gustin *et al.*, 1999). This indicates that net radiation can indirectly affect the gaseous mercury movement in the soil column and through soil-air interface by changing the surface soil and air temperatures.

Based on the redox reaction schemes, this light-enhancement of mercury volatilization could be promoted by the production of Hg (0) through photolytic reactions in the aqueous and solid soil phases (Zhang and Lindberg, 1999). Some examples of the proposed potential controlling reactions are given below.

In the aqueous solution phase, most of the redox reactions are directly light-induced. For example, both Hg (OH)₂ and Hg (II)-organic acid complexes can transform into Hg (0) by direct photolysis, expressed as (Zhang and Lindberg, 1999):

- $Hg(OH)_2 + light \rightarrow Hg(0) + 2 \cdot OH$
- $Hg(II)\text{-organic acid complex} + light \rightarrow Hg(0) + CO_2 + products$

On the soil particle surface, in addition to the aforementioned redox reaction of Hg (II)-organic acid complexes and Hg (OH)₂, the redox reaction of Fe (III) bound with organic acid are also photolytic and produce organic free radicals to promote the redox reaction of inorganic Hg (II) (Zhang and Lindberg, 1999).

2.4.3.2 Precipitation effect

During the Nevada STORMS campaign, several unexpected rain cells impacted the site and an immediate and steep rise in the ambient air Hg concentration were observed following the rainfall (Lindberg *et al.*, 1999; Poissant *et al.*, 1999). The immediate and sharp increase in mercury fluxes caused by rain event called for further investigation on

the relationship between soil moisture and gaseous mercury volatilization (Lindberg et al., 1999; Poissant et al., 1999).

The strong correlation between mercury flux and water vapour mixing ratio showed that the underlying mechanism was not only a physical transfer of mercury but also included mercury redox reactions and mobility of Hg (II) in aqueous phase (Poissant et al., 1998). The precipitation effect is a comprehensive effect, involving many rain parameters such as rain intensity, rain interval, rain temperature, and rain pH. These rain parameters can directly affect mercury emissions.

Soil moisture can be greatly increased by a rain event, and soil hydraulic conductivity is determined by rain intensity and rain interval. As introduced in Section 2.4.1.4, an enhancement of mercury flux can be caused by a quick physical displacement of the interstitial soil air by infiltrating water (Zhang and Lindberg, 1999). The mercury existing in soil air and adsorbed on soil particles can be replaced by incoming water to cause an increased mercury emission. The enhancement of mercury volatilization can also be caused by a promoted Hg (II) redox reaction in aqueous phase or enhanced mobility of Hg (II) in soil solution (Zhang and Lindberg, 1999; Lindberg *et al.*, 1999). With more water coming into the soil column, a greater volume is provided for the aqueous Hg (II) reaction to produce Hg (0) resulting in enhanced mercury volatilization. Additionally, rain temperature can affect mercury volatilization flux by changing soil and air temperatures. Likewise, rain pH can change soil acidity, thus potentially affecting the production of gaseous mercury as well.

Based on the results observed from Nevada STORMS campaign field tests during the precipitation event, increasing soil moisture was predicted to be responsible for the immediate increase in mercury emission fluxes and the following decreasing pattern of mercury emission fluxes after the precipitation event. As stated before, the possible controlling processes of rain-induced soil moisture effects are the physical displacement of soil air by the incoming water, aqueous divalent mercury redox reaction, or enhanced mobility of Hg (II) in the liquid phase. However, no definitive conclusions regarding the control process in terms of the precipitation effects have been drawn due to the convolution of the field flux data with other environmental parameters. More research on precipitation effects is required for a better understanding of the underlying mechanism.

2.5 Research Objectives

One of the largest current knowledge gaps of soil mercury emission is the underlying mechanism of the observed increase in mercury emission just after a precipitation event, especially the relationship between mercury emissions and surface soil moisture, which needs to be isolated and studied for a better understanding.

Therefore, the research objectives are:

- (1) to design and construct a laboratory DFC system to simulate the field-observed increases in gaseous elemental mercury fluxes due to precipitation under laboratory-controlled conditions; and

(2) to determine the precipitation effects on mercury emissions to better understand the suspected underlying mechanisms during and after a rain event. based on the experimental results of simulated precipitation events under different soil conditions.

CHAPTER 3. EXPERIMENTAL APPARATUS AND METHODOLOGY

To study the underlying mechanism of precipitation effects, the field-observed increases in gaseous elemental mercury fluxes due to precipitation were simulated in a controlled laboratory experiment. In this manner, the specific effects that precipitation and the ensuing soil moisture have on the magnitude of mercury emissions can be isolated and studied. In comparison with micrometeorological methods, dynamic flux chamber methods are good at controlling operating conditions, which are more suitable for the study of specific effects on mercury emission. A laboratory apparatus based on the dynamic flux chamber method was designed and applied for the purpose of this research. The descriptions of the experimental apparatus and research methodology based on this set-up are presented in this chapter.

3.1 Experimental apparatus

The experimental apparatus was composed of a DFC (dynamic flux chamber) system, a parameter measuring system, and a data acquisition system. These three systems are introduced in detail, respectively. The diagram of this set-up is presented in Figure 3-1.

Figure 3-1: Diagram of the experimental apparatus

3.1.1 Laboratory dynamic flux chamber system

The laboratory DFC system was made up of an interior precipitation generator, a dynamic flux chamber, a soil lysimeter containing soil naturally enriched with mercury and sampling paths. The structure of this DFC system is shown in Figure 3-2. The dimensions of the soil lysimeter is given in the diagram, while the dimensions of the precipitation generator and flux chamber are presented in Figure 3-3 and Figure 3-5, respectively.

Figure 3-2: Diagram of the dynamic flux chamber system
(Note: all the dimensions are in inches in this diagram.)

3.1.1.1 Dynamic flux chamber

In DFC methods, the mercury fluxes are estimated by measuring the mercury concentration difference between the inlet and the outlet of the chamber. To reflect the real mercury fluxes from the soil substrate as closely as possible, a good air flow pattern inside the chamber is required. However, the major drawbacks of DFC methods are the stagnant regions inside the chamber and corresponding pressure effects on mercury flux caused by the enclosed chamber structure. As shown in Figure 3-3, an octagonal chamber with airflow transition zones at the inlet and outlet was designed to improve the air-transport condition in the chamber.

Figure 3-3: Diagram of the laboratory dynamic flux chamber
(Note: all the dimensions are in inches)

For an additional presentation, the pictures of the real chamber are given in Figure 3-4 and Figure 3-5. Combining the advantages of the perforated-inlet design (Gillis and Miller, 2000) and the baffle design (Gao, 1997), the transition zones at the inlet and outlet consisted of two perforated boards and a baffled section. Going through the transition zones, the airflow was split into small airstreams and traveled through the chamber without stagnant zones, as observed by a smoke test. The details of the smoke test are introduced in Section 3.2.1.1. The details of the chamber transition zones are presented in Figure 3-5.

Figure 3-4: Picture of the dynamic flux chamber
(constructed by Taylor Roumeliotis)

Shown in Figure 3-4a, the flux chamber was made of transparent polycarbonate with relatively low adsorption of mercury and was fairly inexpensive (Kemp, 2001). The transparent nature could help with the experimental observation and the potential studies on light effects. A smoke test was done to check the stagnant regions inside the flux

chamber. The results of the smoke test validated the air flow pattern inside the flux chamber. Detailed procedures and results of the smoke test are given in Section 3.2.1.1.

Figure 3-5: The chamber transition zone

3.1.1.2 Interior precipitation generator

To introduce rain events into the experiment, a precipitation generator was integrated into the DFC system and mounted on the top of the chamber. The precipitation generator was made of Plexiglas with a polycarbonate board base, which was the same as the material of the chamber. In doing so, the mercury adsorption on all the interior walls of the chamber would be similar.

The diagram and the photo of the precipitation generator are presented in Figure 3-6 and Figure 3-7, respectively. As shown in Figure 3-6, the precipitation generator was a rectangular container with a maximum volume of 6.8L. Twenty evenly spaced syringe

needles (length= 1.52cm, outer diameter= 0.51mm, inner diameter= 0.29mm) were carefully inserted through the bottom of the rain generator to extend into the DFC, and evenly covered the circular soil surface with an area of 95 in² (0.0613m²).

(a) Top view

(b) Side view

Figure 3-6: The diagram of the precipitation generator
(Note: all the dimensions in this figure is in inches)

The synthetic rain was produced by filling the precipitation generator with water, which drips down through the syringe needles to form the rain. Due to the function of the gravity of water and surface tension, different rain rates can be generated by adding different volumes of water in the precipitation generator. The synthetic rain rate range

produced by this precipitation generator was 1~12mm/h at atmospheric pressure. Higher rain rates to simulate a downpour could be reached by pressurizing the rain generator with a regulated pressurized air cylinder.

Figure 3-7: The picture of the precipitation generator (constructed by Taylor Roumeliotis)

3.1.1.3 Soil substrate

The soil lysimeter was filled with soil naturally enriched with mercury and attached to a flask at the bottom to collect any leachate. The soil lysimeter refers to a soil container with a draining system, the basic definition of which was referred from a lysimeter design for soil mercury study (Schlüter *et al.*, 1995). The structure of the lysimeter in this research is illustrated in Figure 3-8.

A soil naturally enriched with a high mercury concentration was used in the experiment to ensure the response of mercury emission to rain events on a magnitude that exceeded the background mercury concentration in the air. The soil was collected from Clyde Forks, Ontario area. To get homogenous texture and soil properties, the soil was laid out and air dried for 48 hours and sifted through a 2mm sift to remove big rocks and plant residues. Sifted soil samples were tested in the lab and at the University of Guelph Laboratory Services (2003) for mercury concentration and other soil properties. The results of these tests are summarized in Table 3-1. The soil properties measured in the School of Engineering lab are marked with "*" in Table 3-1 and the measurement procedures of these properties are introduced in Section 3.2.1. After soil sampling, the soil was loosely packed in the soil lysimeter.

Table 3-1: Soil properties of the Clyde Forks soil

Mercury concentration	290 μ g/g soil
Soil texture	Loamy sand
Inorganic carbon concentration	1.78% dry by weight
Organic carbon concentration	1.31% dry by weight
Total carbon concentration	3.09% dry by weight
pH	7.5
Bulk density*	1400 kg/m ³
Porosity*	0.47 m ³ /m ³ soil column
Field capacity*	0.25 m ³ /m ³ soil column
Saturated hydraulic conductivity*	9.26 $\times$ 10 ⁻⁶ m/s

(Summarized based on the School of Engineering laboratory test results and the University of Guelph Laboratory Services, 2003)

In most of the DFC designs in the past, the dynamic flux chamber was skirted in the soil substrate, which had a larger area than the chamber footprint. In this case, the outside soil air was pulled into the chamber via a vacuum pump. To avoid any infiltration of outside air into the chamber, the soil substrate was contained in a lysimeter that was

sealed to the bottom of the flux chamber. In doing so, the entire soil surface was covered by the chamber, thus external air infiltration due to the DFC system design were avoided. In order to collect any water percolation through the soil lysimeter and to conduct a water mass balance estimation, a flask was connected to the bottom of the lysimeter.

Figure 3-8: Picture of the soil substrate

3.1.1.4 Pumps and sampling paths

In DFC methods, flushing airflow condition and sampling paths are directly related to the accuracy of mercury flux measurement. Based on the previous DFC system designs (Kemp, 2001), the flushing airflow line and sampling paths were designed to improve the operating conditions.

Outdoor air was supplied to flush through the DFC system by a vacuum pump (GAST[®], 23 Series Oil-less Vacuum Pump), due to the low mercury concentration of outdoor air. Constant air flow rates were required in the chamber to ensure a steady operating condition within the chamber. To prevent indoor air infiltration into the DFC system, airtight tube fittings (Swagelok[®], Niagara fittings) were used in all the paths.

As shown in Figure 3-9, sampling lines at the inlet and outlet were connected to the Tekran[®] Analyzer (mercury vapour analyzer) with the Tekran[®] sampling flow rate of 1.5 L/min (Tekran[®], 1996). To measure the mercury concentration at both the inlet and outlet, the sampling line switched between the inlet and outlet after each sampling period. However, the valve-switching interrupted the balance of airflow inside the chamber. An equalizing path was introduced in the system operating at the same flow rate as the Tekran[®] sampling line to keep the airflow balanced in the chamber. Shown in Figure 3-9, two solenoid valves were used on the sampling line (solid path in Figure 3-9) and equalizing line (dashed path in Figure 3-9). When the sampling was working on the inlet (Figure 3-9 (a)), the airflow with the same rate of 1.5L/min was supplied by the equalizing pump on the outlet. In the next sampling period (Figure 3-9 (b)), the sampling line switched to the outlet by the control solenoid valve. At the same time, the valve on the equalizing line switched to make the equalizing line active on the inlet line. In doing so, the sampling process was executed without flow rate changes in the main path.

(a) Sampling inlet

(b) Sampling outlet

Figure 3-9: Scheme of valve switching between sampling periods
(Note: black paths represent sampling paths in this figure; not to scale.)

As shown in Figure 3-9, a flow rate of 21.5 L/min was supplied by the vacuum pump in the main path. With a constant flow rate on the outlet of 1.5 L/min, a flow rate of 23 L/min inside the chamber was maintained through and between sampling periods and was in the recommended flow rate range of 15~40 L/min (Lindberg *et al.*, 2003)

3.1.2 Parameter measuring system

Parameters measured included mercury fluxes at the inlet and outlet of the chamber, air temperatures and relative humidities at both the inlet and outlet of the flushing chamber, soil temperatures at two different soil depths, and soil moistures at four different soil depths.

As stated in the introduction of the DFC methods in Chapter 2, mercury fluxes were estimated by the mercury concentration difference between the chamber inlet and outlet as measured by a Tekran[®] 2375A total gaseous mercury analyzer. Some important specifications for the Tekran[®] 2537A are listed in Table 3-2 (Tekran Inc., 1996).

To monitor the temperatures and relative humidities at the inlet and outlet of the chamber, two CS500 temperature and relative humidity probes (Campbell-Scientific Inc., 1994) were plugged and sealed tightly into the top of the inlet and outlet transition zones of the chamber. The positions of the temperature and relative humidity probes are given in Figure 3-1.

Table 3-2: Specifications for Tekran[®] 2537A (adapted from Tekran Inc., 1996)

Detection limit	<0.01ng/m ³
Range	0.10 ~ 1000 ng/m ³
Linearity	(1 ~ 200 ng/m ³) 2%
Sampling flow rate	1.5 L/min
Sample cycle time	5 min

Two soil temperature thermometer probes were inserted in the soil lysimeter at 7cm and 15cm depth, respectively. To get a soil moisture profile, four TDR soil moisture probes were also inserted into the soil lysimeter at 1cm, 5cm, 10cm and 20cm depth, respectively. The soil moisture measurement of the TDR probes were based on the electrical conductivity variations with water content in the soil (Campbell-Scientific Inc., 2002). However, the available TDR probes were longer than the diameter of the lysimeter resulting in a partial exposure of the probes in the air. The electrical conductivity of air is very sensitive to temperature and relative humidity changes, which will introduce more error in soil moisture measurement. To eliminate the error, Styrofoam blocks were used to cover the part of the probes exposed in the air. With the probes covered by isothermal material, the noises in soil moisture measurement due to surrounding air changes were reduced. Although the Styrofoam is isothermal and of stable electrical conductivity, introducing Styrofoam blocks can shorten the effective length of TDR probes. Therefore, a calibration procedure was conducted on the TDR probes. The details of TDR calibration procedures and results are presented in Appendix A.

All the meteorological and soil probes were connected to a CR23X datalogger (Campbell-Scientific, 1999) for further data transmission and storage. Details about the data transmission and storage are introduced in the following section.

3.1.3 Data acquisition system

An automatic data acquisition system was designed and improved based on Kemp's (2001) system design. The detailed description of this system is presented in Figure 3-10.

Shown in Figure 3-10, the computer-interfaced National Instrument analog to digital data acquisition card (National Instruments Inc., 1994) served as the central control unit of the whole system. The SCB68-connector was used as an extension of the NI-DAQ card to communicate with other data transmission and storage units in the system (National Instruments Inc., 1995). A CR23X datalogger was used to transform voltage signals from the meteorological and soil probes into data with an execution time of 20 seconds, and transfer the average values over every sampling period to the SCB-68 and subsequently to the NI-DAQ for further data storage. The Tekran[®] mercury analyzer was directly connected to the SCB-68 connector for data transfer and communication.

All the data were synchronized to reflect the real-time precipitation effect on mercury emission. As the central control unit in the system, the NI-DAQ card sent out commands every 10 minutes to SCB-68 to synchronize data collection from the Tekran[®] mercury analyzer and the CR23X datalogger. In between, the NI-DAQ manipulated the two solenoid valves through a relay box to switch the mercury sampling line between the inlet

and outlet of the chamber. All the data were eventually transferred to the central computer (PC3 in Figure 3-10) for storage and display. The other two computers (PC1 and PC2) were connected to the Tekran[®] analyzer and the CR23X datalogger respectively for data back up. The program codes for the NI-DAQ card and CR23X datalogger are included in Appendix D.

Figure 3-10: Diagram of the electrical connections of the data acquisition system and the parameter measuring system

3.2 Research methodology

A laboratory dynamic flux chamber system with an interior precipitation generator was designed to study precipitation effects on mercury soil volatilization under controlled

conditions. In this section, descriptions of the system validation and preparation are presented, which were used to test the capability and limitation of this experimental set-up design. More importantly, the detailed descriptions of the experimental methodology and procedures are presented in this section.

3.2.1 System validation

For an innovative dynamic flux chamber system design, a series of system validation tests were executed to test the reliability and limitations of the experimental set-up design. These tests included the air-transport condition test, system waterproof and airproof tests and rain rate test. The details of these tests are included in this section.

