Smoke off the Water:
Determination of Mass Emission Rates from Off-Gassing Surfaces Using a Flux Chamber

By

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Abstract

A flux chamber is an effective and recognized means of sampling off gassing surfaces, such as landfills and settling ponds. Because there has been little discussion on the survey patterns used for deploying flux chambers. This thesis looks into developing a scalable survey pattern as part of a flux chamber test methodology that can accurately give a representative sample of the emission components and the emission rate of the entire area of interest. The test methodology evolved out of literature review and experiences of two case studies which are discussed within this thesis.

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List of Acronyms

AQL: Acceptable Quality Level

Bbl: Barrels of Fluid

BTEX: Benzene, Toluene, Ethyl benzene, and Xylene

CAA: Clean Air Act

CEM: Continuous Emission Monitoring

CEMS: Continuous Emission Monitoring Systems

CEPA: Canadian Environmental Protection Act, 1999

CH_4 Methane

CO_2 Carbon Dioxide

DEM: Digital Elevation Model

EPA: United States Environmental Protection Agency

FID: Flame Ionization Detector

GHG: Greenhouse Gases

GIS: Geographic Information System

HAP: Hazardous Air Pollutants

N_2O Nitrous Oxide

O_3 Ozone

Ppm: Parts Per Million

TPH: Total Petroleum Hydrocarbons

THC: Total Hydrocarbons

VOC: Volatile Organic Compounds

List of Equations

Determination of a Chamber Flux Rate

$$F_c = \frac{\left(\frac{V_c}{A_c}\right)dC}{dt}$$

Determination of Chamber Volume

$$V_c = t * Q$$

Determination of Chamber Area

$$A_c = \frac{V_c\left(\frac{dC}{dt}\right)}{F_c}$$

Determination of Total Surface Flux Rate

$$F_{total} = \left(\frac{1}{n}\sum_{i=1}^{n}F_{ci}\right) \times A_{total}$$

Determination of Size for Hexagons

$$b \approx \sqrt{\frac{a}{n} * \frac{2}{3\sqrt{3}}}$$

Determination of Error Bias

$$Error(\%) = \frac{predicted\ flux - calculated\ flux}{predicted\ flux} * 100$$

Determination of Cumulative Emissions

$Emission\ Estimate\ (kg\ emissions)$

$$= Emission\ Factor\ \left(\frac{kg\ emissions}{inhabitant}\right) * Population\ Density\ \left(\frac{inhabitants}{unit\ area}\right)$$

$$* Area\ (total\ area)$$

Determination of Number of Sampling Points

$$n^* = [TR(V)/1^T V1]n$$

List of Variables

a   The Area of Study

A_c Cross-Sectional Area of the Chamber (m^2),

A_{total} Total Surface area (m^2),

b   The Side of the Hexagon,

dC/dt   Concentration Gradient of the Component Gas (g/m^3/*unit of time),*

F_c Surface flux Rate (gm^{-2} *unit of time*$^{-1}$),

F_{ci} Surface flux Rate Iterations (gm^{-2} *unit of time*$^{-1}$),

F_{total} Total Surface Flux (gm^{-2} *unit of time*$^{-1}$),

g   Grams (g),

i   Iterations,

mg   Milligrams (mg),

n   Equals a Given Sample Size,

n*   Effective Sample Size,

Q   Flow Rate of the Gases into the Chamber,

t   Time,

TR   Denotes the Matrix Algebra Trace Operator

$1^T V1$ Redundant Statistical Information

V_c Volume of the Chamber (m^3),

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1   Introduction

1.1   Background

Public pressure during the 1960s and 1970s forced governments to require industry to quantify the emission of pollutants allowing them to be regulated (Jahnky, 2000). Measuring and monitoring is one of the feedback loops in a system, which provides indications of changes within the system. To quantify the emissions of a pollutant, it needs to be measured precisely and repeatable while being representative of the source.

Humans can never fully control all parts of a system that generate pollutants but can only affect small parts of it (Meadows, 2001). The resulting effects from the changes can create cascading changes within the system. Those changes can be neutral, positive or negative depending on the observer (Draper, 2002). The more knowledge one has about a system, the better one can see the effects they have on the system. The more feedback loops within a system, the more difficult it is to identify forces of changes within the system. The amount of pollution generated by a system depends on the relationships between the various parts in the system, for example the link between combustion temperature and the formation of nitrogen oxides within an engine (Meadows, 2001). Measuring the emissions of a pollutant is the first part of understanding a feedback loop within the system, so that one can better manage the generation of that pollutant within the system.