3.2.1.1 Air-transport condition test

The typical DFC is a rectangular box with one inlet and one outlet, skirted in the soil substrate. The nature of the one-inlet and one-outlet chamber design is not efficient at spreading the airflow to flush over the entire soil surface inside the chamber. In other words, this nature causes the heterogeneity of airflow and stagnant air-transport regions inside the chamber. As a result, the effective soil surface area is less than the actual area and can lead to the underestimation of mercury emissions. In light of this, an improved DFC was designed to minimize the short circuit in the flushing airflow.

Figure 3-11: The smoke test for the air-transport conditions in the chamber

To validate this structure design, an air-transport condition test was carried out shown in Figure 3-11. Smoke was blown into the chamber to check the air transport inside the chamber. As shown in Figure 3-11, the smoke stream was instantly and evenly spread out into many small streams through the inlet transition zone and going through the chamber. It demonstrated the homogeneity of air-transport with airstreams going above all the area of the soil surface.

3.2.1.2 Chamber and precipitation generator seal test

To ensure that the experiment is running under controlled conditions, the whole DFC system was sealed to avoid indoor air infiltration. Airtight tube fittings (Swagelok[®], Niagara Falls fittings) were used in all the flushing and sampling lines. The sealings on

the flux chamber and the precipitation generator required leakage checks to avoid indoor air infiltration. The leakage check of the flux chamber was done by submerging the chamber in a container filled with water, while the precipitation generator was filled with water for waterproof test.

3.2.1.3 DFC system seal test

After the waterproof check of the chamber and the rain generator, all the units of the system were connected together and sealed. The DFC system was disconnected from the flushing and sampling line. A soap solution was applied on all the suspected leakage areas and connections between different units. With the inlet and sampling line openings sealed, air was blown into the chamber system from the outlet, and the leakage was checked by looking for bubbles in suspected areas.

After the leakage check of the DFC system, the chamber system was reconnected to the flushing and sampling lines. Soap solution was applied onto all the fitting connections in the sampling and flushing lines. High flow rates of 40L/min in the flushing line and 5L/min in the equalizing line were applied by the vacuum pumps to check the leakage in the tubing lines.

3.2.1.4 Rain rate test

To simulate and study the mercury emission changes in response to rain in the field, the rain generator has to be able to produce precipitation with a reasonable rain rate range

experienced in the real world. Additionally, future potential studies on rain rate effects still require the rain generator to produce different rain rates up to high rain rates to simulate downpours.

The rain rate tests were carried out to test the rain generation capability of the precipitation generator. Shown in Figure 3-7, the rain was produced by adding water into the rain generator, and the water dripped down through the syringe needles attached to the bottom of the rain generator to form the rain. Under atmospheric pressure, the rain rate was controlled by the difference between the head of the water and capillary forces in the needles, depending on the depth of the water. The more water was applied into the rain generator, the higher rain rate was generated due to the higher water pressure. Based on this scheme, rain rates at atmospheric pressure were tested by measuring the volume of rain in one minute at certain water levels. The rain rate curve of the precipitation generator is presented in Appendix A. Additionally, a downpour rain rate could be tested by measuring the volume of rain in a minute while pressurizing the water in the rain generator. A maximum downpour rain rate generated by the precipitation generator was 40mm/hr for the average of soil surface.

3.2.1.5 Soil property tests

Soil bulk density, porosity, field capacity and saturated hydraulic conductivity were measured in the lab by using some simple experimental set-ups. The soil bulk density was obtained by measuring the weight of certain volume of dry soil contained in a scaled

cylinder. The total porosity was estimated by the bulk density through an empirical formula:

$$\phi = 1 - \frac{\bar{\rho}_b(\text{soil})}{\rho_p(\text{particle})} \quad (3.1)$$

where $\bar{\rho}_b$ is the soil bulk density. ρ_p is the soil particle density (typically 2.65g/ml) (Craig, 1997).

Figure 3-12: Soil permeameter used in saturated hydraulic conductivity and field capacity tests

The saturated soil hydraulic conductivity was measured using a falling-head method (Craig, 1997). Shown in Figure 3-12, a pre-sifted soil sample is loosely filled in the soil

permeameter using the same soil-packing method filling the soil lysimeter, and then it was placed in an empty container higher than the permeameter itself. To measure the saturated hydraulic conductivity, the soil must be fully saturated without any interstitial air in the soil column. The experimental set-up of soil saturation process is presented in Figure 3-13. Water was slowly pumped from one water container (on the right) to the other dry container (on the left) containing a soil permeameter full of soil sample. In doing so, the soil sample in water was slowly immersed to expel the interstitial air in the soil column. Once all the water was transferred into the container with the soil permeameter, the pump was stopped with the permeameter staying in the container to saturate the soil for over 48 hours.

Figure 3-13: Experimental set-up for soil saturation process

The falling-head test experimental set-up is presented in Figure 3-14, and the basic principle is described as (Craig, 1997):

$$k = \frac{aL}{a't} \ln \frac{h_1}{h_2} \quad (3.2)$$

where k = saturated hydraulic conductivity, cm/s

a = cross-sectional area of buret or other standpipe, cm^2

a' = cross-sectional area of soil sample, cm^2

t = elapsed time of test, s.

h_1 = hydraulic head across sample at beginning of test ($t=0$)

h_2 = hydraulic head across sample at end of test ($t = t_{\text{test}}$)

L = soil sample length, cm

Figure 3-14: Experimental set-up for falling-head test (adjusted from Craig, 1997)

Based on the above equation, the cross-sectional area of the buret and the dimensions of the soil permeameter were measured as required. The soil permeameter was connected to the buret by a rubber tube with air expelled out of the system. The elapse time of water level dropping from a certain point (point B in Figure 3-14) to the other on the buret (point A in Figure 3-14) were measured three times and averaged to get the t in the equation. The sample calculation is given in Appendix B.

The same soil permeameter was used to measure soil field capacity as presented in Figure 3-12 after the saturated hydraulic conductivity test was completed. To make sure that the soil was saturated after the falling head test, water was filled into the soil permeameter until the soil was completely immersed by the water. The soil permeameter was placed in a container for draining over 24 hours with the top of the permeameter covered to avoid evaporation. When the water stopped dripping from the bottom of the permeameter, the soil was considered at field capacity. Several samples of saturated soil was weighed and dried in the oven at 105°C for 24 hours. The oven-dried soil samples were weighed and compared with the saturated soil weight. The ratio of the weight difference between saturated soil and oven-dried soil sample was the field capacity, which was estimated at 0.25 m³/m³ for the soil used in this research.

3.2.2 Experimental methodology

As introduced in Chapter 2, soil moisture is an important soil parameter controlling soil mercury emission by influencing (1) the transformation of mercury species in and

between different soil phases and (2) the mobilization of mercury species between three soil phases within the soil column. According to the hypothesized controlling mechanism introduced in Chapter 2, predicted mercury flux changes in response to precipitation over soils with different soil moisture are given below.

When a rain event is conducted over a fairly dry soil, elemental mercury existing in interstitial soil air is possibly expelled by the infiltrating water (refer to the solid black path in Figure 2-8), which can possibly lead to a temporary increase in the mercury emission flux. In terms of the mobility of Hg (II) or redox reaction of reactive Hg (II) in the aqueous phase, the increase in the mercury flux is predicted to be observed when the rain is applied over a fairly dry soil.

When a rain event is conducted over the moist soil, physical displacement effect is greatly reduced due to the limited displaceable interstitial air. Based on the mechanism of the aqueous redox reactions or mobility of Hg (II), no huge changes in the mercury flux are expected once soil moisture reaches certain level, since the moist soil environment has already favoured either of these two processes before the precipitation.

To further investigate these hypothesized controlling processes, six sets of experiments were designed and conducted to apply rain events at various surface soil moistures under controlled conditions. The detailed experimental methodology and procedures are given below, while the sequence of all the procedures is presented in Figure 3-15.

Before starting the experiment, the DFC system and sampling paths were acid-washed to remove adsorbed mercury (U.S. EPA, 1999). Due to mercury adsorption and desorption to and from the interior wall of the chamber, a chamber blank test was done before starting the first experiment and after finishing all the experiments to correct the mercury fluxes measured by DFC methods (BT in Figure 3-15). The blank of this flux chamber was $0.000356 \text{ ng m}^{-2} \text{ s}^{-1}$, indicating a negligible mercury adsorption inside the chamber. The details of acid-wash procedure (U.S. EPA, 1999) and chamber blank test are included in Appendix A.

3.2.2.1 Single rain events

The purpose of the single rain events was to simulate the field-observed increases in gaseous elemental mercury flux due to precipitation under controlled conditions when the soil was close to air-dry. The air and soil temperatures were fairly constant with minor fluctuations due to changes in outdoor conditions. Outdoor fresh air was supplied with a constant flow rate of 20 L/min through the chamber. Deionized water was used to simulate rain events and to avoid pH effects from the water. Lab test showed no significant Hg concentrations in the deionized water. The rain event in both sets of experiments was set at the same rain rate and rain duration.

One litre of deionized water was added into the precipitation generator, creating a rain with a constant mid-rain rate of 11mm/hr lasting for a duration of 1.5 hours. The rain was applied when the surface soil was fairly dry (<5%). Mercury concentrations at the inlet and outlet of the chamber as well as other environmental parameters were

continuously monitored to keep track of all the parameter changes and mercury flux variations in response to precipitation. Measurements commenced one day prior to the rain event, and continued through the rain event and lasted for an extended period after the precipitation. As the soil dried back to approximately the same initial conditions, the experiment was repeated to verify the observed behaviour.

The period for data collection for both single rain events lasted about 6 days to focus on the phenomena during and shortly after the rain events (1S, 2S in Figure 3-15), while the drying process (1S', 2S') continued until the soil moisture returned to the initial condition for approximately 6 more days after the data-collection period.

After the single rain events, the system was open and a surface soil sample at 1mm was taken for a lab analysis of the total mercury concentration before starting the experiment (A in Figure 3-15). After the soil sampling, the soil in the top 5 cm in the lysimeter was taken out of the lysimeter, remixed and air-dried under the light (B in Figure 3-15). When the soil moisture was close to 5%, the soil was returned to the lysimeter and loosely packed as before. The second surface soil sample was taken for total mercury concentration test before the system was sealed (A in Figure 3-15).

3.2.2.2 Double rain event

A double rain event (D in Figure 3-15) was conducted to observe and compare the mercury flux changes with the rain applied over the soil with very different water

content, including at fairly dry soil and very moist soil shortly after the first rain event (1 day).

This set of experiments consisted of monitoring mercury emissions from a fairly dry surface again, but the initial rain event was followed by a subsequent rain event of the same magnitude and duration on the next day. In doing so, the second rain was applied on a quite moist soil surface (soil moisture ~20%) compared to the soil condition before the first rain. Same as in the single rain events, the mercury emissions and other environmental parameters were monitored and the soil was allowed to dry until it reached the same initial conditions.

One complete double rain experiment from starting the rain event with fairly dry soil until the soil moisture returned to the approximate initial condition lasted 19 days.

3.2.2.3 Triple rain events

After experimenting with rain event on fairly dry and moist soils, rain events at intermediate conditions were executed to gain a better understanding of the underlying mechanisms.

Triple rain event with a 1-day and 5-day delay: The experiment repeated the initial double rain event as introduced earlier but with an added third rain event of the same magnitude and duration five days after the second rain event when the soil moisture was approximately 12% (1T in Figure 3-15). All the operating conditions and other

experimental procedures were kept the same as in the previous experiments. Likewise, the mercury fluxes and environmental parameters were continuously monitored for an extended period after the precipitation event. The system was opened to remix the soil using the method introduced previously.

Triple rain event with an 8-day and 5-day delay: The experiment started with a double rain event with an 8-day interval between two precipitation events, which allowed the surface soil moisture drop back to approximate 10% before the second rain event (2T in Figure 3-15). A third rain with the same magnitude was added 5 days after the second rain event, when the surface soil moisture dropped back to around 10%. Same as in all the other experiments, operating conditions were controlled through the complete experiment period. The mercury fluxes and environmental parameters were measured before, during and after the precipitation event until the soil moisture dropped down to the condition before the second rain in this set of triple rain events.

Figure 3-15: Chronology of experimental procedures
 (Note: "W" is a 3L single rain event that was not included in the experimental methodology.
 The valuable results of this experiment are discussed in Chapter 4.)

CHAPTER 4. EXPERIMENTAL RESULTS AND DATA ANALYSIS

In this chapter, experimental results are presented, followed by the discussion and analysis of the experimental data. The relationships between mercury emission and some specific parameters related to precipitation effects were analyzed to explain the underlying mechanisms.

4.1 Raw data processing

The presented experimental data include the mercury flux, other measured environmental parameters mentioned in Chapter 3, and the calculated water vapour flux in the chamber. A brief introduction of data processing including important parameter calculations and corrections for environmental condition variation is included in this section.

The calculated mercury fluxes were blank corrected and determined from the averaged concentration difference measured by the two cartridges of the Tekran[®] analyzer. As stated in Chapter 3, the Tekran[®] analyzer operates by trapping mercury onto two gold cartridges located within the instrument. The Tekran[®] analyzer was auto-calibrated by an internal permeation source before each experimental run to eliminate the transient bias on each cartridge and the bias between two cartridges. The scheme of auto-calibration of the analyzer is included in Appendix A.

The water vapour flux was estimated based on the difference of water vapour densities between the inlet and outlet of the chamber, which were derived from the relative humidity at these two locations. The calculation of water vapour flux has also been verified by a rough estimation of average water vapour flux based on the amount of rain water applied in the system. The sample calculation of water vapour flux and the calculation check are given in Appendix B.

In all the experiments, the soil and air temperatures were fairly stable but with minor changes within $\pm 3^{\circ}\text{C}$. These minor fluctuations in temperatures caused variations in temperature-sensitive parameters, including the mercury flux, water flux and relative humidity. Therefore, these parameters have all been normalized to a standard temperature at 20°C , which is fairly close to the average temperature (20.18°C) through all the experimental runs. The detailed calculations of normalization for these aforementioned parameters are presented in Appendix B.

4.2 Raw experimental results

Raw experimental results include the first trial of a single rain event, two single rain events, one double rain event with a 1-day interval, one triple rain event with a 1-day and a 5-day interval, a 3L single rain event and one triple rain event with a 8-day and a 5-day interval.

4.2.1 Discovery of the light effect

The first trial of single rain experiment was carried out to validate the experimental set-up and methodology. The mercury flux and other environmental parameters for this single rain event are presented in Figure 4-1 at the end of Section 4.2.

The data in Figure 4-1 indicates that there was a sharp spike in mercury flux immediately after the start of the precipitation event, given by the RE arrow in the graph. After the rain event, the mercury fluxes were still elevated compared to before the rain but decreased in a generally analogous manner to the decreasing surface soil moisture.

However, some unexpected fluctuations (circles in the Hg flux plot of Figure 4-1) occurred in the mercury flux and were neither related to the rain event nor to minor fluctuations in other parameters. A zoom-in graph of the Hg flux in the first trial of single rain event is given in Figure 4-1z. There was a minor decrease in the mercury flux starting at around midnight. Around 8:30am in the morning, the mercury flux started to gradually recover. This gradual increase in mercury flux lasted for a couple of hours, and then mercury flux fell back to the initial decreasing pattern. This fluctuation in mercury flux occurred diurnally through the complete experiment. The only exception was the 2-day interval between the first two fluctuations.

As indicated by the dashed lines in Figure 4-1z, these times when the minor decrease and increase in the mercury flux happened matched the times when the lab fluorescent lights were turned off by midnight and on in the morning, respectively. The 2-day interval

between the first fluctuations was due to a constant lights-on period during the weekend. This phenomenon indicates that the light generated by fluorescent lights can influence Hg emissions from the soil presumably through a photolytic conversion of Hg (II) to Hg (0) at the soil surface.

To control the suspected light effects on mercury emissions during the experiments, the fluorescent lights were kept on through all the remaining experiments. As indicated by the experimental results in single rain events (Figure 4-2 and Figure 4-3), the fluctuation in mercury fluxes due to the light effect disappeared, which confirmed that the fluorescent light intensity changes do have an influence on mercury emissions. Considering that the focus of this research is the precipitation effects on mercury emissions, no further study on the light effects were conducted but is recommended to be investigated in the future.

4.2.2 Single rain events

In the following six experiments, the mercury flux, water vapour flux and relative humidities were all normalized to 20°C to correct the temperature effect as introduced in Section 4.1. The normalized mercury flux and other environmental parameters for the two single rain events are presented in Figure 4-2 and Figure 4-3, respectively.

In both single rain events, the soil temperatures and air temperature at the inlet and outlet of the chamber were fairly stable as a result of the near constant indoor air temperature

(~20°C). The relative humidity at the inlet of the chamber was fairly stable in the first single rain event, as the cold outdoor air was heated up to about 20°C by the constantly warm indoor air (~20°C) before entering the chamber. In the second single rain experiment, the relative humidity at the inlet of the chamber was fluctuating due to the outdoor precipitation events during the early spring, which potentially introduced more uncertainty into the results.

The single rain event resulted immediate increase in the surface soil moisture (at 1 cm), as indicated by an arrow in both Figure 4-2 and Figure 4-3. The moisture levels deeper in the soil matrix are slower to respond with less of an increase in magnitude as the rain water percolates through the soil column. As a result of the single precipitation event, a corresponding sharp increase in the water flux and relative humidity at the outlet of the chamber was observed in both single rain events.