Monitoring gas emissions from area sources, such as sewage lagoons, tailing ponds, settling ponds, bogs and landfill sites, presents unique set of challenges. The research that will be discussed in this paper is part of a growing interest in emissions from these types of sources as they are sources of fugitive air pollution, which are difficult to measure and can have an impact on the local environment. Due to the nature of the emissions and the difficulty in sampling them, well-defined methods have not been developed to measure the pollutants being emitted from bodies of water.

1.2   Objectives

The easiest pollutants to measure are the easiest to manage; for example household waste is measured by weight and managed by disposal in an engineered solid waste management facility (this ignores secondary pollutants like odours, and leachates). Pollutants like gases, which are often invisible, are more difficult to measure. If the source of a gas is not easily identifiable, the difficulty in measurement increases and often requires specialized equipment and trained technicians to conduct the measurements. The objective of this thesis is to present a method to measure these more difficult sources of pollution, providing consistent comparable results.

Identification of pollutants is important because many have health effects, and thus measurement methods need to measure accurately at the levels that affect human health. Furthermore, pollutants may impact human health at differing levels of concentration (i.e., some are related to short term, with high or low dose exposure, while others only impact health over a long period of time at a high or low dosage). For

pollutants that are either difficult to identify or that come from an indirect source,

quantification can be a significant challenge. For something to be measured it needs an

accurate, repeatable methodology to derive metrics for it so that the source can thus be

monitored for changes over time. Hence, more complex methods are often required to

measure them and the sensitivity of the measurement methods is important. This thesis

will touch on some of the current sampling methods and explore some of the limitations

of fugitive gas emission monitoring from area sources, like swage lagoons. Within this

paper, a sampling method that can provide reasonably consistent comparable results

will be suggested.

1.3   Approach

Using a review of the literature and case studies, this paper provides an overview

of test methodologies for measuring flux emissions from non-point sources and the

considerations involved in the proper execution of the test methodology to get a

representative sample of the emissions. Some of the theoretical background to the

problem of pollution from bodies of water will be covered. A discussion of some of the

sources of subsurface pollutants and the factors that generate their fluxes will build an

understanding towards the developing of the proposed sampling methodology.

A flux chamber is a device for determining the emissions of gases over a small

area at a single location. The flux chamber allows the gases to collect in order to be

measured. Discussing the specifics of using a flux chambers to sample gases released

from bodies of water is the major focus of this paper. The issue is whether the small

area covered by the flux chamber at that point is representative of the entire area. The

question becomes how many sample points are needed to create a representative

sample of the emissions and balance that with the practicalities of collecting those

samples. The paper also discusses considerations when it comes to the specialized

equipment needed to conduct the proposed sampling methodology.

2   Context

2.1   *Basics of Pollution Sources*

Pollution is prevalent in all parts of our environment and is found in various forms in air, water, and land. In general, pollution comes from either, point sources or non-point sources. A basic understanding of the differences and the challenges of measuring non-point source verses point sources are highlighted below.

Point sources are generally considered to be emissions from stacks or pipes. It is easier to create measurement systems for point sources as they have well-defined boundaries that concentrate the pollutant into a small area. Point sources are often directly linked to an industrial process. Typically pollution releases can be correlated to process controls during production. These process controls and indicators such as operation temperatures and feed rates can be measured indirectly or directly. For example the amount of fuel used by an engine or a boiler is directly related to the pollutants released into the atmosphere and can either be determined by monitoring the pollutant release or the fuel feed rate.

Non-point sources have less solidly defined boundaries. Difficulties in defining the release area affect the accuracy of the calculated mass emission rate. Non-point sources are sources that are difficult to define spatially such as a field, a pond, or an accumulation of smaller sources, such as vehicles, livestock, or leaking valves. For these types of sources the sampled population or number of sampling points needs to be statistically representative of the whole population or sample area. This will be

discussed in greater detail later in the paper. Non-point sources are also known as

diffuse sources; the terms are used interchangeably in the literature so for the purpose

of this paper they will be considered the same (Ministry of Housing, Spatial Planning

and the Environment of the Netherlands, 1998).

The emission discharge rates of non-point sources are not necessarily

dependent on the production process and can be subject to many variables. When a

garbage incinerator (point source) is operating, it is generating gaseous emissions, turn

it off and the emissions from the incinerator stop. A landfill is always generating

gaseous emissions regardless of waste being added or not. This also means that

process controls often cannot be used to control the emissions especially for large area

sources like tailing and municipal settling ponds. A single snap shot of the emissions

from a non-point source may not have the same correlation as a snap shot from a point

source. Many of the issues highlighted in the collection and reporting of results using

flux chamber sampling methods for bodies of water can also apply to landfills,

agricultural fields, bogs and marshes.