More significantly, as shown in Figure 4-2 and Figure 4-3, immediately after the start of the rain event, the mercury flux increased dramatically and started to decrease sharply once the rain event ended. This observed spike in the mercury flux during the rain event was consistent with the physical displacement of mercury-containing interstitial soil air by infiltrating rain water. A calculation check was also done to compare the amount of mercury purely contributed by physical displacement in the mercury flux peak (between the two bars on the Hg flux curve in Figure 4-2) and the available gaseous mercury in soil air that can be displaced by 1L of rain water. The details of this calculation check are included in Appendix B. The calculation results were 0.97µg Hg in the mercury flux

spike and $3.2\mu\text{g}$ Hg available in the interstitial air to be displaced by 1L rain water. It should be noted that the theoretical maximum of $3.2\ \mu\text{g}$ Hg was calculated assuming equilibrium conditions between all soil phases and that all the Hg (II) in the soil matrix was readily available for potential conversion to Hg (0). As a matter of fact, the distribution of mercury species in the soil matrix can barely reach an equilibrium in a short period of time, while only a small portion of Hg (II) can be potentially converted to Hg (0). Therefore, the mass of Hg in the spike of the Hg flux is smaller than but comparable with the theoretical maximum value. Based on the timing and duration of the spike in the Hg flux with the rain event and the support from the theoretical calculation, the temporary spike in the mercury flux during the precipitation event was caused by a physical displacement process.

After the rain event, the mercury flux was still elevated above that observed for the fairly dry soil and decreased in the same pattern as the decreasing surface soil moisture. This pattern suggested a correlation between soil moisture and the mercury emission flux whereby an increase in soil moisture would enhance the production of elemental mercury in the soil matrix possibly through an aqueous mercury redox reaction. As discussed in Chapter 3, the production of Hg (0) through the soil solution phase was possibly enhanced by the increasing volume of rain water by (1) a more dissolved Hg (II) from soil particles into the soil solution (mobilization of Hg (II)), or (2) a promoted transformation of reactive Hg (II) to Hg (0) in the soil solution. In terms of the enhanced aqueous redox reaction, no specific redox reaction formulas in the soil are known, due to the unknown mercury species and metals in the soil.

Although similar patterns of mercury flux changes were observed in both single rain experiments, the magnitude of the peak in mercury flux of the first run was greater than that in the second run. One explanation of the smaller peak in mercury flux of the second run is the surface depletion effects. After an experimental run of 12 days, the accumulative loss of mercury from the soil was $41.9\mu\text{g}$ based on the integration of the mercury flux curve. Based on the concentration of total mercury in the soil before the experiment ($290\mu\text{g/g}$ soil) and using the surface area of the lysimeter, this would result in the complete ideal depletion of total mercury in the upper 1.68mm soil. Realistically, however, the depletion front would not be a step function but a gradual change with depth. As introduced in the methodology, two soil samples were taken right before and after the soil remixing that was conducted after the second single rain event. The results of the total mercury concentration for the two soil samples were $250\mu\text{g/g}$ soil before (University of Guelph Laboratory Services, 2004a) and $280\mu\text{g/g}$ soil after the soil remixing (University of Guelph Laboratory Services, 2004b), confirming the depletion of mercury in the soil surface.

Due to the surface Hg depletion over time, less Hg (II) would be available at the soil surface for conversion to Hg (0) in the interstitial soil air. This would result in a smaller spike in the mercury flux during the rain event, provided the surface interstitial air is the first to be depleted.

In addition, the smaller peak in the mercury flux in the second run could also be related to the higher initial surface soil moisture. When the surface soil moisture was higher,

interstitial air from deeper in the soil column would have to be displaced by the incoming rain water. At deeper soil levels, the enhanced production of Hg (0) through unidentified mechanism would not be present, resulting in interstitial air that has smaller mercury concentrations than at the soil surface.

4.2.3 Double rain event

To get further insight into the potential relationship between soil moisture and the gaseous elemental mercury flux, a double rain experiment with one-day delay was conducted. The normalized mercury fluxes and other parameters for the double rain event are given in Figure 4-4.

The two precipitation events were conducted with one day interval, as indicated by the two arrows on the time axis which were also reflected by the two sharp spikes in the surface soil moisture (at 1cm). Corresponding increases due to the double rain events in the outlet relative humidity and water vapour flux were also observed in the first rain event, but not in the second event.

As for the mercury flux, a similar spike with a greater magnitude was observed for the first rain event as for the single rain events. This was followed by a second spike, of smaller magnitude, during the second rain event on the following day, which was possibly a result of the higher soil moisture before the second rain, and insufficient time for the surface interstitial air to reach equilibrium with soil bound mercury at the surface.

Surface soil depletion was not considered as a major factor contributing to the smaller peak in this case, since the time interval (1 day) between the two peaks in the mercury flux was too short for significant mercury depletion at the soil surface.

Note however that after the second rain event finished, the mercury flux dropped back to the same decreasing pattern as before the second rain event and did not rise in an analogous manner to the surface soil moisture. This indicates that the added rain water in the second precipitation event did not enhance the underlying mechanism (either the mobility or redox reaction) of mercury emissions any more than prior to the rain event.

4.2.4 Triple rain events applied at different soil moistures

To further investigate the effect of soil moisture before the precipitation event on the mercury flux, several triple rain events were performed with the precipitation event applied at a soil surface with different soil moistures. The results are presented and analyzed in this section.

4.2.4.1 Triple rain event with 1-day and 5-day delay

To repeat a double rain event and look at the behaviour of the mercury flux when precipitation event is applied at a soil surface with an intermediate soil moisture (~12%), a triple rain event was executed in sequence after the double rain event. The experimental results are presented in Figure 4-5.

The inlet relative humidity was fluctuating through the entire period of the triple rain event, due to the variable outdoor humidity. As a result of the simulated precipitation events, three sharp peaks were observed in the surface soil moisture. A sharp increase was also observed in the water vapour flux and outlet relative humidity after the first rain event, but not after the second and third rain event.

As for the mercury flux, the behaviour in the double rain events was repeated in the first two rain events of the triple rain events. However, smaller peaks in the mercury flux were observed after the first two rain events, which was probably due to the mercury depletion in the soil column especially at the surface and the higher soil moisture as introduced in Section 4.2.2. For the third rain event, a spike in the mercury flux was again observed during the rain event. However, after the rain event, there was a slight increase in the mercury flux pattern compared to before the third event. This suggests that the soil moisture prior to the third rain event had dropped to a level that no longer supported the maximum conversion of Hg (II) to Hg (0). The observed behaviour of the mercury flux after the third rain event indicated that the mercury flux emitted from soils after a rain event was not only dependent on the quantity of infiltrating rain but also on the soil moisture content prior to the rain event.

4.2.4.2 Discovery from a 3L rain event

To further confirm the conclusion drawn from the previous triple rain event, a rain event when the surface soil moisture reaches about 10% was originally designed. However,

instead of 1L, 3L of rain water was added into the system. Although not following the original methodology, some interesting results are still worthwhile to discuss and serve as a recommendation for future work (W in Figure 3-15). The experimental results are summarized in Figure 4-6.

As opposed to the original design, a 3L rain was added when the surface soil moisture was around 10%, as indicated by the sharp increase in surface soil moisture (1cm). Unlike the 1L rain event, the 3L rain event lasted long enough to make the soil moisture reach field capacity ($0.25\text{m}^3/\text{m}^3$). As indicated in the soil moisture plot, after the rain event, the soil moistures at different depths maintained a similar behaviour with a minor gradual decrease during the 19-day drying process. After the surface soil moisture reached the field capacity, the infiltrating rain started moving downward after the rain event. However, the soil moisture at 20cm was maintained near field capacity, as there is no natural percolation of water with a sealed flask at the bottom of the lysimeter.

As for the mercury flux, only a minor pulse was observed during the rain event, indicating that surface depletion played a factor since the soil was last turned 6 weeks ago. After the precipitation event, only a minor elevation in the mercury flux was observed compared to before the rain event, which was probably due the downward movement of infiltrating rain water. More specifically, once the soil moisture reached field capacity, the infiltrating water was no longer staying at the surface but moving downwards to the bottom of the lysimeter. Therefore, the mercury emission flux is not only related to the volume of the precipitation, but possibly affected by the movement of

water flux in the soil matrix. Additionally, some obvious pulse in the mercury flux after the precipitation event was also observed, which was possibly influenced by the fluctuations in the water vapour flux influenced by the fluctuations in the inlet relative humidity. Details of the relationship between water vapour flux and the mercury flux is discussed in Section 4.4.

In light of all these, further experimentation on precipitation events over a soil surface with soil moisture exceeding the field capacity is recommended as future work. In addition, inlet relative humidity should be controlled ($RH = 100\%$) by using saturated air in the flushing line to avoid relative humidity effect on mercury emissions (Poissant and Casimir, 1998).

4.2.4.3 Triple rain event with 8-day and 5-day delay

To investigate the mercury flux behaviour, a triple rain event was conducted with an 8-day and 5-day delay between the first and last two rain events, respectively. In doing so, the surface soil moisture dropped down to around 10% before the second and the third rain event. The experimental results for this run are given in Figure 4-7.

After the 3L rain event, the soil was close to saturation, which slowed the drying process and caused a depletion of mercury in the surface soil. Therefore, as indicated on the time axis, the DFC system was opened and the soil (within 10cm depth) was remixed to speed the drying process and to increase the gaseous mercury concentration in the surface soil.

As shown in Figure 4-7, a diurnal fluctuation was observed in the inlet and outlet air temperature, which was due to the turning on and off of the air conditioner in the lab and the outdoor air temperature changes. The outdoor rain events caused dramatic fluctuations in the inlet relative humidity, resulting in significant fluctuations and even slight negative values in the water vapour flux.

Three sharp increases in the surface soil moisture (1cm) resulted from the three precipitation events. Compared to the soil moisture at the top three levels, the soil moisture at 20cm depth maintained at a near constant level of 17.5% due to the massive volume of water from the 3L rain event. Similar to the last triple rain event, the outlet relative humidity and water vapour flux were not affected by the rain event.

The behaviour of the mercury flux observed in the single rain event was repeated in the first rain event of this triple rain event. Unfortunately, the valve-switching control was interrupted by a temporary power shut off on June 29th and was not recovered until July 5th. As a result, only the outlet mercury concentration was measured from June 29th to July 5th. As the inlet mercury concentrations were fairly constant, the mercury flux during this period was calculated by using the measured outlet mercury concentration and the average inlet values before June 29th in this experiment based on Equation (2.5). Shown in the mercury flux plot, immediately after the second rain event, a smaller spike in the mercury flux was observed compared to after the first rain event. After the second

rain event, compared to before the rain event, the elevation in the mercury flux was also observed, which again demonstrated the enhancement of mercury emissions.

To justify the recovered data after the second rain event, a third rain event was conducted at a similar soil condition. Similar results, especially the minor elevation in mercury emissions after the rain event, were obtained and presented in the mercury flux plot.

The observed behaviour of the mercury flux after the second and third rain event confirmed that the mercury flux after a rain event was dependent on both the quantity of infiltrating rain and the soil moisture content prior to the rain event. More specifically, the mercury volatilization could no longer be enhanced when the soil moisture was at a magnitude that the production of Hg (0) through soil solution phase had reached an equilibrium. One possible scenario is that the Hg emission was controlled by the dissolution of Hg (II) into soil solution, whereas the factor limiting the dissolution of Hg (II) is possibly the contact surface area of soil particles with water.

When the soil is fairly dry, soil water predominantly exists close to the contact points of soil particles, while most of the soil particles are only covered by a very thin water film (indicated in Figure 2-7a). When the rain is applied on a fairly dry soil surface, the contact surface area of soil particles with water increased with increasing soil moisture, which promotes the mobility of Hg (II) into soil solution phase and results in higher mercury emissions in consequence. Once the soil moisture exceeds a certain level (i.e. transitional soil moisture), the contact surface area of soil particles with water probably

has reached maximum (indicated in Figure 2-7b). In this case, adding more water will not promote the mobility of Hg (II), which is possibly limited by the contact surface area of soil particles with water. Therefore, no enhancement in mercury emission after precipitation is observed when the rain event happens on a fairly moist soil.

Therefore, the mobility of Hg (II) into soil solution phase is suspected as a limiting process of mercury emissions after precipitation. However, no concrete conclusions on the limiting process after a rain event can be drawn without knowing Hg species in the soil column, which helps understanding the redox potential and mobility of different Hg (II) species in the aqueous phase.

Figure 4-1: Hg flux and environmental parameters for the first trial of single rain experiment

(Note: RE represents one rain event in all the graphs in this chapter. Circles indicate the fluctuations in the Hg flux caused by light effects in Figure 4-1.)

Figure 4-1z: Light effects on Hg emission flux in the first trial of single rain event

Figure 4-2: Hg flux and other parameters for the first single rain event, normalized to 20°C
 (Note: the peak in Hg flux between the two bars is suspected as a result of physical displacement)

Figure 4-3: Hg flux and other parameters for the second single rain event, normalized to 20°C

Figure 4-4: Hg flux and other parameters for the double rain event, normalized to 20°C

Figure 4-5: Hg flux and other parameters for the triple rain event with a 1-day and 5-day interval, normalized to 20°C

Figure 4-6: Hg flux and other parameters for the 3L rain event, normalized to 20°C

Figure 4-7: Hg flux and other parameters for the triple rain event with 8-day and 5-day interval, normalized to 20°C

4.3 Water vapour flux and Hg flux

Based on the basic principle of mass transfer, fluxes from the soil substrate are usually related (Kemp, 2001). Therefore, water vapour flux was either possibly an influencing factor for mercury emissions, or controlled by the same factors controlling mercury emissions. In order to further study the relationship between the water vapour flux and mercury flux, the correlation between these two fluxes is discussed in this section based on the analysis of experimental results.

4.3.1 Single rain events

The mercury flux and water vapour flux for the single rain events are presented in Figure 4-8 and Figure 4-9, respectively for a better presentation. Shown in Figure 4-8, the curve of the mercury flux for the first single rain event was fairly smooth, while the water vapour flux being fairly stable as well. For the second single rain event shown in Figure 4-9, perturbations in the water vapour flux curve corresponded to the noise in the mercury flux, as indicated by the dashed lines.

Plots of the water vapour flux versus the mercury flux for the single rain events are presented in Figure 4-10 and Figure 4-11. However, no definitive correlation between the water vapour flux and the mercury flux were observed in the drying processes for both the single rain event experiments.

4.3.2 Double rain event

The mercury flux and water vapour flux for the double rain event are shown in Figure 4-12. The mercury flux was decreasing smoothly after the first and the second rain event, but started to fluctuate once the surface soil moisture dropped below 10% (indicated in Figure 4-4) around March 19th. These perturbations in the mercury flux corresponded to the fluctuation in the water vapour flux, as indicated by the bars in Figure 4-12.

To further investigate the any relationship between the water vapour flux and the mercury emission flux, a plot of the mercury flux versus the water vapour flux is given in Figure 4-13. However, as shown in Figure 4-13, the curve for the drying process after the second rain did have a slight correlation between the water flux and the mercury flux during the drying process.

4.3.3 Triple rain events at different soil moisture

The mercury flux and water vapour flux for the two different triple rain events are presented in Figure 4-14 and Figure 4-16, respectively. As indicated by the bars in Figure 4-14, some slight corresponding perturbations in the mercury flux to the water vapour were observed. Compared to Figure 4-14, the mercury flux curve in Figure 4-16 was fairly smooth, although the water vapour flux was fluctuating dramatically in response to the outdoor precipitation events. In addition, no correlation between water vapour flux and mercury flux for these two different triple rain events were observed in the data plotted in Figure 4-15 and Figure 4-17, which indicates that the slight correlation

between the water vapour flux and mercury flux in Figure 4-13 might be due to the influence of another environmental parameter (e.g. soil moisture) on both the two fluxes.

The 3L rain event data and the correlation between the water vapour flux and mercury flux are also presented in Figure 4-18 and Figure 4-19, respectively. Although both the mercury flux and water vapour flux had many perturbations during this event, these perturbations in both fluxes appear to be unrelated as indicated in Figure 4-19.

In summary, the water vapour flux does appear to have a weak positive correlation with mercury emissions in the drying process, but this influence is not significant enough to control mercury emissions.

Figure 4-8: Hg fluxes and water vapour flux for the first single rain event, normalized to 20°C

Figure 4-9: Hg fluxes and water vapour flux for the second single rain event, normalized to 20°C

Figure 4-10: Correlation between mercury flux and water vapour flux for the first single rain event

Figure 4-11: Correlation between mercury flux and water vapour flux for the second single rain event

Figure 4-12: Hg flux and water vapour flux for the double rain event, normalized to 20°C

Figure 4-13: Correlation between the Hg flux and water vapour flux for the double rain event

Figure 4-14: Hg flux and water vapour flux for the triple rain event with a 1-day and 5-day delay

Figure 4-15: Correlation between Hg flux and water vapour flux for the triple rain event with a 1-day and 5-day delay

Figure 4-16: Hg flux and water vapour flux for the triple rain event with an 8-day and 5-day delay

Figure 4-17: Correlation between Hg flux and water vapour flux for the triple rain event with an 8-day and 5-day delay

Figure 4-18: Hg flux and water vapour flux for the 3L rain event

Figure 4-19: Correlation between Hg flux and water vapour flux for the 3L rain event

4.4 Soil moisture and Hg flux

As discussed previously, the mercury emission is not only related to the volume of infiltrating rain water, but also the soil moisture before the rain event. To further investigate the enhancement of mercury emissions by a precipitation event, the relationship between soil moisture and the mercury flux for the different precipitation events were analyzed.

4.4.1 Single rain events

Correlations between soil moisture and the mercury flux for both single rain events are presented in Figure 4-20. Each single circle represented one run of single rain event. Wetting process and drying process in all the rain events were differentiated with color for a better presentation. As presented in Figure 4-20, the smaller peak in the mercury flux for the second single rain event suggested a depletion of Hg in the soil matrix. The curves show a repeatable pattern between the surface soil moisture and mercury volatilization during the drying process of the single rain events. This pattern indicated a correlation between the surface soil moisture and the mercury emission flux, as the two curves had an analogous decreasing pattern with time (see Figure 4-2 and Figure 4-3).

4.4.2 Double rain event

A correlation between the mercury flux and soil moisture for the double rain event is presented in Figure 4-21. Different from in the single rain events, the two drying curves

after the two rain events did not show a similar repeating pattern between the mercury flux and the surface soil moisture, although low mercury fluxes always corresponded to low surface soil moistures in both drying processes. This behaviour between the mercury flux and surface soil moisture suggested that the magnitude of infiltrating rain water was not the only controlling factor in the enhancement of the mercury emission flux in the precipitation events.

4.4.3 Triple rain events at different soil moistures

Correlations between the mercury flux and surface soil moisture at 1cm for the triple rain events (with a 1-day and 5-day delay and an 8-day and 5-day delay) are presented in Figure 4-22 and Figure 4-23, respectively. Similar to the double rain event, the curves for the three drying processes showed different relationships between the mercury flux and soil moisture, which was determined by the wetting/drying cycles of the soil.

Shown in Figure 4-22 and Figure 4-23, dryer surface soil moisture before the rain event led to a stronger positive correlation between the soil moisture and mercury flux at the beginning of the drying process after the precipitation event. As shown in Figure 4-22 and Figure 4-23, once the soil moisture dropped to about $0.15\text{m}^3/\text{m}^3$ during the drying process, however, the curves of the drying processes started to converge to one pattern, whatever the initial soil moisture was before the precipitation event.

Figure 4-20: Correlation between Hg fluxes and surface soil moisture for the single rain events

Figure 4-21: Correlation between the Hg flux and surface soil moisture for the double rain event

Figure 4-22: Correlation between Hg flux and surface soil moisture for the triple rain event with a 1-day and 5-day delay

Figure 4-23: Correlation between Hg flux and surface soil moisture for the triple rain event with an 8-day and 5-day delay

4.4.4 Transitional soil moisture and precipitation enhancement factor

Based on the observation of the data of six different experiments, a negative relationship between the surface soil moisture before a precipitation event and the enhancement of mercury emissions after a precipitation event is indicated. In other words, the higher surface soil moisture before the rain event, the less elevation in mercury emissions is generated after the rain event. A transitional soil moisture before precipitation is indicated, above which the mercury emission can not be promoted more than before the precipitation event.

To further investigate the effect of the surface soil moisture before a precipitation event on the enhancement of mercury emissions, the surface soil moistures and the mercury fluxes before and after a precipitation event (SM_{BF} , SM_{AFT} , $F_{Hg,BF}$, $F_{Hg,AFT}$, respectively) in the six experiments (only 1L rain event experiments are included) are summarized in Table 4-1. An example annotating aforementioned soil moistures and mercury fluxes in the first single rain event is given in Figure 2-24.

As shown in Table 4-1, data for ten different rain events in six experiments are listed and ranked by the soil moisture before a precipitation event. The precipitation enhancement factor f is defined as:

$$f = \frac{F_{Hg,AFT} - F_{Hg,BF}}{F_{Hg,BF}} \quad (4.1)$$

A plot of the precipitation factor f versus the surface soil moisture before a rain event SM_{BF} in Table 4-1 is presented in Figure 4-25. The precipitation enhancement factor f

and the corresponding surface soil moisture at 1cm before precipitation SM_{BF} follows a good negative correlation in the form of $f = 137.67e^{-48.062SM_{BF}}$ ($R^2 = 0.8782$) as presented in Figure 4-25. As indicated in the graph, the dryer soil before a precipitation event, the greater enhancement in the mercury flux will be promoted after the rain event. Once the surface soil moisture reaches and exceeds the transitional soil moisture (in a range of 13% ~ 15%), the precipitation enhancement of mercury emissions approaches zero.

Figure 4-24: Surface soil moisture and Hg flux before and after the first single rain event

Table 4-1: Summary of soil moistures and mercury fluxes before and after a precipitation event in the six experiments

Rain event	SM _{BF}	$F_{Hg, BF}$	SM _{AFT}	$F_{Hg, AFT}$	Precipitation enhancement factor
1 st single	0.04340	0.2199	0.2468	2.833	11.88
1 st rain event in double	0.05672	0.1917	0.1744	3.329	16.37
2 nd single	0.06457	0.2716	0.2256	1.699	5.254
1 st rain event in triple-1-5	0.06619	0.5271	0.2293	2.522	3.786
1 st rain event in triple-8-5	0.07257	0.1788	0.2061	1.022	4.716
3 rd rain event in triple-8-5	0.1117	0.3700	0.2264	0.7189	0.9430
2 nd rain event in triple-8-5	0.1277	0.3718	0.1856	0.7074	0.9026
3 rd rain event in triple-1-5	0.1321	0.9059	0.2293	1.119	0.2353
2 nd rain event in double	0.1483	2.275	0.2367	2.315	0.01790
2 nd rain event in triple-1-5	0.1731	1.520	0.2558	1.610	0.05950

(Note: triple-8-5 represents triple rain event with an 8-day and 5-day delay; triple-1-5 means triple rain event with a 1-day and 5-day delay. SM_{BF} is the surface soil moisture before a rain event, while SM_{AFT} is the surface soil moisture after a rain event.)

As discussed in Section 4.2.4.3, the mobility of Hg (II) (the dissolution of Hg (II) from soil particles into the soil solution) is possibly the controlling process in mercury emissions after a rain event, which is limited by the contact surface area of soil particles with water. When the soil moisture reaches possibly the transitional level (13% ~ 15%), the mobility of Hg (II) reaches an equilibrium, as the contact surface area of soil particles with water reaches maximum. As a consequence, the aqueous redox reaction of reactive Hg (II) can not be promoted to enhance the mercury emission after a rain event event.

Figure 4-25: Precipitation enhancement factor versus surface soil moisture before a rain event for 6 experiments

Enhancement in mercury emissions after a 1L rain event from this type of soil substrate can be predicted based on the exponential relationship between the precipitation enhancement factor and surface soil moisture for a rain event, which helps modellers deal with one type of major climate changes, precipitation in the Hg emission inventories.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

In an attempt to investigate the underlying mechanism of precipitation effects on mercury volatilization from soils, a DFC system incorporated with a precipitation generator and a gaseous mercury analyzer (Tekran[®] 2537A) was designed. A series of laboratory experiments were performed under controlled conditions to isolate the effects of precipitation on mercury emission from bare soils based on this laboratory DFC system. Several conclusions have been drawn based the analysis of experimental results and are summarized below, followed by recommendations for future research in terms of experimentation and instrumentation improvement.

5.1 Conclusions

In terms of the hypothesized controlling processes in the enhancement of soil mercury volatilization in response to precipitation event, it can be concluded that:

- a reliable laboratory DFC system with an internal precipitation generator has been successfully designed and applied to simulate field-observed enhancement in mercury emissions in response to precipitation under different soil conditions.
- water vapour flux does have a slight positive correlation with mercury soil emissions, but it is not responsible for the enhancement of the mercury emission flux in response to precipitation.

- the spike in mercury emissions during the rain event is due to the physical displacement of Hg-containing interstitial soil air by infiltrating rain water.
- the mercury flux emitted from soils after a rain event is dependent on not only the quantity of infiltrating rain water but also the soil moisture content prior to the rain event.
- A correlation between the precipitation enhancement of mercury emission after a rain event and the surface soil moisture prior to a rain event has been obtained based on experimental data. The mercury emission can not be promoted after more than before a rain event, when the surface soil moisture reaches or exceeds the transitional soil moisture range of 13% ~ 15%.
- the controlling mechanism during the drying process is possibly the mobility of Hg (II) from soil particle phase to soil solution, which is limited by the contact surface area of soil particles with water.

5.2 Recommendations

According to the limitations of the experimental apparatus and methodology and new discoveries made during the experiments, some recommendations for future work include:

- to eliminate the effect of fluctuations of the relative humidity at the inlet of the chamber, inlet air with controllable RH (~100%) is recommended to be used as the flushing air.

- Hg speciation in the soil matrix is strongly needed to obtain a better understanding of the mechanism of the specific aqueous redox reactions of Hg (II), as well as the mobility potential for each Hg (II) species.
- Experiments on rain duration are recommended to look at precipitation effects on the mercury volatilization from soils at different soil moistures, especially when the soil moisture exceeds the field capacity after the rain event.
- Experiments on light effects on mercury emissions are recommended to be conducted, as a noticeable enhancement in mercury emission flux has been observed in this research.

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APPENDIX A: INSTRUMENT CALIBRATION

A.1 System cleaning and chamber blank test

Before the chamber blank test, the system was cleaned to remove absorbed mercury. All the tubing, the flux chamber, the precipitation generator and the soil lysimeter were acid soaked and washed by 0.1% nitric acid (U.S. EPA, 1999), rinsed by deionized water, and eventually air-dried.

Due to the requirement of continuous data collection in the experiments and stable indoor environmental conditions, the blank tests were not executed during the running experiments but operated before the first and after the last experiment. The chamber was separated from the soil substrate and the rain generator, with the top and bottom of the chamber covered by polycarbonate boards. Using the same material for the top and bottom cover as for the chamber body ensured similar sorption/desorption properties inside the chamber. The inlet and outlet mercury concentration was regularly taken by the Tekran[®] for 24 hours to measure the blank concentration inside the chamber.

The blank was calculated by using (Kemp, 2001):

$$Blank = (C_{outlet} - C_{inlet}) \cdot Q / A \cdot CF \quad (A.1)$$

where C_{outlet} (ng m⁻³) is the mercury concentration leaving the chamber, C_{inlet} (ng m⁻³) is the mercury concentration before entering the chamber, Q (23 L min⁻¹) is the flushing flow rate, A (0.0613m²) is the area of the base the chamber, and CF (1000×60)⁻¹ is the units correction factor. Obtained by averaging the blank value through the two blank test

results, the blank of this chamber was $0.000356 \text{ ng m}^{-2}\text{s}^{-1}$, showing no significant change before and after the test.

The mercury fluxes were corrected by using (Kemp, 2001):

$$Flux_{corrected} = Flux_{uncorrected} - Blank \quad (A.2)$$

The blank can be positive or negative. Positive blank indicates the mercury adsorption on the chamber interior walls, while the negative blank indicates the mercury desorption from the chamber. In this case, a negligible mercury adsorption inside the chamber was indicated, since the blank was only 0.3% of the average mercury flux measured in all the experiment.

A.2 Calibration of the Tekran[®] mercury analyzer

The Tekran[®] mercury analyzer was auto-calibrated before and after each experimental run. A full calibration included cleaning, zero, and span operation on both cartridges of the Tekran[®] analyzer. Clean operation was executed to purge the cartridges before the zero and span operation. Based on the zero and span operation results, a linear calibration curve was determined to present the relationship between the span peak area and the mass of mercury as shown in Figure A-1.

Zero operation was conducted to find the blank area (Blarea in Figure A-2), the peak area when no mercury was supplied to either of the cartridges. A known quantity of mercury,

Figure A-1: Calibration curve of the Tekran® mercury analyzer

from an interior mercury source, was collected onto each cartridges of the Tekran® analyzer in sequence. The source mercury concentration (SC) was usually the same with a value of 14.096 ng/m^3 on two cartridges, while span peak area (Sparea) varied from each calibration runs as a response to this known mass of mercury (point A). The Blarea was zeroed to calibrate the curve going through the origin. The adjusted span peak area (Adjarea) (point B) was obtained by subtracting Blarea from Sparea. In doing so, the detected TGM was proportionally reflected by the ratio of the detected mercury peak area to Adjarea.

A.3 Calibration of TDR soil moisture probes

As introduced in Chapter 3, Styrofoam blocks were used to cover the exposed part of the TDR probes and to block off air condition variation effects on the probes (shown in

Figure 3-6). Although not sensitive to the surrounding air condition changes, the electrical conductivity of Styrofoam is still different from the soil.

Figure A-2: Calibration curve of the TDR soil moisture probes
(Note: SM in the linear fit equation represents soil moisture)

The calibration experiment was carried out using a soil bucket deep enough to plug in the whole TDR probe. The bucket was filled with air-dried soil. Soil moistures were measured both (1) with the bare probe completely buried in the soil and (2) with the probe partly covered by the Styrofoam block and the rest in the soil. After each set of measurement, a certain amount of water was added to the soil bucket to change the water content in the bucket, and the measurement was repeated until the soil moisture

approached 0.7, which was great enough to include the field capacity (0.25) in the effective range of the calibration curve.

The calibration curve is plotted and regressed based on the experimental soil moisture data. Due to the stable electrical conductivity of Styrofoam, the relationship between the raw soil moisture measured by the probes with the measurement error with Styrofoam on the probes was linear in the form of:

$$SM_{\text{calt}} = 1.0796 \cdot SM_{\text{raw}} + 0.00489 \quad (\text{A.3})$$

This relationship is also presented in Figure A-2.

APPENDIX B: SAMPLE CALCULATIONS

B.1 Saturated hydraulic conductivity

As introduced in Chapter 3, the saturated hydraulic conductivity was measured using a falling head method. The basic principle is presented as Equation (3.2) in Chapter 3. Following the experimental procedure introduced in Chapter 3, the experiment was repeated three times and with the results presented in Table B-1.

Test no.	h_1 , cm	h_2 , cm	t , s	a , cm^2	A , cm^2	L , cm
1	176.8	135.7	65.9	1.13	63.6	13.3
2	176.8	135.7	67.3			
3	176.8	135.7	67.6			

Table B-1: Results of the falling head experiment

The three sets of experimental results were substituted back into Equation (3.2), and the calculated saturated hydraulic conductivities (k) were averaged to obtain a value of 9.26×10^{-6} m/s.

B.2 Water vapour flux, estimation based on rain volume

For the sample calculations on the water vapour flux, a set of raw data on Jan. 23 from the first rain event was used. Relevant parameters are listed below:

$$T_{\text{inlet}} = 19.822^\circ\text{C} = 292.97\text{K}, T_{\text{outlet}} = 19.715 = 292.86\text{K}.$$

$$RH_{\text{inlet}} = 16.447, RH_{\text{outlet}} = 62.676.$$

In addition, the flushing flow rate was $Q = 23\text{L/min} = 0.000382\text{m}^3/\text{s}$ and the substrate area was $A = 0.0613\text{m}^2$.

The saturation water vapour pressure was calculated using a correlation with temperature (Daubert and Danner, 1981):

$$e_s = \exp\left(73.679 - \frac{7.2582 \times 10^3}{T} - 7.3037 \times \ln T + 4.1653 \times 10^{-6} \times T^2\right) \quad (\text{B.1})$$

where e_s is the saturation vapour pressure (Pa) and T is the temperature (K). Taking $T_{\text{inlet}} = 292.97\text{K}$ and $T_{\text{outlet}} = 292.86\text{K}$ into Equation (B.1), gives:

- $e_{s, \text{inlet}} = 2312.6\text{Pa}$
- $e_{s, \text{outlet}} = 2298.3\text{Pa}$

According to the definition of relative humidity, the actual water vapour pressure was calculated using:

$$e = e_s \cdot RH\% \quad (\text{B.2})$$

where e is the actual water vapour pressure, e_s is the saturation water vapour pressure (Pa) at the same temperature, and $RH\%$ is the relative humidity at the same temperature.

Taking $RH_{\text{inlet}} = 16.447$, $RH_{\text{outlet}} = 62.676$, $e_{s, \text{inlet}} = 2312.6\text{Pa}$, and $e_{s, \text{outlet}} = 2298.3\text{Pa}$ into Equation (B.2), gives:

- $e_{\text{inlet}} = 380.5\text{Pa}$
- $e_{\text{outlet}} = 1440.5\text{Pa}$

The water vapour density was derived from the ideal gas law:

$$\rho_{\text{wv}} = \frac{e \cdot MW}{R^* T} \quad (\text{B.3})$$

where ρ_{wv} is the water vapour density ($\text{g} \cdot \text{m}^{-3}$), e is the actual water vapour pressure (Pa), MW is the molecular weight of water ($18 \text{g} \cdot \text{mol}^{-1}$), R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$), and T is the temperature (K). Taking the inlet values $e_{\text{inlet}} = 380.5 \text{ Pa}$ and $T_{\text{inlet}} = 292.97 \text{ K}$ and outlet values of $e_{\text{outlet}} = 1440.5 \text{ Pa}$ and $T_{\text{outlet}} = 292.86 \text{ K}$ into Equation (B.3), gives:

- $\rho_{\text{wv, inlet}} = 0.002818 \text{ kg/m}^3$
- $\rho_{\text{wv, outlet}} = 0.010654 \text{ kg/m}^3$

Similar to the calculation of mercury fluxes, water vapour fluxes were estimated using:

$$F_{\text{wv}} = \frac{Q \cdot (\rho_{\text{wv, outlet}} - \rho_{\text{wv, inlet}})}{A} \cdot CF \quad (\text{B.4})$$

where F_{wv} is the water vapour flux ($\text{g} \cdot \text{m}^{-2} \text{s}^{-1}$), Q is the flushing flow rate ($23 \text{ L} \cdot \text{min}^{-1}$), $\rho_{\text{wv, out}}$ and $\rho_{\text{wv, in}}$ are the water vapour density at the inlet and outlet of the chamber, A is the surface area of the soil substrate (0.0613 m^2), and $CF (1000 \times 60)^{-1}$ is a unit correction factor. Taking $\rho_{\text{wv, inlet}} = 0.002818 \text{ kg/m}^3$ and $\rho_{\text{wv, outlet}} = 0.010654 \text{ kg/m}^3$ into Equation (B.4), results in a water vapour flux of $F_{\text{wv}} = 0.04898 \text{ g m}^{-2} \text{s}^{-1}$.