2.2   *Pollution Sampling*

In order to measure a pollutant, the pollution source needs to be defined as well

as the sampling methods. Non-point sources also known as fugitive emissions are

becoming more important. The emissions that escape the controlled environment via

leaking valves, dust from stockpiles, or emissions from industrial lagoons are

considered to be fugitive emissions. Fugitive emissions are, for some facilities, their

largest source of pollutants being emitted into the environment. Non-point sources can also be made up of a several smaller point sources, such as cars, wood burning fireplaces or livestock.   Nationally, emissions from non-point sources such as cumulative small point sources associated with transportation are becoming the largest sources of emissions.

Non-point sources are not directly linked to a single specific production process as point sources are. As a result, they are more difficult to measure directly. In order to understand how to measure a non-point source, a basic level of understanding of existing point source measurement theory is required to maintain the comparable standards of data quality.

Point sources are far easier to identify, and sampling from them makes quantifying those emissions straightforward. Quantification has led to better pollution control systems for emissions from point sources. It is still common practice for samples from point sources to be manually extracted and analyzed (Jahnky, 2000). Direct sampling is often used interchangeably with manual sampling within the literature. Manual sampling methods for this paper are defined as methods in which a human has to be present to oversee parts of the extraction and analysis of the physical samples. The drawbacks to manual source test methods are that they require coordination and preparation, and can result in the source's operating conditions being optimized for the testing (Jahnky, 2000). Therefore, the test may not accurately reflect the emissions being produced by the source overall. Unless the sampling is continuously repeated,

manual source test methods only provide a snapshot of the emissions from a source

and may not truly represent the day-to-day emissions (Jahnky, 2000).

Manual sampling of point sources has led to improvements in pollution control

equipment. Increased efficiencies in pollution control and monitoring systems has

resulted in lower amounts of pollutants being emitted. Industries and regulators are

driving this, as many industries are charged by the amount of pollution emitted per year.

As emissions of pollutants become lower, then regulators can lower the air quality

permit limits. This has led to improvements in the detection limits of the sampling

equipment and the sampling methods. This has also led to the development of

automatic sampling methods and technologies, which are independent of human control

for the collection and analysis of a sample. Automatic sampling methods require

configuration of sensors, analysers and data acquisition systems; all requiring on-going

maintenance. Automatic sampling methods can provide continuous real-time

information about the pollution discharge rates.

Pollution sampling equipment, similar to the pollution sources, is roughly broken

down into two different categories. The sampling equipment provides either direct

sampling or remote sampling. Remote sampling detects the pollution in the

environment, for example by camera, lasers or radars, and does not interfere with the

source or the environment to conduct its measurements. Direct sampling removes

samples from the environment by inserting a probe into the area of interest and

extracting a sample for analysis.

The sampling equipment can be further classified as either using automated or manual sampling methods. Direct manual sampling methods extract a representative sample at a specific time. Manual sampling methods typically involves technicians going to the source to collect a sample. With automated sampling methods the equipment is set up to constantly take measurements from the source. Determining the most suitable method requires evaluating the source, the pollutant and the limitations of the method. An example of direct manual sampling would be the US Environmental Protection Agency (US EPA) Method 5, *Determination of Particulate Matter Emission from Stationary Sources* where the sampling system and the operator, conducting the measurements are next to a smoke stack (United States Goverment , 1990). Direct automated sampling methods are generally referred to as Continuous Emission Monitoring (CEM) systems. US EPA Method 7E *Determination of Nitrogen Oxides Emissions from a Stationary Source (Instrumental Analyzer Procedure)* is an example of the CEM method. An example of a remote manual method would be the use of infrared cameras to detect leaking valves. Automated remote methods can also include the use of satellites and aerial photography to collect information about the site. Measuring a non-point source often relies on a combination of both manual and continuous methods. Because the proposed method for measuring fugitive emissions from bodies of water is a direct sampling method, more focus will be paid to understanding that sampling method.

Ambient monitoring systems, while not in-situ to a source, would be considered as direct automatic sampling, because they are often automated systems that may alter the environment when they collect the samples. While ambient monitoring systems can be useful in determining the ambient impact of a pollutant, they cannot directly determine the source or the emission rate. However, the available data, such as wind direction, may allow technicians to indirectly determine likely sources and emission rates. In an area with a high concentration of different sources, determining the emission rate of a single source, by ambient monitoring can be next to impossible.

2.3   Emission Sampling in Context

The accuracy of determining emission discharge rates depends on the accuracy of the measurements at the sources. The less accurate the measurements, the less confidence there is in the emission discharge rates. Emission discharge rates derived from direct measurements are generally considered more accurate than emission rates calculated from indirect measurements and by calculated emission factors. Direct sampling is often quicker for point sources, more accurate and in many cases, cheaper than calculated emission factors. However, the same cannot always be said for direct measurements of non-point sources. Specifically, there is no standardized method for emission measurements from large area sources. In addition, these methods are often impractical due to the time required for the sampling and the resultant cost of conducting the testing. Currently there are few means of sampling gases directly from large area sources. There are also few regulators pushing for direct sampling of non-

point sources, thus the cost of creating the equipment and the testing method has been

left in the hands of researchers and forward thinking industries.