The calculation of water vapour flux was checked by the rough estimation of the maximum average water evaporation rate. The total volume of rain water applied in this experiment was 1L. According to Figure 4-2, the drying process lasted for at least 4 days to bring the surface soil moisture back to the initial conditions. With a substrate area of 0.0613 m^2 , the maximum average water vapour flux can be estimated by:

$$F_{\text{wv, max}} = \text{Mass of rain water} / (\text{time} \times \text{substrate area}) = 0.0472 \text{ g m}^{-2} \text{s}^{-1}$$

In the meantime, the average water vapour flux after the rain event for the first single rain event calculated using Equation (B.1) ~ (B.4) is $0.04061 \text{ g m}^{-2}\text{s}^{-1}$, which was comparable but smaller than the estimated $F_{\text{wv,max}}$. This indicates that the drying process was longer than 4 days and collaborated the results of the calculation method used for the water vapour flux.

B.3 Normalization of mercury flux, water vapour flux, RH

As mentioned in Chapter 4, to correct the temperature effect on the mercury flux, water vapour flux and relative humidity at the inlet and outlet of the chamber, the raw data were normalized to 20°C .

The same set of raw data on Jan 23 for the first single rain event was used for the sample calculations listed below:

$T_{\text{soil, 7cm}}$ ($^\circ\text{C}$)	$T_{\text{soil, 15cm}}$ ($^\circ\text{C}$)	T_{inlet} ($^\circ\text{C}$)	T_{outlet} ($^\circ\text{C}$)	T_{average} ($^\circ\text{C}$)	RH_{inlet}	RH_{outlet}	Hg flux ($\text{ng m}^{-2}\text{s}^{-1}$)
18.108	18.2	19.822	19.715	18.961	16.447	62.676	3.2303

Table B-2: A set of raw data from the first single rain event

where T_{average} is the average temperature of the two soil temperatures and the air temperature at the inlet and outlet of the chamber to present the surface soil temperature that was required in normalization of the mercury flux. Detailed derivations and calculations are included in this section.

B.3.1 Mercury flux

Mercury fluxes were normalized to 20°C based on the strongest empirical correlation – (Arrhenius equation) between the mercury emission rate and soil temperature (Scholtz *et al.*, 2003), described as:

$$\ln(F_{Hg}) = \ln A' - \frac{E_a}{RT} \quad (B.5)$$

where F_{Hg} is the elemental mercury flux ($\text{ng m}^{-2}\text{s}^{-1}$), A' is a correlation constant, E_a is the activation energy with a value of 14kcal/mol, R is the gas constant with a value of 8.314J $\text{mol}^{-1} \text{K}^{-1}$, and T is the soil temperature (K).

Based on Equation (B.5), F_{Hg} at certain temperature can be expressed as:

$$F_{Hg,T} = A' \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (B.6)$$

With $T = 293\text{K}$ (20°C), F_{Hg} can be expressed as:

$$F_{Hg,293K} = A' \cdot \exp\left(-\frac{E_a}{R \cdot 293}\right) \quad (B.7)$$

Therefore, the mercury flux normalized to 20°C can be calculated using:

$$F_{Hg,293K} = F_{Hg,T} \left[\exp\left(-\frac{E_a}{R \cdot 293} + \frac{E_a}{RT}\right) \right] \quad (B.8)$$

Taking $T_{\text{average}} = 18.961^\circ\text{C} = 292.11\text{K}$ into Equation (B.8) gives $F_{Hg,293K} = 4.044 \text{ ng m}^{-2}\text{s}^{-1}$, which is greater than the original value $3.7148 \text{ ng m}^{-2}\text{s}^{-1}$ due to the positive correlation between the mercury flux and temperature.

B.3.2 Relative humidity and water vapour flux

Based on the definition of relative humidity, the normalized relative humidity can be calculated using:

$$RH\%_{293K} = \frac{e}{e_{s, 293K}} \quad (B.9)$$

where e is the actual water vapour pressure (Pa) at the real temperature, introduced earlier in this chapter, and $e_{s, 293K}$ is the saturation water vapour pressure (Pa), calculated using Equation (4.1). Taking $e_{inlet} = 380.5\text{Pa}$, $e_{s, inlet} = 2312.6\text{Pa}$, $e_{outlet} = 1440.5\text{Pa}$ and $e_{s, outlet} = 2298.3\text{Pa}$ as calculated in Section B.2, gives:

- $RH_{inlet, 293K} = 16.27$
- $RH_{outlet, 293K} = 61.58$

Normalized water vapour flux was calculated using Equation (B.3) and (B.4) but with the normalized relative humidity $RH_{inlet, 293K} = 16.27$, $RH_{outlet, 293K} = 61.58$ with $T = 293\text{K}$. Therefore, $F_{wv, 293K} = 0.04898\text{g m}^{-2}\text{s}^{-1}$.

Comparisons between the original and normalized mercury flux, water vapour flux and relative humidity at the inlet and outlet of the chamber are presented in Figure 4-3. Shown in the graphs, normalized mercury flux was greater than the original values with an average increase of $0.3\text{ng m}^{-2}\text{s}^{-1}$, since the experiment was done in the winter at an average temperature around 19°C . Normalized relative humidity at the inlet and outlet of the chamber were lower than the original values, due to a lower saturation vapour pressure at higher temperatures. Compared to the relative humidity and mercury flux,

water vapour flux was slightly lower after normalization, due to a slight decrease in the relative humidity difference between the inlet and outlet of the chamber.

B.4 Calculation check for physical displacement

As introduced in Chapter 4, a calculation check was done to justify the hypothesis that the temporary increase in the mercury flux during the rain event was due to a physical displacement of Hg-containing interstitial soil air by infiltrating rain water.

As indicated in Figure 4-2, the mass of Hg contributing to the temporary increase (the area between the two bars) in the Hg flux spike was calculated using:

$$M_{Hg} = \sum_{i=0}^{i=11} \left(\frac{(F_{Hg,i} + F_{Hg,i+1})}{2} - F_{Hg,AFT} \right) \cdot t \cdot A \quad (B.10)$$

where M_{Hg} (ng) is the total mass of mercury, F_{Hg} (ng m⁻²s⁻¹) is the raw mercury flux in Table B-2, $F_{Hg,AFT}$ is the mercury flux after the spike in response to the rain event (2.776 ng m⁻²s⁻¹), i is the numbering of the mercury flux in the table, t (20min) is the sampling interval, and A is the soil surface area covered by the chamber (0.0613m²). The raw data of the mercury flux during this time is listed in Table B-3. Taking all the data in Table B-3 into Equation (B.10), the total mass of Hg in the temporary increase is 952.4ng.

Figure B-1: Original and normalized Hg flux and other parameters for the first single rain event

Time (min)	Hg flux (ng m ⁻² s ⁻¹)
0	2.598
20	4.044
40	4.681
60	4.878
80	4.905
100	4.680
120	4.418
140	4.104
160	3.258
180	2.979
200	2.850
220	2.776

Table B-3: Hg flux in the peak from the first single rain event

To demonstrate that the increase in the mercury flux during the rain event was the result of gaseous mercury in the interstitial soil air being displaced by 1L of rain water, the mass of mercury in 1L of interstitial air was also calculated as below.

In general, the equilibrium ratio of Hg (II)/Hg (0) in soil particle phase is 0.99/0.01 (McKay *et al.*, 1995). The total mercury concentration in the soil was measured at 290g/g soil using acid digestion (University of Guelph Laboratory Services, 2003). Therefore, the Hg (0) concentration in soil particle phase can be estimated as: $C_{S,Hg(0)} = C_{S,Hg(II)} \times 0.01/0.99 = 290\mu\text{g/g} \times 0.01/0.99 \times 10^{-3} \text{ g g}^{-1} \mu\text{g kg}^{-1} = 0.00293\text{g/kg}$.

In general, the adsorbed-liquid partitioning relationship of Hg (0) follows (Scholtz *et al.*,

2003):

$$C_s = K_D C_l \quad (\text{B.11})$$

where C_s (g/kg soil) is the mercury concentration in soil particle phase, K_D (m^3/kg) is the adsorbed-liquid partition coefficient, and C_l (g/m^3 soil solution) is the mercury concentration in the soil. This partition coefficient K_D has a relationship with organic carbon distribution coefficient K_{OC} as:

$$K_{OC} = K_D / f_{OC} \quad (\text{B.12})$$

where f_{OC} is the fraction of organic carbon in the soil ($f_{OC} = 1.31\%$ in Table 3-1).

The vapour-liquid partition is assumed to follow a linear relationship given by Henry's law as:

$$C_g = K_H C_l \quad (\text{B.13})$$

where C_g is mercury concentration in soil air phase, K_H is Henry's law constant and C_l mercury concentration in liquid phase. Henry's law constant varies with temperature and is approximated by the Clausius-Clapeyron equation (Scholtz *et al.*, 2003):

$$\ln \left(\frac{K_H(T_1)}{K_H(T_2)} \right) = - \frac{\Delta H_f}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{B.14})$$

where T_1 , T_2 are temperatures in Kelvin, R is the gas constant with a value of 8.314 J/mol/K, and ΔH_f is the enthalpy of phase change (KJ/mol). Partition coefficients and related properties of Hg (0) are listed in Table B-4 (McKay *et al.*, 1995).

	K_H at 25°C	K_{OC} (m^3/kg)	ΔH_f (kJ/mol)
Hg (0)	0.32	20	20

Table B-4: Partition coefficients and enthalpies of phase change for mercury species (adapted from McKay *et al.* 1995)

Taking K_H at 25°C and ΔH_f value in Table B-4 into Equation (B.14), Henry's constant of Hg (0) at 20°C is $K_{H, \text{Hg}(0)}(20^\circ\text{C}) = 0.271$. Based on Equation (B.12), $K_{D, \text{Hg}(0)} = K_{OC} f_{OC} = 0.262 \text{ m}^3/\text{kg}$.

The Hg (0) concentration in soil solution $C_{L, \text{Hg}(0)} = C_{S, \text{Hg}(0)} / K_D = 0.00293 \text{ g/kg} / 0.262 \text{ m}^3/\text{kg} = 0.0112 \text{ g/m}^3$ soil solution. Taking $C_{L, \text{Hg}(0)} = 0.0112 \text{ g/m}^3$ soil solution in Equation (B.13), the equilibrium Hg (0) concentration in soil air is $C_{G, \text{Hg}(0)} = C_{L, \text{Hg}(0)} K_{D, 293\text{K}} = 0.0032 \text{ g/m}^3$ air.

Therefore the total mass of displaceable Hg (0) in 1L of air can be calculated as:

$$M_{\text{Hg}(0)} = 0.0032 \text{ g/m}^3 \text{ air} \times 0.001 \text{ m}^3 \times 10^9 \text{ ng/g} = 3200 \text{ ng}$$

This value is a theoretical maximum and greater than the mass of Hg (0) measured during the rain event of $M_{\text{Hg}(0)} = 966.3 \text{ ng}$. The larger mass calculated using a theoretical approach assumes equilibrium conditions between all three phases and that all of the mercury in the soil phase is readily available and mobile. This calculation, however, demonstrates that the temporary and sharp increase in the mercury flux during the rain event can be readily explained by the physical displacement of the soil air by incoming rain water.

APPENDIX C: ERROR ANALYSIS

C.1 Direct measurement errors

Direct measurement errors contain the uncertainty contained within the measured experimental variables, which are usually ingrained with the accuracy of the instruments. The directly measured parameters include air temperature, relative humidity, soil temperature, soil moisture, flushing flow rate and mercury concentration. Calculations of direct measurement errors based on instrument accuracy are given below.

C.1.1 Relative humidity and air temperature

Relative humidity and air temperature at the inlet and outlet of the chamber was measured by CS500 Temperature and Relative Humidity Probes (Campbell-Scientific Inc., 1994). The temperature measurement range is between -40°C to 60°C . The accuracy of temperature measurement is $\pm 0.4^{\circ}\text{C}$ when the average temperature is around 20°C (Campbell-Scientific Inc., 1994), while the relative error $E_r(T)$ around 20°C is $\pm 2\%$. The accuracy for relative humidity measurement $E_r(RH)$ is $\pm 3\%$ for the range of 10 to 90% and $\pm 6\%$ for the range of 90 to 100% (Campbell-Scientific Inc., 1994). As the RH values in the experiments were predominantly in the range of 10 ~ 90%, $E_r(RH)$ is considered as $\pm 3\%$.

C.1.2 Soil temperature

The soil temperatures at two different depths were measured using Copper - constantan soil thermocouples (Brock, 1994) with an accuracy of $\pm 0.8^{\circ}\text{C}$. Considering the average measured soil temperature of 20°C , the relative accuracy of soil moisture $E_r(T_s)$ is $\pm 4\%$.

C.1.3 Soil moisture

TDR100 soil moisture probes were used to measure soil moistures in this research. The accuracy of these probes is $\pm 0.5\%$ (Campbell-Scientific Inc., 2002). Considering a maximum soil moisture value of $0.3 \text{ m}^3 \text{ water/m}^3 \text{ soil}$, the absolute error of soil moisture is $\pm 0.0015 \text{ m}^3 \text{ water/m}^3 \text{ soil}$.

C.1.4 Flushing flow rate

The flushing flow rate was measured by a high-flow correlated flowmeter (Cole-Parmer Instrument Company, 2004). The accuracy of this flowmeter is $\pm 2\%$ full-scale. Considering a flow rate of 23 L/min , the absolute error of the flow rate is $\pm 0.46 \text{ L/min}$.

C.1.5 Hg concentration

A Tekran[®] Mercury Vapour Analyzer (Model 2537A) was used to measure the mercury concentration at the inlet and outlet of the chamber. The calibration is generally considered accurate if the calibration source is within $\pm 5\%$ of expected concentrations. Only interior permeation source was applied for calibration through the entire course of experimentation, and is considered fairly accurate with the relative errors around $\pm 5\%$.

C.2 Propagation of errors into other results

The direct measurement errors are transferred into the following parameters that are calculated based on directly measured parameters introduced previously. If express the indirectly measured parameter y is expressed as a function of directly measured parameters x_i , the relationship can be written as: $y = f(x_1, x_2, \dots, x_n)$. The errors of indirectly measured values were calculated using a root-sum-square (RSS) method (John, 1982) which is given by:

$$D(y) = \left(\sum_{i=1}^n D(x_i)^2 \right)^{1/2} \quad (C.1)$$

where $D(y)$ is the absolute error of the indirectly measured values, and $D(x_i)$ is the absolute error of different directly measured values. The relationship of the relative error and absolute error is give by (John, 1982):

$$E_r(y) = D(y)/|y| \quad (C.2)$$

where E_r is the relative error, and $|y|$ is the absolute value of the average measured parameter. Therefore, E_r can be expressed as (John, 1982):

$$E_r(y) = \frac{D}{|y|} = \sqrt{\sum_{i=1}^n \left(\frac{\partial y}{\partial x_i} \cdot \frac{D(x_i)}{y} \right)^2} \quad (C.3)$$

C.2.1 Hg flux

According to Equation (2.5) and Equation (C.3), the relative error of the calculated mercury flux can be written as:

$$E_r(HgF) = \sqrt{(E_r(HgC))^2 + (E_r(Q))^2} \quad (C.4)$$

where HgF is mercury flux, HgC is mercury concentration, and Q is flow rate. As $Er(HgC)$ is 5% and $Er(Q)$ is $\pm 2\%$, the propagated $Er(HgF) = \pm 5.38\%$, which is mainly from the errors in mercury concentration measurement.

C.2.2 Water vapour flux

Recalling Equation (B.1) ~ (B.4) used for the water vapour flux calculation.

$$e_s = \exp\left(73.679 - \frac{7.2582 \times 10^3}{T} - 7.3037 \times \ln T + 4.1653 \times 10^{-6} \times T^2\right) \quad (B.1)$$

$$e = e_s \cdot RH\% \quad (B.2)$$

$$\rho_{wv} = \frac{e \cdot MW}{R^* T} \quad (B.3)$$

$$F_{wv} = \frac{Q \cdot (\rho_{wv, outlet} - \rho_{wv, inlet})}{A} \cdot CF \quad (B.4)$$

Incorporating Equation (B.1) and Equation (C.1), the relative error of e_s is given as:

$$E_r(e_s) = \frac{D(e_s)}{|e_s|} = \frac{\sqrt{\left(\frac{\partial e_s}{\partial T_{ave}} D(T)\right)^2}}{|e_s|} \quad (C.5)$$

$$= \sqrt{D^2(T) \left(\frac{7.2582 \times 10^3}{T^2} - \frac{7.3037}{T} + 2 \times 4.1653 \times 10^{-6} \times T \right)^2}$$

Considering an average temperature of 20°C, the absolute error of T is $\pm 0.4^\circ\text{C}$. Taking

$D(T_{ave})$ back to Equation (C.5), $E_r(e_s) = \pm 2.48\%$.

Incorporating Equation (B.2) and Equation (C.1), the relative error of e is given as:

$$E_r(e) = \sqrt{(E_r(e_s))^2 + (E_r(RH))^2} = \sqrt{(\pm 2.48\%)^2 + (\pm 3\%)^2} = \pm 3.89\%$$

Incorporating Equation (B.3) and Equation (C.1), the relative error of ρ_{wy} is given as:

$$E_r(\rho_{wy}) = \sqrt{(E_r(\varphi))^2 + (E_r(T))^2} = \sqrt{(\pm 3.89\%)^2 + (\pm 2\%)^2} = \pm 4.37\%$$

Incorporating Equation (B.4) and Equation (C.1), the relative error of F_{wy} is given as:

$$E_r(F_{wy}) = \sqrt{(E_r(\rho_{wy}))^2 + (E_r(Q))^2} = \sqrt{(\pm 4.37\%)^2 + (\pm 2\%)^2} = \pm 4.81\%$$

which is mainly due to the errors in air temperature measurement.

APPENDIX D. SOURCE CODES

D.1 Main Program for NI-DAQ Card

Note: The programming language is in C code.

```
/* Preprocessor Directives */

/*Written by Gireesh Dharwar*/
/*Calculates flux from inlet and outlet of chamber*/
/*Interfaced with datalogger to collect 10 minute averages from temperature/RH probes.
2 thermocouples. and 4 TDR soil moisture probes*/
/*these parameters are also reported on the screen and written to file*/

#include <stdio.h>
#include <conio.h>
#include <time.h>    /* time functions header */
#include <string.h>  /* string functions header */
#include <stdlib.h>  /* standard library header */
#include <graphics.h> /* graphics header */
#include "nidaq.h"   /* NI-DAQ function definitions */
#include "nidaqerr.h" /* NI-DAQ error code definitions */
#include "nidaqcns.h" /* NI-DAQ constants definitions */

/* Function Prototypes */
int menu (void);          void initCard (void);
void data (void);

/* *****Global Variable List***** */
/* NI-DAQ Variables */
int deviceNumber = 1. /* AT-MIO-16X is device number 1 */
err.             /* the error code for the NIDAQ calls */
gain[8] = {1, 1, 1, 1, 1, 1, 1, 1}. /* gain for all channels */
chan = 1.        /* position of the valves - upper or lower */
portA = 0.       /* digital port used to control Tekran One */
portB = 1.
lineNo0 = 0.     /* line number zero - ??? */
lineNo1 = 1.     /* line number one - cartridge B */
lineNo2 = 2.     /* line number two - chart output status */
lineNo3 = 3.     /* line number three - ??? */

stateA0.        /* status of bit A0 */
stateA1.        /* status of bit A1 */
stateA2.        /* status of bit A2 */
stateA3.        /* status of bit A3 */
```

```

stateB0.          /* status of bit B0 */
stateB1.          /* status of bit B1 */
stateB2.          /* status of bit B2 */
stateB3:          /* status of bit B3 */

/* Graphing Range Parameters */
float maxValueHg = 1000.0. /* maximum value of mercury (ng/m3) */
      baseLineHg = 0.0. /* minimum value of mercury (ng/m3) */
      rangeHg = 1000.0. /* range of concentration of mercury */
      maxHg = 1000.0: /* value of the Chart-Output of the Tekran */

/* Tekran Parameters */
float tubeDelay = 3.00:

/*chamber parameters*/
float chamberFlow = 15.0/(1000.0*60.0): /*15 L/min -> m^3/s*/
float chamberArea = 0.12: /*m^2*/

/* Interrupt Counters */
unsigned long int inCounter = 0: /* counts the # of interrupts */
int dcCounter = 0. /* controls the valve */
      concCounterHg = 0. /* counts the total number of Hg concentration positions */
      sampleCounter = 0:

int ii:
int SAMPLES = 25:
int aCount = 0. bCount = 0:
int sampleTime = 300:
/* Interrupt Flags */
int intFlag = 0. /* indicates an interrupt */
      valveFlag = 0. /* indicates a valve switch */
      firstFlag = 0. /* indicates the first usable valve data */
      pFlag = 0. /* indicates that the THD concentration file can be updated */
      aFlag = 1. /* indicates that the cartridge is on A */
      bFlag = 0.
      halfFlag = 0.
      waitFlagA = 0.
      waitFlagB = 1: /* must start as one */

/* Data Values */
double voltage[8]. /* voltage from each channel */
      convert[8]: /* converted voltages for all channels */

```



```

/* Calculated Values */
double sumConcHg = 0.0;
    cartA.      /* Cartridge A average */
    cartB.      /* Cartridge B average */
    L.
    A[900].
    B[900].
concAB = 0.;
    avgAHg.      /* overall average at position A */
    avgBHg.      /* overall average at position B */
    avgdiffAB.
    diffAB.
    avgFlux:

double soilTempAv[2], ambTempAv[2], rhAv[2], soilMoistAv[4];
double soilTempAv[2], ambTempAv[2], rhAv[2], soilMoistAv[4];
double soilTempCnt[2], ambTempCnt[2], rhCnt[2], soilMoistCnt[4];

/* File Pointers */
FILE *LPtr;
FILE *HPtr: /* high resolution data file */
char filenameL[20] = {0}; /* low resolution data file name mmmdd.dat */
    filenameH[20] = {0}; /* high resolution data file name */

    /*debug files*/
FILE * ADebug. * BDebug. * SDebug. * PDebug. * ST1Debug. * ArdDebug.
    * BSDebug. * SigDbg:

/* ++++++ */

void main(void)
{
    /* Initialize and Declare the Variables */
    int selection. /* main menu choice */
        flag = 1: /* indicates that exit has been requested */
    char stuff[5]; /* response buffer */

    /* Place Welcome on the Screen */
    clrscr();
    printf("bbbbbb THE NORTHERN EXPOSURE PROGRAM - Alert bbbbbb\n");
    printf("Please be gentle with this program. It can be very temperamental!\n\n");

    /* Initialize the Data Acquisition Card */
    initCard();

```

```

while(flag)
{
    /* Display the Menu and Obtain the Appropriate Selection */
    selection = menu();

    /* Go to the Selection */
    switch(selection)
    {
        /* Data */
        case 1:
            // Do data stuff
            data();
            break;

        /* Reset the Parameters. Scale, Equipment */
        case 2:
            initCard():
data():
            break;

        /* exit */
        case 3:
            printf("\nThank you for using this program. Have a nice
day.\n");

            printf("\t\t\tGoodbye!!\n\n");
            flag = 0;
            break;

        default:
            flag = 1;
            printf("\nYour selection is incorrect. Please enter it
again.\n");
    }
}

int menu(void)
{
    int answer; /* menu selection */
    char stuff[5]; /* response buffer */
    ans; /* response to circle */

    /* Display menu */
    clrscr();

```

```

printf("MENU\n\n");
printf("1.   Record Data \n");
printf("2.   Repeat the Initialization Procedures\n");
printf("3.   Exit\n");

printf("\nPlease enter the number of your selection now: ");
gets(stuff);
sscanf(stuff, "%d", &answer);

printf("\n");

return answer;
}

void data(void)
{
    /* Variable Declarations */
    char string[20];      /* User's Menu Selection and Filename */
    *namePtr = NULL;     /* Creation of the Default Filename */
    hold[30];            /* Creation of Default Filename */
    time_t t;            /* Time Variable */

    /* External Variables are Defined in Main */
    extern FILE *LPtr, *HPtr;
    extern int err, deviceNumber, portA, lineNo0, lineNo3, stateA0, stateA3;
    extern char filenameL[20], filenameH[20];

    /* Obtain the Filename for Storing Concentration Data */
    printf("\nEnter a Filename for Concentration Data Storage.\n");
    printf("The default is cmmdd.dat. Filename: ");
    gets(string);
    sscanf(string, "%s", filenameH);

    /* Obtain the filename for storing data */
    printf("\nEnter a Filename for Concentration Average Storage (default is mmmdd.dat): ");
    gets(string);
    sscanf(string, "%s", filenameL);

    if (strcmp(filenameL, "") == 0)
    {
        time(&t);
        strcat(hold, ctime(&t));
        namePtr = strtok(hold, " ");
        namePtr = strtok(NULL, " ");
    }
}

```

```

        strcpy(filenameL, namePtr);
        namePtr = strtok(NULL, " ");
        strcat(filenameL, namePtr);
        strcat(filenameL, ".txt");
    }

    /* Create the Default Filename */
    if (strcmp(filenameH, "") == 0)
    {
        strcpy(filenameH, "c");
        strcat(filenameH, filenameL);
    }

    /* Open the File */
    if ((HPtr = fopen(filenameH, "a")) == NULL)
    {
        /* Ensure that the file could be opened */
        exit(0);
    }

    fclose(HPtr);

    /*printf("\nEnter the chamber flow in m^3/s: ");
    gets(string);
    sscanf(string, "%f", chamberFlow);*/

    /* Clear the Analog Input of the NI-DAQ */
    err = AI_Clear(deviceNumber);
    ErrPrint("AI_Clear", err);

    printf("\nWaiting for the Tekrans\n");

    err = DIG_In_Line(deviceNumber, portA, lineNo0, &stateA0);
    ErrPrint("DIG_In_Line", err);

    while (stateA0 != 0)
    {
        err = DIG_In_Line(deviceNumber, portA, lineNo0, &stateA0);
        ErrPrint("DIG_In_Line", err);
    }

    err = DIG_In_Line(deviceNumber, portA, lineNo3, &stateA3);
    ErrPrint("DIG_In_Line", err);

```

```

while (stateA3 == 0)
{
    err= DIG_In_Line(deviceNumber, portA, lineNo3, &stateA3);
    ErrPrint("DIG_In_Line", err);
}

/*reset Debug files*/
BDebug = fopen("BDebug.txt","w");
fprintf(BDebug,"buffer concCounterHg pFlag dataLoggerCom avgSigSent\n");
fclose(BDebug);

ADebug = fopen("ADebug.txt","w");
fprintf(ADebug,"buffer concCounterHg pFlag dataLoggerCom avgSigSent\n");
fclose(ADebug);

SDebug = fopen("SDebug.txt","w");
fclose(SDebug);

PDebug = fopen("PDebug.txt","w");
fprintf(PDebug,"Time ConcCounter\n");
fclose(PDebug);

ST1Debug = fopen("ST1Debug.txt","w");
fclose(ST1Debug);

ArdDebug = fopen("ArdDebug.txt","w");
fclose(ArdDebug);

BSDebug = fopen("BSDebug.txt","w");
fclose(BSDebug);

SigDbg = fopen("SigDbg.txt","w");
fclose(SigDbg);

/* Display the User Screen */
screen();

/* Begin the Scanning Sequence */
interrupter();

/* Get a Character to End Data Collection Mode */
getch();

/* Close the Graphics Mode */
closegraph();
}

```

D.2 Interrupt Service Routine Program for NI-DAQ Card

Note: The programming language is in C code.

```
/* Version 1.0 - Alert - 2001 */

/* Written by Gireesh Dharwarkar */
/* Adjusted by Taylor Roumeliotis and Xiaoxi Song */

/* **NOTE:
    This is an interrupt service routine. You can NOT compile this
    program with Test Stack Overflow turned on and get an executable
    file which will operate correctly. */

/* Preprocessor Directives */
#include <stdio.h> /* standard input and output library */
#include <stdlib.h> /* standard library */
#include <string.h> /* string functions library */
#include <dos.h> /* dos functions library */
#include <conio.h> /* console input and output library */
#include <time.h> /* time functions library */
#include <graphics.h> /* graphics function library */
#include <math.h> /* math library */

#define INTR 0X1C /* clock tick interrupt */

#define LEFT_COL_STRT 75
#define LEFT_COL_END 149
#define RIGHT_COL_STRT 215
#define RIGHT_COL_END 300
#define AV_OFFSET_LEFT 320
#define AV_OFFSET_RIGHT 320
#define TOO_MUCH_TIME 50
#define AV_WINDOW 9
#define ERROR -9999.99

/* Function Prototypes */
void interrupt iHandler(); void interrupt (*oldhandler)();
void reset (void); float julian (void);

int loggerSampleCounter=0, loggerDataReady = 0, dataLoggerCom = 0,
    dataLoggerError = 0, comCounter = 0;
double soilTemp[2][AV_WINDOW], ambTemp[2][AV_WINDOW],
    rh[2][AV_WINDOW], soilMoist[4][AV_WINDOW];
double sumSoilTemp[2] = {0.0}, sumAmbTemp[2] = {0.0}, sumRH[2] = {0.0},
    sumSoilMoist[4] = {0.0,0.0,0.0,0.0};
```

```

int valuesRetrieved[5] = {0.0,0.0,0.0}; /*indicated that the corresponding pair of values
were received successfully*/
int index = 0;
int getDataPair[4] = {1.0,0.0,0.0}; /*these avoid sampling from the data logger more than 25
times unnecessarily*/

void interrupt ihandler()
{
    /* Global Variables (defined in Main) */
    extern unsigned long int inCounter;
    extern int deviceNumber, ii, err, gain[8], chan, portA, portB, lineNo0,
        lineNo1, lineNo2, lineNo3, stateA1, stateA2, stateB0, stateB1, stateB2,
stateB3, sampleTime, halfFlag,
        waitFlagA, waitFlagB, firstFlag, intFlag, valveFlag, timeFlag,
        aFlag, bFlag, pFlag, dcCounter, concCounterHg, sampleCounter,
SAMPLES:
    extern double voltage[8], convert[8], sumConcHg, cartA, cartB;
    extern float tubeDelay, maxHg;
    short int turnedOff = 0;

    int j;
    static int avgSigSent = 0;

    extern FILE * BDebug, * SDebug, * ADebug, * ST1Debug, * ArdDebug, *
BSDebug, * SigDbg;

    char buffer[200];
    time_t t;

    time(&t);

    /*if(avgSigSent)
    {
        SigDbg = fopen("SigDbg.txt", "a");
        fprintf(SigDbg,"avgSigSent inCounter=%d", inCounter);
        fclose(SigDbg);
    } */

    /* Each Interrupt, Increment the Counters */
    inCounter++;    dcCounter++;

    if(dataLoggerCom)
        comCounter++; /*keep track of time elapsed between retrieval of values*/

    if(comCounter > 50)
        dataLoggerError = 1;

```

```

/* Reset the Half Hour Flag (delay) */
if (inCounter == 22 * sampleTime)
{
    firstFlag = 1;
}

/* Alter the Valve Position */
if (dcCounter == (int) (18.2 * (sampleTime - tubeDelay)) && firstFlag)
{
    /* chan = 0 - UP, chan = 1 - DOWN */
    if (chan == 0) /* valve is B */
    {
        /* AB Level */
        err = AO_VWrite(deviceNumber, 0, 3.5); /* Tekran Control */
        chan = 1; /* force valve to A */
    }
    else /* chan == 1 - valve is A */
    {
        /* AB Level */
        err = AO_VWrite(deviceNumber, 0, 0.0); /* Tekran Control */
        chan = 0; /* force valve to B */
    }
    valveFlag = 1; /* set the valveFlag */
}

/* Read the Digital Channels */
/* Line 1 - Cartridge Type, Line 2 and 3 - Chart Output */
err = DIG_In_Line(deviceNumber, portA, lineNo1, &stateA1);
err = DIG_In_Line(deviceNumber, portA, lineNo2, &stateA2);

/* datalogger data lines status */
if(dataLoggerCom)
{
    err = DIG_In_Line(deviceNumber, portB, lineNo0, &stateB0);
    err = DIG_In_Line(deviceNumber, portB, lineNo1, &stateB1);
    err = DIG_In_Line(deviceNumber, portB, lineNo2, &stateB2);
    err = DIG_In_Line(deviceNumber, portB, lineNo3, &stateB3);
}
else
{
    stateB0 = 0;
    stateB1 = 0;
    stateB2 = 0;
    stateB3 = 0;
}

```



```

        if(stateB0 && getDataPair[0]) /*capture first set of values from datalogger*/
                                           /*temps from the two
RH/temp probes*/
    {
        ST1Debug = fopen("ST1Debug.txt", "a");
        fprintf(ST1Debug,"comcounter=%d. loggerSampleCounter=%d\n",
comCounter, loggerSampleCounter);
        fclose(ST1Debug);

        comCounter = 0; /*reset the elapsed time between values form 23X*/
        if(!turnedOff)
        {
            err = AO_VWrite(deviceNumber, 1, 0.0); /* turn off initiation com
with 23X */
            turnedOff = 1;
        }

        for (ii = 5; ii < 7; ii++)
        {
            err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
            convert[ii] = voltage[ii] * 10;
        }

        for(j=0;j<2;j++)
        {
            sumAmbTemp[j] += convert[j+5];
        }

        loggerSampleCounter++;

        if(loggerSampleCounter == SAMPLES)
        {
            for(j=0;j<2;j++)
            {
                ambTemp[j][index] = sumAmbTemp[j]/SAMPLES;
            }

            loggerSampleCounter = 0;

            for(j=0; j<2; j++)
            {
                sumAmbTemp[j] = 0;
            }
        }
    }

```

```

    }

    ST1Debug = fopen("ST1Debug.txt", "a");
    fprintf(ST1Debug, "av samp
values=%f,%f\n", ambTemp[0][index], ambTemp[1][index]);
    fclose(ST1Debug);

    getDataPair[0] = 0;
    getDataPair[1] = 1;
    valuesRetrieved[0] = 1;
}
}

else if(stateB1 && getDataPair[1]) /*capture second set of values from
datalogger.*/
{
    /*rh from from the
two rh/temp probes*/
    comCounter = 0; /*reset the elapsed time between values form 23X*/
    for (ii = 5; ii < 7; ii++)
    {
        err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
        convert[ii] = voltage[ii] * 1000/100 * 2 ;
    }

    for(j=0;j<2;j++)
    {
        sumRH[j] += convert[j+5];
    }

    loggerSampleCounter++;

    if(loggerSampleCounter == SAMPLES)
    {
        for(j=0;j<2;j++)
        {
            rh[j][index] = sumRH[j]/SAMPLES;
            sumRH[j] = 0;
        }

        loggerSampleCounter = 0;

        getDataPair[1] = 0;
        getDataPair[2] = 1;

        valuesRetrieved[1] = 1;
    }
}

```

```

    }
else if(stateB2 && !stateB3 && getDataPair[2]) /*first pair of thermocouples*/
{
    comCounter = 0; /*reset the elapsed time between values form 23X*/
    for (ii = 5; ii < 7; ii++)
    {
        err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
        convert[ii] = voltage[ii] * 1000/100;
    }

    for(j=0;j<2;j++)
    {
        sumSoilTemp[j] += convert[j+5];
    }

    loggerSampleCounter++;

    if(loggerSampleCounter == SAMPLES)
    {
        for(j=0;j<2;j++)
        {
            soilTemp[j][index] = sumSoilTemp[j]/SAMPLES;
            sumSoilTemp[j] = 0;
        }

        loggerSampleCounter = 0;

        getDataPair[2] = 0;
        getDataPair[3] = 1;

        valuesRetrieved[2] = 1;
    }
}

else if(!stateB2 && stateB3 && getDataPair[3]) /*first pair of TDR*/
{
    comCounter = 0; /*reset the elapsed time between values form 23X*/
    for (ii = 5; ii < 7; ii++)
    {
        err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
        convert[ii] = voltage[ii] * 1000/100;
    }

    for(j=0;j<2;j++)