In deciding which method of sampling to use, the practicality of the given test

methodology needs to be taken into account. For example measuring particulate matter

from point sources requires that the particulate be extracted isokinetically, requiring a

specific length of straight ducting (Alberta Environmental Protection Services, 1996).

Isokinetic sampling is the extracting of gas and particulate matter at the same energy

level as the flue gas, thereby extracting an equal portion of the large and small particles

found within the gas stream. In other cases the hazards of the sampling location may

also dictate the choice of sampling methods. The goal of what the sampling is to

achieve also plays a role in the choice of sampling methods. The type of emission and

the type of source can be measured using different sampling methods. A point source is

not sampled in the same manner as an area source or a fugitive source. The results of

the sampling methods and what can be inferred about the sources also differ. The

sampler needs to understand what the sampling methods do in order to apply them

correctly and attain the desired results.

A test method can be designed to be highly accurate and precise but may be too

expensive, cumbersome or labour intensive to be widely adopted. Tests that are

required to be carried out routinely to check pollutant levels need to be relatively

inexpensive and simple to execute. If the testing is too difficult or expensive, they will

not be conducted regularly because it is financially punitive for the polluter to test at

intervals to be useful for determining emission trends. Tests designed to monitor a

pollutant, need to be conducted regularly enough to provide environmental information

of value that outweighs the cost of conducting the testing. Another consideration in

designing a test methodology is that it needs to be flexible enough to be adaptable to a

variety of different situations. Each facility where the tests are preformed has its own

slight variations in the way the facility operates, and in the location where the testing is

performed. The testing methods need to be adaptable to slightly different test

environments that exist at the facility being tested.

The test methodologies need to be reliable enough to give consistent results,

regardless of the source being tested or competency of those conducting the tests.

Environmental sampling is about collecting a representative sample. This often requires

answering several questions dependent on the site itself. Specifically it is important to

determine the number of points to sample for an area, and how frequently the source

should be sampled during a specific time period. This of course must be balanced

between the cost of conducting the sampling and the value of the information generated

from the sample.

2.4 Fluxes and Why They Need to be Measured

Current industrial society generates a lot of waste materials. Landfills are created

for solid wastes and settling or tailing ponds are created for liquid wastes. Groundwater

can become contaminated through leaching of toxicants from these waste sites or

through spills thereby creating large areas of contaminated soils. Chemical and

biological processes start to break down the waste, which in turn can generate small amounts of toxic gases. These gases build up and migrate through the subsurface and can even cross surface boundaries releasing the gases into the atmosphere. The rate at which a particular compound passes through a boundary between two media is known as the flux. The summation of several fluxes of a pollutant across a non-point source is the pollutant's discharge emission rate, or how much of the pollutant is being released per unit of time. While the flux from an individual point can be minor, when accumulated over a larger area the total amount of gases released can become substantial. The potential emission of large amounts of gases from area sources is a major reason why emissions from non-point sources needs to be better monitored despite the challenges in getting accurate direct measurements. A source could be such a large area that it is impractical for it to be sampled as a whole. Unless the sampling is part of an automated system that monitors the entire area, any sampling is a snap shot of the emissions at the time and location of the sampling.

Contaminated sites including settling ponds and sewage lagoons, can release many kinds of contaminants for example: Volatile organic compounds (VOCs) released into the air at levels that exceed the transportation of those compounds through groundwater (Murthy, 1993). Under the USA Clean Air Act (CAA) regulation, 40 CFR 51.100(s) reactive VOCs are defined broadly as any volatile compound of carbon that takes part in photochemical reactions in the atmosphere (Dicataldo, Richins, Spiroff, & Nelson, 2009). These VOCs contribute to the creation of ground level ozone. Ozone

(O_3) in the upper atmosphere protects us from harmful ultraviolet rays but on the ground it is toxic to humans, vegetation, and animals, and hence these emissions are detrimental to human health and the environment (Dicataldo, Richins, Spiroff, & Nelson, 2009). Furthermore, birth defects, cancer, and respiratory illness are some of the direct effects on human health from exposure to VOCs (Murthy, 1993).

Health issues prompted the US Environmental Protection Agency (US EPA) to regulate VOC emissions into the air at facilities that were subject to the 1984 Resource Conservation and Recovery Act Amendments (Murthy, 1993). That act was replaced by the CAA in 1990, with an updated list of chemicals including VOCs that had to be regulated. The CAA also gave the US EPA the ability to add and delete chemicals (Murthy, 1993). In Canada the enabling legislation that requires the measurement and control of pollutants is the Canadian Environmental Protection Act, 1999 (CEPA, 1999). At this time there are no regulations directly requiring non-point sources to be tested or how they are to be tested. Currently it is up to the individual industries and local authorities to decide on the best approach for industrial facilities to meet their environmental commitments and reporting requirements. As emission limits shrink and cap and trade emission schemes grow, the need to more accurately measure the emission of non-point sources will also grow.