```

```

        {
            sumSoilMoist[j] += convert[j+5];
        }

loggerSampleCounter++;

if(loggerSampleCounter == SAMPLES)
{
    for(j=0;j<2;j++)
    {
        soilMoist[j][index] = sumSoilMoist[j]/SAMPLES;
        sumSoilMoist[j] = 0;
    }

    loggerSampleCounter = 0;

    getDataPair[3] = 0;
    getDataPair[4] = 1;

    valuesRetrieved[3] = 1;
}
}

else if(stateB2 && stateB3 && getDataPair[4]) /*TDR (soil moisture)*/
{
    comCounter = 0; /*reset the elapsed time between values form 23X*/

    for (ii = 5: ii < 7: ii++)
    {
        err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
        convert[ii] = voltage[ii] * 1000/100;
    }

    for(j=2; j<4; j++)
    {
        sumSoilMoist[j] += convert[j+3];
    }

    loggerSampleCounter++;

    if(loggerSampleCounter == SAMPLES)
    {
        for(j=2;j<4;j++)
        {
            soilMoist[j][index] = sumSoilMoist[j]/SAMPLES;
            sumSoilMoist[j] = 0;
        }
    }
}

```

```

    }

    loggerSampleCounter = 0;
    dataLoggerCom = 0;
    loggerDataReady = 1;
    getDataPair[4] = 0;

    valuesRetrieved[4] = 1;

    }
}

/* Cartridge Position */
if ((stateA1) && waitFlagA)
{
    if (waitFlagB == 0)
    {
        aFlag = 1;
        waitFlagB = 1;
    }

    /* if(firstFlag)
    {
        BSDebug = fopen("BSDebug.txt", "a");
        fprintf(BSDebug, "firstflg=%d.
avgSigSent=%d\n", firstFlag, avgSigSent);
        fclose(BSDebug);
    } */

    if (firstFlag && !avgSigSent)
    {
        //send signal to 23X to calculate averaged parameters for last 10
minutes*/

        SDebug = fopen("SDebug.txt", "a");
        fprintf(SDebug, "about to send signal\n");
        fclose(SDebug);

        err = AO_VWrite(deviceNumber, 1, 5.0);
        turnedOff = 0;

        SDebug = fopen("SDebug.txt", "a");
        fprintf(SDebug, " about to set avgSigSent\n");
        fclose(SDebug);

        avgSigSent = 1;

```

```

/*raise flag to commence data logger com*/
SDebug = fopen("SDebug.txt", "a");
fprintf(SDebug, "raising datalogger com flag\n");
fclose(SDebug);

dataLoggerCom = 1;

SDebug = fopen("SDebug.txt", "a");
fprintf(SDebug, "about to set index\n");
fclose(SDebug);

index = concCounterHg % (AV_WINDOW);

strcpy(buffer, ctime(&t));
SDebug = fopen("SDebug.txt", "a");
fprintf(SDebug, "%s done\n", buffer);
fclose(SDebug);
}

/* Read Cartridge A Data on the Tekran */
if (stateA2)
{
    /* Read the Voltages from the Card */
    for (ii = 7; ii < 8; ii++)
    {
        err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
    }

    convert[0] = voltage[7] * maxHg * 0.2;
    ArdDebug = fopen("ArdDebug.txt", "a");
    fprintf(ArdDebug, "concCounter=%d, sampleCnt=%d,
value=%f\n", concCounterHg, sampleCounter, convert[0]);
    fclose(ArdDebug);

    sumConcHg += convert[0];
    sampleCounter++;

    if (sampleCounter == SAMPLES)
    {
        waitFlagA = 0;

        /* Lower Level */
        cartA = sumConcHg / SAMPLES;

        sumConcHg = 0.0;
    }
}

```

```

        sampleCounter = 0;

        ADebug = fopen("ADebug.txt","a");
        strcpy(buffer, ctime(&t));
        fprintf(ADebug, "%s %d %d %d %d\n", buffer,
concCounterHg, pFlag, dataLoggerCom, avgSigSent);
        fclose(ADebug);
    }
}

if (waitFlagB && (!(stateA1))) /* Cartridge-a is sampling*/
{
    if (waitFlagA == 0)
    {
        bFlag = 1;
        waitFlagA = 1;
        dcCounter = 0;
    }

    /* Read Cartridge B Data on Both Tekrans */
    if (stateA2)
    {
        for (ii = 7; ii < 8; ii++)
        {
            err = AI_VRead(deviceNumber, ii, gain[ii], &voltage[ii]);
        }

        convert[0] = voltage[7] * maxHg * 0.2;

        sumConcHg += convert[0];
        sampleCounter++;

        if (sampleCounter == SAMPLES)
        {
            waitFlagB = 0;
            cartB = sumConcHg / SAMPLES;

            avgSigSent = 0; /*reset the sent-signal-to-23X-flag for next
time*/

            sumConcHg = 0.0;
            sampleCounter = 0;

            pFlag = 1;

```

```

        concCounterHg++;

        BDebug = fopen("BDebug.txt","a");

        strcpy(buffer, ctime(&t));
        fprintf(BDebug,"%s %d %d %d %d\n", buffer,
concCounterHg, pFlag, dataLoggerCom, avgSigSent);

        fclose(BDebug);
    }
}

if (firstFlag == 0) waitFlagB = 0;
}

if (inCounter == 32760)
{
    halfFlag = 1;
    inCounter = 0;
}

intFlag = 1;
}

void interrupter(void)
{
    int j, k,          /* index */
        done = 1,      /* indicates that the loop is done executing */
        x = 21,        /* horizontal coordinate */
        y = 0,         /* vertical coordinate (Hg - Tekran 1) */
        maxPix = 200,  /* maximum number of pixels in graphing region */
        spread = 0,
        dayFlag = 0,   /* new day indicator */
        pchan;
    float julianDay; /* julian date */
    static float flux = 0;
    char *timePtr = NULL, /* used in string functions to break time */
        hold[30],         /* used as a hold buffer */
        day[15],
        buffer[200],      /* used as the output buffer */
        *namePtr = NULL, /* used in string functions to break names */
        keyhit;
    time_t t;             /* time indicator */

```



```

/* External Variable Declarations - (Defined in Main) */
extern int chan, err, deviceNumber, intFlag, valveFlag, pFlag, halfFlag,
        aFlag, bFlag, outFlag, concTime, aCount, bCount, portA, portB,
        concCounterHg, sampleTime;
extern float baseLineHg, rangeHg, chamberFlow, chamberArea;
extern char filenameL[20], filenameH[20];
extern FILE *LPtr, *HPtr;
extern double cartA, cartB, concAB, avgAHg, avgBHg, L, A[900], B[900],
diffAB,
        avgdiffAB, avgFlux;
extern double soilTempAv[2], ambTempAv[2], rhAv[2], soilMoistAv[4];
extern double soilTempCnt[2], ambTempCnt[2], rhCnt[2], soilMoistCnt[4];

char soilTempStr[4][20], ambTempStr[2][20], rhStr[2][20], soilMoistStr[4][20];
char *error = "ERR";

extern FILE * PDebug;
/* Output Initial Voltage to Force the Valve to Position A */
err = AO_VWrite(deviceNumber, 0, 3.5);

/* Set begin com with 23X signal to zero initially*/
err = AO_VWrite(deviceNumber, 1, 0);

/* Initial Screen Settings - Valve Position */
settextstyle(DEFAULT_FONT, HORIZ_DIR, 1);
setcolor(WHITE);
outtextxy(200, 8, "SAMPLE-Inlet");
/*outtextxy(x+6, 261, "A");*/
x = x + 30;
setlinestyle(DOTTED_LINE, 0, NORM_WIDTH);

/* Initial Screen Settings - Julian Date, Half Hour Number */
julianDay = julian();
bar(70, 200, 90, 220);
gcvt(julianDay, 6, buffer);
outtextxy(70, 200, buffer);

/* Save the old interrupt vector */
oldhandler = getvect(INTR);

/* Install the new interrupt handler */
setvect(INTR, ihandler);

do
{
        if (intFlag)

```

```

{
    time(&t);
    bar(10, 220, 300, 230);
    outtextxy(10, 220, ctime(&t));

    strcpy(hold, ctime(&t));
    timePtr = strtok(hold, " ");
    timePtr = strtok(NULL, " ");
    timePtr = strtok(NULL, " ");
    timePtr = strtok(NULL, " ");
    strcpy(day, timePtr);
    if ((strcmp(day, "00:00:00") == 0)) dayFlag = 1;

    intFlag = 0;
}

if (aFlag)
{
    bar(200, 23, 300, 33);
    outtextxy(200, 23, "Cart. a");
    aFlag = 0;
}

if (bFlag)
{
    bar(200, 23, 300, 33);
    outtextxy(200, 23, "Cart. b");
    bFlag = 0;
}

if (valveFlag)
{
    if (chan == 1)
    {
        bar(200, 8, 320, 18);
        outtextxy(200, 8, "SAMPLE-inlet");
        outtextxy((x+6), 261, "in");
        line(x, 261, x, 459);
    }
    else /* chan == 0 */
    {
        bar(200, 8, 320, 18);
        outtextxy(200, 8, "SAMPLE-outlet");
        outtextxy((x+6), 261, "out");
        line(x, 261, x, 459);
    }
}

```

```

        valveFlag = 0;
    }

    if (pFlag && (loggerDataReady || dataLoggerError))
    {

        PDebug = fopen("PDebug.txt","a");
        strcpy(buffer, ctime(&t));
        fprintf(PDebug,"%s concCounter=%d\n", buffer,
concCounterHg);

        if (spread == 1)
        {
            // Open the High Res File
            HPtr = fopen(filenameH, "a");

            // Calculate the Average
            L = (cartA + cartB) / 2.0;

            /*Output cart A value*/
            bar(LEFT_COL_STRT, 38, LEFT_COL_END, 77);
            gcvt(cartA, 5, buffer);
            outtextxy(LEFT_COL_STRT, 38, buffer);

            /*Output cart B value*/
            bar(RIGHT_COL_STRT, 38, RIGHT_COL_END, 77);
            gcvt(cartB, 5, buffer);
            outtextxy(RIGHT_COL_STRT, 38, buffer);

            if (chan == 0) /* on B belongs to A(Inlet) */
            {
                A[aCount] = L;
                aCount++;
                bar(LEFT_COL_STRT, 58, LEFT_COL_END, 79);
                gcvt(A[aCount-1], 5, buffer);
                outtextxy(LEFT_COL_STRT, 58, buffer);
                pchan = 1;
            }
            else /* on A - belongs to B(Outlet) */
            {
                B[bCount] = L;
                bCount++;
                bar(RIGHT_COL_STRT, 58, RIGHT_COL_END,
79);

                gcvt(B[bCount-1], 5, buffer);
                outtextxy(RIGHT_COL_STRT, 58, buffer);
            }
        }
    }
}

```

```

        pchan = 0;
    }

    y = 460 - (int) (((L - baseLineHg) * maxPix)/ rangeHg);

    if (y < 261)
    {
        setcolor(LIGHTMAGENTA);
        line(x, 260, x+30, 260);
    }
    if (y > 459)
    {
        setcolor(LIGHTMAGENTA);
        line(x, 460, x+30, 459);
    }
    if (y >= 260 && y <= 449)
    {
        setcolor(LIGHTCYAN);
        line(x, y, x+30, y);
    }
    setcolor(WHITE);

    if (x >= 630)
    {
        x = 21;
        bar(21, 260, 320, 459);
    }

    if (x == 291) bar(320, 260, 633, 459);

    x = x + 30;
}

if (spread == 3)
{
    if (concCounterHg > 1)
    {
        diffAB = B[bCount - 1] - A[aCount - 1];
        flux = diffAB * chamberFlow/chamberArea;
    }

    if (concCounterHg >= 9)

```

```

{
/* concAB = ((B[bCount-4]-((A[aCount-4]+A[aCount-
3])/2.0)) +
((B[bCount-4]+B[bCount-3])/2.0)-
A[aCount-3]) +
(B[bCount-3]-((A[aCount-3]+A[aCount-
2])/2.0)) +
(((B[bCount-3]+B[bCount-2])/2.0)-
A[aCount-2]) +
(B[bCount-2]-((A[aCount-2]+A[aCount-
1])/2.0)) +
(((B[bCount-2]+B[bCount-1])/2.0)-
A[aCount-1])) / 6.0;*/

if (concCounterHg % 3 == 0)
{
// Average Mercury Concentration at
Each Valve Height
// One and a half hour averages
updated every half-hour after the first hour and a half
if(concCounterHg % 2 == 1)
{
concAB = ((B[bCount-4]-((A[aCount-
5]+A[aCount-4])/2.0)) +
(((B[bCount-4]+B[bCount-
3])/2.0)-A[aCount-4]) +
(B[bCount-3]-((A[aCount-
4]+A[aCount-3])/2.0)) +
(((B[bCount-3]+B[bCount-
2])/2.0)-A[aCount-3]) +
(B[bCount-2]-((A[aCount-
3]+A[aCount-2])/2.0)) +
(((B[bCount-2]+B[bCount-
1])/2.0)-A[aCount-2])+
(B[bCount-1]-((A[aCount-
2]+A[aCount-1])/2.0)))/ 7.0;

avgAHg = (A[aCount-5] + A[aCount-4] +
A[aCount-3] + A[aCount-2] + A[aCount-1])/5.0;
avgBHg = (B[bCount-4] + B[bCount-3] +
B[bCount-2] + B[bCount-1])/4.0;
}
else
{

```

```

4])/2.0)-A[aCount-4]) +
4]+A[aCount-3])/2.0)) +
3])/2.0)-A[aCount-3]) +
3]+A[aCount-2])/2.0)) +
2])/2.0)-A[aCount-2]) +
2]+A[aCount-1])/2.0)) +
1])/2.0)-A[aCount-2])) / 7.0:

```

```

concAB = (((B[bCount-5]+B[bCount-
(B[bCount-4]-((A[aCount-
(((B[bCount-4]+B[bCount-
(B[bCount-3]-((A[aCount-
(((B[bCount-3]+B[bCount-
(B[bCount-2]-((A[aCount-
(((B[bCount-2]+B[bCount-

```

```

A[aCount-2] + A[aCount-1])/4.0:
B[bCount-3] + B[bCount-2] + B[bCount-1])/5.0:
}

```

```

avgAHg = (A[aCount-4] + A[aCount-3] +
avgBHg = (B[bCount-5] + B[bCount-4] +

```

```

avgdiffAB = avgBHg - avgAHg;
avgFlux =

```

```

concAB*chamberFlow/chamberArea:

```

```

/*Calculate Avg 23X values*/
/*extern double soilTempAv[2],
ambTempAv[2], rhAv[2], soilMoistAv[4];*/
/*extern double soilTempAvCnt[2],
ambTempAvCnt[2], rhAvCnt[2], soilMoistAvCnt[4];*/

```

```

for(j=0; j<2; j++)
{
soilTempAv[j] = 0;
ambTempAv[j] = 0;
rhAv[j] = 0;

soilTempCnt[j] = 0;
ambTempCnt[j] = 0;
rhCnt[j] = 0;
}

```

```

for(j=0; j<4; j++)
{

```

```

soilMoistAv[j] = 0;

```

```

soilMoistCnt[j] = 0;
}

/*sum the values*/
for(j=0; j<9; j++)
{
    for(k=0; k<2; k++)
    {
        if(soilTemp[k][j] !=
ERROR)
        {
            soilTempAv[k] += soilTemp[k][j];
            soilTempCnt[k]++;
        }

        if(ambTemp[k][j] !=
ERROR)
        {
            ambTempAv[k] += ambTemp[k][j];
            ambTempCnt[k]++;
        }

        if(rh[k][j] != ERROR)
        {
            rhAv[k] +=
            rhCnt[k]++;
        }
    }

    for(k=0; k<4; k++)
    {
        if(soilMoist[k][j] !=
ERROR)
        {
            soilMoistAv[k] += soilMoist[k][j];
            soilMoistCnt[k]++;
        }
    }
}

```

	}
	/*calculate the averages*/
	for(j=0; j<2; j++)
	{
	if(soilTempCnt[j]>0)
	{
soilTempAv[j]/soilTempCnt[j]:	soilTempAv[j] =
	}
	else
	{
ERROR:	soilTempAv[j] =
	}
	if(ambTempCnt[j]>0)
	{
ambTempAv[j]/ambTempCnt[j]:	ambTempAv[j] =
	}
	else
	{
ERROR:	ambTempAv[j] =
	}
	if(rhCnt[j]>0)
	{
rhAv[j]/rhCnt[j]:	rhAv[j] =
	}
	else
	{
	rhAv[j] = ERROR;
	}
	}
	for(j=0;j<4;j++)
	{
	if(soilMoistCnt[j]>0)
soilMoistAv[j]/soilMoistCnt[j]:	soilMoistAv[j] =
	else


```

                                {
                                    soilMoistAv[j] =
ERROR:
                                }
                                }

                                LPtr = fopen(filenameL, "a");
                                strcpy(buffer, ctime(&t));
                                buffer[19] = '\0';
                                fprintf(LPtr, "%s %.5e %.5e %.5e
%.5e %.5e %.5e %.5e %.5e %.5e %.5e %.5e %.5e %.5e\n", buffer,
                                concAB, avgdiffAB, avgAHg,
                                avgBHg, avgFlux, ambTempAv[0], ambTempAv[1], rhAv[0], rhAv[1], soilMoistAv[0],
                                soilMoistAv[1], soilMoistAv[2], soilMoistAv[3], soilTempAv[0], soilTempAv[1]);
                                fclose(LPtr);

/* Output Values to Leftside*/

                                bar(LEFT_COL_STRT+AV_OFFSET_LEFT, 38,
                                LEFT_COL_END+AV_OFFSET_LEFT, 178);

                                gcvt(avgAHg, 5, buffer);

                                outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 38, buffer);

                                gcvt(concAB, 4, buffer);

                                outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 58, buffer);

                                gcvt(avgFlux, 4, buffer);

                                outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 78, buffer);

                                if(ambTempAv[0] == ERROR)
                                    strcpy(buffer, error);
                                else
                                    gcvt(ambTempAv[0], 5,
buffer);

                                outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 98, buffer);

                                if(ambTempAv[1] == ERROR)
                                    strcpy(buffer, error);
                                else