Additionally greenhouse gases (GHGs) which have been identified as one of the causes of global warming, can be released from contaminated sites (Demarty & Bastien, 2009). The potential impact that these gases have on the global climate has

led to the need to develop better instruments to quantify GHG emissions (Senevirathna, Achari, & Hettiaratchi, 2007). Much work has been done to reduce GHG emissions from point sources and hence the focus is now switching to area sources of GHG.

Reported emission rates are often assumed constant over the course of a year yet the actual emission rates may vary greatly depending on a variety of factors. If the direct sampling of a sewage pond is done on a cool day in the wintertime the flux would be lower than on a hot day in the summer (Nagaraj & Sattler, 2005). This is the limitation of using a fixed emission rate over such a long period of time. The facility could be reporting higher rates than are actually being emitted leading to unfair penalization for emitting more than is actually released or vice versa emissions could be underreported. The underlying issue for doing direct measurements is to get accurate emission rates for a given time interval, usually a year.

2.5   Non-Point Source Pollution

One of the common gases released by non-point sources is methane, which is a flammable, colourless odourless greenhouse gas. Methane is produced by the decomposition of organic material under anaerobic conditions, found in landfills, settling ponds, bogs and marshes. Depending on the pollutants in the subsurface a whole host of volatile organic compounds could be released, including those that are hazardous to human health. The VOC's could include compounds like acetone, glycol ether from unused paints and benzene from waste fuels and plastics. Other potential released gases include other greenhouse gases such as carbon dioxide and carbon monoxide.

There is public pressure on governments to reduce greenhouse gas emissions, because of the link to climate change that was put forward by the Intergovernmental Panel on Climate Change (IPCC) (Gore, 2007; Spencer, 2010; IPCC, 2007).

Carbon dioxide (CO_2) is one of the GHGs and is created, along with methane (CH_4) and Nitrous Oxide (N_2O), by bacterial degradation of organic material in water and sediment. The degradation increases the concentration of the gases within the body of water (Demarty & Bastien, 2009). Photosynthesis in a body of water has the reverse effect; the dissolved gases are turned into building blocks for the photo synthesizer's continued growth thus reducing the concentrations and the flux (Demarty & Bastien, 2009). Fluxes can also be used to indicate volcanic activity or other geological processes taking place below the surface (Smithsonian National Museum of Natural History, 2008).

In aquatic systems the concentration of GHGs depends on a number of chemical and biological factors, such as the nutrient and algae concentrations (Demarty & Bastien, 2009). These factors influence ambient air pollution concentrations, emission rates and dispersion rates of non-point sources (Nagaraj & Sattler, 2005). Places like landfills and wastewater treatment facilities can even generate enough GHGs (mainly methane) that it can be extracted and used.

In places such as wastewater treatment plants, volatilization and biological activity within the treatment ponds change with temperature. Biological activity in the ponds breaks down organic matter generating GHGs dissolved in water (Demarty &

Bastien, 2009). Depending on a number of factors within the water and the surrounding environment, the emission rate of the gases dissolved in water can change drastically. If the concentration of the gases in the water is higher than the concentration in the air, the gases will be released from the water into the atmosphere until the concentration is balanced (Demarty & Bastien, 2009). The reverse is also true. If the concentration of GHG in the air is higher than in the water, the GHGs will be absorbed into the water (Demarty & Bastien, 2009). This ability to have positive and negative fluxes of gases across a surface is why there is a need to have a reliable direct measure of the gases being emitted to the atmosphere. Soil samples and ambient air samples provide indications of concentration; they do not indicate which way the pollutant is traveling. Tracking the fluxes can also help identify substrates that absorb GHGs. The more the processes affecting fluxes are understood, the better chance there is of manipulating these to suit society's needs. Ultimately this is about pollution control based on the monitoring of the emission rates of harmful pollutants.

3   Fugitive Emissions

The release of pollutants from surfaces like soils and bodies of water into the atmosphere has received comparatively little attention in the scientific literature relative to other sampling technologies. This is possibly due to a belief that surface emissions are not considered a significant transport method relative to other processes (Tillman Jr., 2003). The concentration gradient of the pollutant is relatively small, however given the large interfacial areas; the surface fluxes may represent a significant pathway for the emission of pollutants (Tillman Jr., 2003). In a simulation conducted by Tillman over the course of a 30 day sampling period, it was estimated that roughly 1.718 million litres of gas left the soil in a 6.07 ha plot (Tillman Jr., 2003). If only 1% percent of that gas was a pollutant or GHG it would still mean 17,890 litres were released every 30 days. To put this in perspective, an average car in the US, which burns 3.7 litres every 32.6 kilometers, will have released the same amount of pollutants roughly every 152,800 km (US EPA, Office of Transportation and Air Quality, 2005). According to the US EPA, the average passenger car travels 19,300 km each year therefore it will take just under 8 years for one car to release the same amount of GHG as one contaminated field could in a month (US EPA, Office of Transportation and Air Quality, 2005). This was only a simulation and there are a huge number of factors that affect the amount of gas respiring in and out of a soil. However Tillman's study does put in perspective the potential emission rates that these surfaces have and the size of the pathway. The total

area may be releasing significant amounts of pollutant yet the pollution released per

square meter could be barely detectable.

On the other hand some locations like municipal sewage settling ponds with their

high biological content can have high enough fluxes that bubbles can be seen on the

water's surface. The fluxes within some of these ponds can be high enough that the

methane formed in the pond could be collected and used for generating power.

3.1   Forces Moving Gases Below the Surface

Barometric pressure is a measure of the downward force of a column of air (Oke,

1987). Changes in air pressure will change the flux in soils. As pressure drops, a

relative vacuum is created over the surface drawing more of the pollutant out of the soil.

The changes in atmospheric pressure over soils create an almost respiratory effect

(Tillman Jr., 2003). The flow rate of this 'respiration' was recently recorded as being as

high as 20 litres per minute in and out of a 2.54 cm test well. (Tillman Jr., 2003). The

'respiration' of the soil means that pollutants can travel both in and out of a porous soil.

The 'respiration' rates are dependent on the porosity of the soil, the moisture content

and the cycling of atmospheric pressure. It has been found that methane fluxes in

landfills rise dramatically during periods of lower barometric pressure (Tillman Jr., 2003)

and hence changes in barometric pressure can have a large impact on the fluxes of

gases over soils. Barometric pressure changes have been observed tens of meters

down in unsaturated soils (Tillman Jr., 2003). The atmospheric pressure near the

surface is constantly changing, due to short-term diurnal fluctuations or longer-term cycles resulting from the passing of weather systems (Tillman Jr., 2003).

Changes in the ground water levels will also create movement of a gaseous pollutant throughout the unsaturated soil that sits on top of the saturated soil that defines the groundwater level. As the ground water level drops, there is more space for gases to fill creating a vacuum, which draws air downwards. Conversely, if the ground water levels rise, it will force the gases in the soil out into the atmosphere (Tillman Jr., 2003).

There are several factors that affect the volatilization rate of waste gases within a soil matrix. For example, increases in soil temperature and porosity tend to increase the emissions of gases while increased moisture content of the landfill waste and the covering soil tends to reduce the emissions (Murthy, 1993). Organic chemical wastes with higher molecular weights volatilize more slowly than those with lighter molecular weights (Murthy, 1993). The organic compounds can also react with other chemicals thus altering their volatilization rates and their fluxes. There are several other processes of diffusion and absorption that can also affect the fluxes of pollutants, which will not be covered in detail in this document.

4   An Emission Isolation Flux Chamber

An emission isolation flux chamber, here after referred to as a flux chamber, provides a simple way to directly measure the emissions coming off a surface. The theory behind how flux chambers work is relatively simple. Gases are generated and through a range of processes those gases can travel across a surface boundary. As noted previously the movement of gases across a surface boundary is the flux. Fluxes work on the basis of molecular diffusion ideally following Fick's first law of diffusion (Murthy, 1993). The flux is the rate that the diffusion across a boundary occurs. The flux chamber is a sealed chamber that allows the gases to build up to a point that they can be measured. This gives the researcher the ability to directly sample the emissions coming from a portion of the surface of a particular area source.

Diffusive gases build within a subsurface, and the flux across the surface can be measured using a chamber to monitor the buildup of gases over a period of time (Matthews, St Louis, & Hasslein, 2003). The concentration over time becomes the emission rate for the area that the flux chamber is covering. By extension that emission rate is also representative of the immediate surrounding area. As the area gets larger the emission rate becomes less representative. Multiple sampling points are used to build a composite emission rate for a larger area. The multiple sampling points can be tested using a network of chambers or an individual chamber that is moved from point to point. The challenge is that the flux of gasses from a surface may be different across the surface depending upon subsurface conditions.

The increase of the concentration of gases in the chamber is used to calculate flux. The flux measured in several chambers is used to estimate gas exchange over a large area (Matthews, St Louis, & Hasslein, 2003).   The flux from the total surface is not measured, but calculated from the individual chamber measurements. The more points measured, the more statistically representative is the estimate.