```

```

buffer):
    gcvv(ambTempAv[1], 5.

    outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 118, buffer);

    if(rhAv[0] == ERROR)
        strcpy(buffer, error);
    else
        gcvv(rhAv[0], 5, buffer);

    outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 138, buffer);

    if(rhAv[1] == ERROR)
        strcpy(buffer, error);
    else
        gcvv(rhAv[1], 5, buffer);

    outtextxy(LEFT_COL_STRT+AV_OFFSET_LEFT, 158, buffer);

    /* Output Values to Right side*/

    bar(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 38,
RIGHT_COL_END+AV_OFFSET_RIGHT, 198);

    gcvv(avgBHg, 5, buffer);

    outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 38, buffer);
    gcvv(avgdifAB, 5, buffer);

    outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 58, buffer);

    if(soilMoistAv[0] == ERROR)
        strcpy(buffer, error);
    else
        gcvv(soilMoistAv[0], 5,
buffer);

    outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 78, buffer);

    if(soilMoistAv[1] == ERROR)
        strcpy(buffer, error);
    else
        gcvv(soilMoistAv[1], 5,
buffer);

    outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 98, buffer);

```

```

        if(soilMoistAv[2] == ERROR)
            strcpy(buffer, error);
        else
            gcvt(soilMoistAv[2], 5,
buffer):

        outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 118, buffer);

        if(soilMoistAv[3] == ERROR)
            strcpy(buffer, error);
        else
            gcvt(soilMoistAv[3], 5,
buffer):

        outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 138, buffer);

        if(soilTempAv[0] == ERROR)
            strcpy(buffer, error);
        else
            gcvt(soilTempAv[0], 5,
buffer):

        outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 158, buffer);

        if(soilTempAv[1] == ERROR)
            strcpy(buffer, error);
        else
            gcvt(soilTempAv[1], 5,
buffer):

        outtextxy(RIGHT_COL_STRT+AV_OFFSET_RIGHT, 178, buffer);
    }
}

if (spread == 2)
{
    strcpy(buffer, ctime(&t));
    fprintf(PDebug, "Spread2  %s  concCounter=%d  \n",
buffer, concCounterHg);

    dataLoggerCom = 0; /*if error occurred com flag would not
be turned off yet so do it now*/

    if (concCounterHg > 1)

```

```

{
    diffAB = B[bCount - 1] - A[aCount - 1];
    flux = diffAB * chamberFlow/chamberArea;
}

/*output flux and data logger values on left side*/
bar(LEFT_COL_STRT, 78, LEFT_COL_END, 178);

if (concCounterHg > 1)
{
    gcvt(flux, 4, buffer);
    outtextxy(LEFT_COL_STRT, 78, buffer);
}

if(valuesRetrieved[0])
{
    gcvt(ambTemp[0][index], 5, ambTempStr[0]);
    gcvt(ambTemp[1][index], 5, ambTempStr[1]);
}
else
{
    strcpy(ambTempStr[0], error);
    strcpy(ambTempStr[1], error);
    ambTemp[0][index] = ERROR;
    ambTemp[1][index] = ERROR;
}
outtextxy(LEFT_COL_STRT, 98, ambTempStr[0]);
outtextxy(LEFT_COL_STRT, 118, ambTempStr[1]);

if(valuesRetrieved[1])
{
    gcvt(rh[0][index], 5, rhStr[0]);
    gcvt(rh[1][index], 5, rhStr[1]);
}
else
{
    strcpy(rhStr[0], error);
    strcpy(rhStr[1], error);
    rh[0][index] = ERROR;
    rh[1][index] = ERROR;
}
outtextxy(LEFT_COL_STRT, 138, rhStr[0]);

```

```

outtextxy(LEFT_COL_STRT, 158, rhStr[1]);

/*output flux and data logger values on right side*/
bar(RIGHT_COL_STRT, 78, RIGHT_COL_END, 198 );

if(valuesRetrieved[2])
{
    gcvt(soilTemp[0][index], 5, soilTempStr[0]);
    gcvt(soilTemp[1][index], 5, soilTempStr[1]);
}
else
{
    strcpy(soilTempStr[0], error);
    strcpy(soilTempStr[1], error);
    soilTemp[0][index] = ERROR;
    soilTemp[1][index] = ERROR;
}
outtextxy(RIGHT_COL_STRT, 158, soilTempStr[0]);
outtextxy(RIGHT_COL_STRT, 178, soilTempStr[1]);


if(valuesRetrieved[3])
{
    gcvt(soilMoist[0][index], 5, soilMoistStr[0]);
    gcvt(soilMoist[1][index], 5, soilMoistStr[1]);
}
else
{
    strcpy(soilMoistStr[0], error);
    strcpy(soilMoistStr[1], error);
    soilMoist[0][index] = ERROR;
    soilMoist[1][index] = ERROR;
}
outtextxy(RIGHT_COL_STRT, 78, soilMoistStr[0]);
outtextxy(RIGHT_COL_STRT, 98, soilMoistStr[1]);


if(valuesRetrieved[4])
{
    gcvt(soilMoist[2][index], 5, soilMoistStr[2]);
    gcvt(soilMoist[3][index], 5, soilMoistStr[3]);
}
else
{
    strcpy(soilMoistStr[2], error);

```

```

        strcpy(soilMoistStr[3], error);
        soilMoist[2][index] = ERROR;
        soilMoist[3][index] = ERROR;
    }
    outtextxy(RIGHT_COL_STRT, 118, soilMoistStr[2]);
    outtextxy(RIGHT_COL_STRT, 138, soilMoistStr[3]);

    strcpy(buffer, ctime(&t));
    buffer[19] = '\0';
    fprintf(HPtr, "%s %.5e %.5e %.5e %8s %8s %8s %8s %8s
%8s %8s %8s %8s %8s %.5e %d\n", buffer, cartA, cartB, L, ambTempStr[0],
ambTempStr[1], rhStr[0], rhStr[1], soilTempStr[0], soilTempStr[1], soilMoistStr[0],
soilMoistStr[1], soilMoistStr[2], soilMoistStr[3], flux, pchan);
    fclose(HPtr);

}

if (spread == 4)
{
    pFlag = 0;
    spread = 0;

    for(j=0; j<5; j++)
    {
        valuesRetrieved[j] = 0;
    }
    dataLoggerError = 0;
    loggerDataReady = 0;
    getDataPair[0] = 1;

}
spread++;
fclose(PDebug);
} // end pFlag

if (halfFlag)
{
    // Find the Julian
    julianDay = julian();
    bar(70, 200, 150, 220);
    gcvt(julianDay, 6, buffer);
    outtextxy(70, 200, buffer);
    halfFlag = 0;
}

```

```

        if (dayFlag)
        {
            // Create a New FileName for Concentration Data
            strcat(hold, ctime(&t));
            namePtr = strtok(hold, " ");
            namePtr = strtok(NULL, " ");
            strcpy(filenameL, namePtr);
            namePtr = strtok(NULL, " ");
            strcat(filenameL, namePtr);
            strcat(filenameL, ".txt");

            strcpy(filenameH, "c");
            strcat(filenameH, filenameL);

            dayFlag = 0;
        }

        if ((bioskey(1)) != 0)
        {
            keyhit = bioskey(0);
            if (keyhit == 'q') done = 0;
        }

    } while (done == 1);

    /* reset the old interrupt handler */
    setvect(INTR, oldhandler);

    /* display text to indicate completion */
    setcolor(LIGHTMAGENTA);
    outtextxy(575, 220, "DONE!!!!");

    /* write a zero to all analog output channels */
    err = AO_VWrite(deviceNumber, 0, 0.00);

    /* ensure that all values are zero */
    reset();

    return;
}

void reset(void)
{
    /* External Variables are Defined in Main */
    extern int chan, intFlag, valveFlag, firstFlag, pFlag, aFlag, bFlag, waitFlagA,

```

```

                                waitFlagB, concCounterHg, dcCounter, sampleCounter, aCount,
bCount:
    extern long unsigned int inCounter:
    extern double sumConcHg, concAB:

    /* Reset the Interrupt Counters */
    inCounter = 0:
    dcCounter = 0:
    sampleCounter = 0:

    /* Reset the Averaging Counters */
    aCount = 0:
    bCount = 0:
    concCounterHg = 0:

    /* Reset the Output Channels */
    chan = 1:

    /* Reset the Flags */
    intFlag = 0:
    valveFlag = 0:
    firstFlag = 0:
    pFlag = 0:
    aFlag = 1:
    bFlag = 0:
    waitFlagA = 0:
    waitFlagB = 1: // must start as one

    /* Reset the Sums */
    sumConcHg = 0.:
    concAB = 0.:

    return:
}

```

D.3 Data collection and averaging program for CR23X datalogger

Note: The programming language is referred from CR23X Datalogger Manual.
 Written by: Gireesh Dharwarkar, Taylor Roumeliotis and Xiaoxi Song

```

:{CR23X}
:
*Table 1 Program
01: 20      Execution Interval (seconds)

```


1: Panel Temperature (P17) : Reference Temperature
1: 1 Loc [panel]

2: Thermocouple Temp (DIFF) (P14) : Thermocouples Measurement
1: 2 Repts
2: 21 10 mV, 60 Hz Reject, Slow Range
3: 1 DIFF Channel
4: 1 Type T (Copper-Constantan)
5: 1 Ref Temp (Deg. C) Loc [panel]
6: 2 Loc [temp_1]
7: 1.0 Mult
8: 0.0 Offset

3: Volt (SE) (P1) : RH Temperature Measurement
1: 2 Repts
2: 24 1000 mV, 60 Hz Reject, Slow Range
3: 5 SE Channel
4: 4 Loc [tempRH]
5: 0.1 Mult
6: -40 Offset

4: Volt (SE) (P1) : Relative Humidity Measurement
1: 2 Repts
2: 24 1000 mV, 60 Hz Reject, Slow Range
3: 7 SE Channel
4: 6 Loc [RH]
5: 0.1 Mult
6: 0.0 Offset :

5: Do (P86)
1: 49 Turn On Switched 12V

6: TDR100 Measurement (P119)
1: 00 SDM Address
2: 0 La/L
3: 1004 MMMP Mux & Probe Selection
4: 4 Waveform Averaging
5: 1 Vp
6: 251 Points

7: 39 Cable Length (meters)
8: 2.0 Window Length (meters)
9: 0.3 Probe Length (meters)
10: 0.085 Probe Offset (meters)
11: 8 Loc [TDR]
12: 0.1138 Mult
13: -0.1758 Offset

7: Do (P86)
1: 59 Turn Off Switched 12V

8: If time is (P92) : Setting Output Flag High
1: 0000 Minutes (Seconds --) into a
2: 10 Interval (same units as above)
3: 10 Set Output Flag High (Flag 0)

9: Real Time (P77)
1: 1110 Year.Day.Hour/Minute (midnight = 0000)

10: Resolution (P78)
1: 1 High Resolution

11: Average (P71)
1: 10 Reps
2: 2 Loc [temp_1]

12: Resolution (P78)
1: 0 Low Resolution

13: If Flag/Port (P91)
1: 15 Do if Flag 5 is High
2: 6 Call Subroutine 6

14: If Flag/Port (P91) :
1: 14 Do if Flag 4 is High
2: 5 Call Subroutine 5

15: If Flag/Port (P91)
1: 13 Do if Flag 3 is High
2: 4 Call Subroutine 4

```

17: If Flag/Port (P91)
1: 11    Do if Flag 1 is High
2: 2     Call Subroutine 2

```

```

19: If Flag/Port (P91)
1: 16    Do if Flag 6 is High
2: 1     Call Subroutine 1

```

*Table 3 Subroutines

```

3: Running Average (P52)
1: 1      Reps
2: 4      First Source Loc [ tempRH  ]
3: 12     First Destination Loc [ avgT_RH  ]
4: 30     Number of Values in Avg Window :

```

5: Analog Out (P133)

1: 1 CAO1
2: 12 mV Loc [avgT_RH]

6: Running Average (P52)

1: 1 Reps
2: 5 First Source Loc [tempRH_2]
3: 13 First Destination Loc [avgT_RH_2]
4: 30 Number of Values in Avg Window

7: Z=X*F (P37)

1: 13 X Loc [avgT_RH_2]
2: 100 F
3: 13 Z Loc [avgT_RH_2]

8: Analog Out (P133)

1: 2 CAO2
2: 13 mV Loc [avgT_RH_2]

9: Delay w/Opt Excitation (P22)

1: 1 Ex Channel
2: 20 Delay W/Ex (units = 0.01 sec)
3: 0000 Delay After Ex (units = 0.01 sec)
4: 0000 mV Excitation

10: Do (P86)

1: 11 Set Flag 1 High

11: Set Port(s) (P20)

1: 9999 C8..C5 = nc/nc/nc/nc
2: 1999 C4..C1 = high/nc/nc/nc

12: End (P95)

13: Beginning of Subroutine (P85) :

Subroutine 2

1: 2 Subroutine 2

14: Do (P86)

1: 21 Set Flag 1 Low

15: Set Port(s) (P20)

1: 9999 C8..C5 = nc/nc/nc/nc

2: 0999 C4..C1 = low/nc/nc/nc

16: Running Average (P52)

1: 1 Repts

2: 6 First Source Loc [RH]

3: 14 First Destination Loc [avgRH]

4: 30 Number of Values in Avg Window

17: Z=X*F (P37)

1: 14 X Loc [avgRH]

2: 50 F

3: 14 Z Loc [avgRH]

18: Analog Out (P133)

1: 1 CAO1

2: 14 mV Loc [avgRH]

19: Running Average (P52)

1: 1 Repts

2: 7 First Source Loc [RH_2]

3: 15 First Destination Loc [avgRH_2]

4: 30 Number of Values in Avg Window

20: Z=X*F (P37)

1: 15 X Loc [avgRH_2]

2: 50 F

3: 15 Z Loc [avgRH_2]

21: Analog Out (P133)

1: 2 CAO2

2: 15 mV Loc [avgRH_2]

22: Delay w/Opt Excitation (P22)

1: 1 Ex Channel


```

32: Running Average (P52)
1: 1      Reps
2: 3      First Source Loc [ temp_2  ]
3: 17     First Destination Loc [ avgTC_2  ]
4: 30     Number of Values in Avg Window

```

```

33: Z=X*F (P37)
1: 17    X Loc [ avgTC_2 ]
2: 100    F
3: 17    Z Loc [ avgTC_2 ]

```

```
34: Analog Out (P133)
1: 2      CAO2
2: 17     mV Loc [ avgTC_2 ]
```

35: Delay w/Opt Excitation (P22)
1: 1 Ex Channel
2: 20 Delay W/Ex (units = 0.01 sec)
3: 0000 Delay After Ex (units = 0.01 sec)
4: 0000 mV Excitation

36: Do (P86)
1: 13 Set Flag 3 High

```
37: Set Port(s) (P20)
1: 9919 C8..C5 = nc/nc/high/nc
2: 9999 C4..C1 = nc/nc/nc/nc
```

38: End (P95)

```

:                               Subroutine 4
39: Beginning of Subroutine (P85)
1: 4       Subroutine 4

```

40: Do (P86)
1: 23 Set Flag 3 Low

```
41: Set Port(s) (P20)
1: 9909 C8..C5 = nc/nc/low/nc
2: 9999 C4..C1 = nc/nc/nc/nc
```

42: Running Average (P52)
1: 1 Repts
2: 8 First Source Loc [TDR]
3: 18 First Destination Loc [avgTDR]
4: 30 Number of Values in Avg Window

43: $Z=X \cdot F$ (P37)
1: 18 X Loc [avgTDR]
2: 100 F
3: 18 Z Loc [avgTDR]

44: Analog Out (P133)
1: 1 CAO1
2: 18 mV Loc [avgTDR]

45: Running Average (P52)
1: 1 Repts
2: 9 First Source Loc [TDR_2]
3: 19 First Destination Loc [avgTDR_2]
4: 30 Number of Values in Avg Window

46: $Z=X \cdot F$ (P37)
1: 19 X Loc [avgTDR_2]
2: 100 F
3: 19 Z Loc [avgTDR_2]

47: Analog Out (P133)
1: 2 CAO2
2: 19 mV Loc [avgTDR_2]

48: Delay w/Opt Excitation (P22)
1: 1 Ex Channel
2: 20 Delay W/Ex (units = 0.01 sec)
3: 0000 Delay After Ex (units = 0.01 sec)
4: 0000 mV Excitation

49: Do (P86)
1: 14 Set Flag 4 High

50: Set Port(s) (P20)
1: 9199 C8..C5 = nc/high/nc/nc

3: 0000 Delay After Ex (units = 0.01 sec)
4: 0000 mV Excitation

60: Do (P86)
1: 24 Set Flag 4 Low

61: Set Port(s) (P20)
1: 9119 C8..C5 = nc/high/high/nc
2: 9999 C4..C1 = nc/nc/nc/nc

62: Do (P86)
1: 15 Set Flag 5 High

63: End (P95)

64: Beginning of Subroutine (P85)
1: 6 Subroutine 6

65: Do (P86)
1: 25 Set Flag 5 Low

66: Set Port(s) (P20)
1: 8009 C8..C5 = input/low/low/nc
2: 9888 C4..C1 = nc/input/input/input

67: End (P95)

End Program