To determine the flux rate from a given flux chamber the following equation is used:

Equation 1   Determination of Flux with a Chamber

$$F_c = \frac{\left(\frac{V_c}{A_c}\right) dC}{dt}$$

Where:

- F_c =Surface flux rate (gm^{-2} *unit of time*$^{-1}$),

- V_c = volume of the chamber (m^3),

- A_c= Cross-sectional area of the chamber (m^2), and

- dC/dt = concentration gradient of the component gas (g/m^3/*unit of time)*

    (Senevirathna, Achari, & Hettiaratchi, 2007).

The flux chamber provides a way of collecting gases so they can be withdrawn and analyzed. The flux chamber is to non-point source sampling what a compound sampling probe is to point source sampling. They are both very versatile and rugged pieces of equipment that can be used to sample a variety of different compounds.

Most sampling techniques have focused on detecting VOC emissions as indicators of ground water contamination (Murthy, 1993). These sampling methods do not characterize the soil gas plume (Murthy, 1993). The flux chamber samples at the boundary of the surface-atmosphere interface where many changes to the VOCs take place and which are not detected by a subsurface sampler (Murthy, 1993). Flux chambers have two basic methods of operation. Closed chambers and open chambers, the following discussion will outline the differences between the two.

4.1   Closed Chambers

A closed flux chamber is a container with an open end which is placed on the surface allowing gases to build up inside, see Figure 4-1. After a period of time the gases are extracted and sent to a lab for analysis. Closed chambers have the advantage of being simple and inexpensive and therefore many can be used simultaneously on an area source at a low cost (Senevirathna, Achari, & Hettiaratchi, 2007). The use of multiple chambers allows for the simulations mapping of flux over an area. Because the closed flux chamber allows the gases to build up inside the chamber over a period of time, even minute fluxes can be measured (Perera, Hettiaratchi, & Achari, 2002).
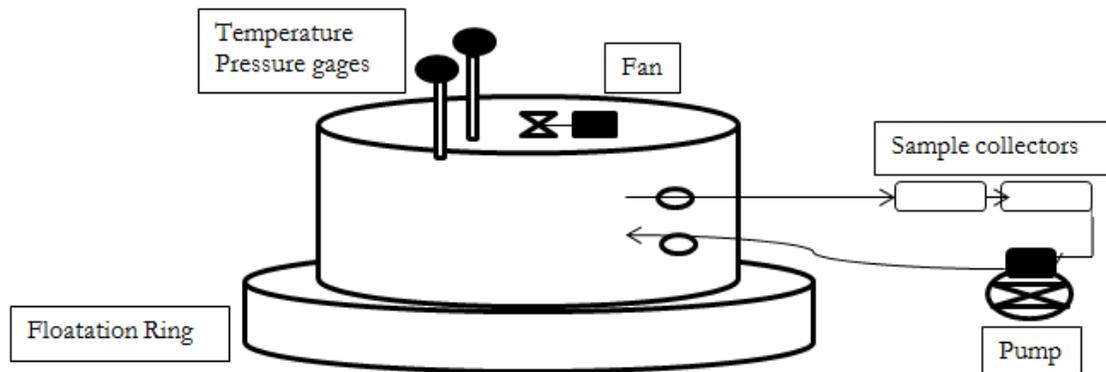
Figure 4-1 Closed Flux Chamber, (Figure created by G, Rutgers. 2013)

The closed chambers allow the gases to build up and then be extracted into something

like a Tedlar bag, or an absorbent material. A popular and simple absorbent material is

activated carbon in glass tubes because it absorbs many of the VOCs found in landfills

(Murthy, 1993). The flux chambers are versatile as the absorbent material can be

changed to match the targeted gases.

The disadvantage of the closed chamber is related to the effect it has on the site

that is being sampled. The closed chamber technique tends to underestimate the gas

fluxes by up to 55% (Perera, Hettiaratchi, & Achari, 2002). Gases flow from areas of

high pressure to low pressure, and this is the basis of the underestimate error (Oke,

1987). If the pressure difference between the inside and the outside of the chamber is

different, the gases will flow toward the lowest pressure and bias the sample. A

chamber with lower pressure than outside air will draw in more gases biasing the

sample high. However if the pressure is too low and the seal between the surface and

the chamber is not complete it may draw in surrounding outside air providing a low bias. If the pressure in the chamber is higher than outside air, less gas will flow into the chamber and bias the sample low. These changes in pressure can result from simple changes in the atmospheric conditions. For example, the sun can warm the chamber causing the temperature of the gases inside to rise thus increasing the pressure inside the chamber forcing the flow of gases out of the chamber (Senevirathna, Achari, & Hettiaratchi, 2007).

Even with all the potential errors that a closed chamber has, they are still popular in studies because they are easy to use, require little maintenance, are logistically convenient, and require no power to operate (Murthy, 1993). Closed chambers are also better suited for low flux environments where the sampling duration for a measureable sample extends beyond a 24 hour period.

The flux chamber is only sampling a small fraction of the total area for the emissions and the researcher needs to be aware that the potential alterations to the microenvironment around the chamber may be large in closed chamber systems (Riechman & Rolston, 2002). Open chamber systems (discussed next) if operated properly, have little effect on the microenvironment (Riechman & Rolston, 2002).

4.2   Open Chambers

In an open flux chamber, gas is simultaneously pumped in and out of the chamber and the gas is continuously monitored by an analyzer, see Figure 4-2. The open system

provides real time fluxes; a closed chamber only provides an average flux for the

sampling duration.
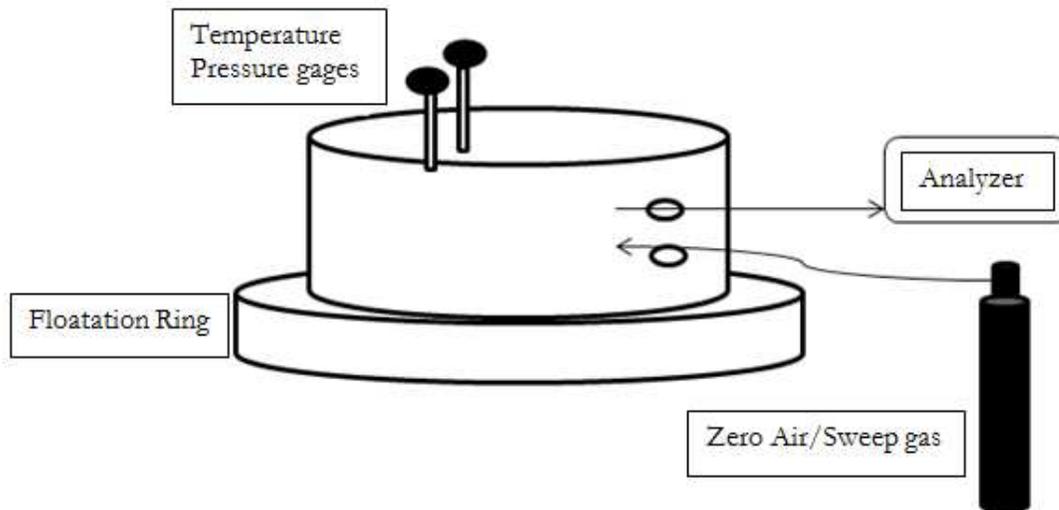
Figure 4-2 Open Flux Chamber (Figure created by G, Rutgers. 2013)

The pressure difference between the inside and the outside of an open chamber is

easier to control by adjustments to the amount of gas flowing in and out of the chamber.

That control can also cause issues. That is, the flow rate into the analyzer needs to be

balanced with the flow rate from the sweep air. Otherwise if the chamber is floating on a

pond and the gas flow in is less than that of the gas being withdrawn, a vacuum is

created inside the chamber. If the flow imbalance is left too long, the chamber will start

to sink as the water climbs into the headspace of the chamber. The opposite happens if

the inflow is greater than the outflow, gas will start to leak out of the bottom edge of the

chamber.

In an open flux chamber the gases inside the chamber are constantly being exchanged with sweep gas. Fluxes are determined by the volume of the chamber. If the volume in an open flux chamber is changing due either to sinking or to over floating the chamber, then a true flux is not determined as the volume of the chamber keeps changing. In an open chamber system the gases are continuously being analyzed. With a constant volume, real time fluxes can be determined. The actual sampling of the flux only starts after the volume of air in the chamber has turned over once. The reason for exchanging the volume of air before sampling is to minimize any buildup of gases within the chamber that would bias the flux. By turning over the volume of gas in the flux chamber it flushes the system so that once sampling begins there is a relative degree of confidence that the gases being sampled are being sampled at the rate they are being emitted. Variations in the flux due to changes in the environment or processes within the substrate can then be observed because other sources of bias have been minimized. It has been found that open flux chamber systems have a reasonable agreement between the aerodynamic methods used on ambient monitor stations to determine emission levels (Riechman & Rolston, 2002). Ambient monitors rely on winds to move the contaminant across a sensor, the fluxes are calculated from the concentration, and predicted dispersion and wind speed (see section 2.2). The use of multiple sampling methods is a way to verify the results.

4.3   Drawbacks of Flux Chambers

There has been a lot of research about details of flux chamber design. Because they are an emerging sampling technology, the chambers are often custom made. The standards and designs of the chambers change from study to study. In a study by Waite and others it was found that the chambers they used, over-turned aluminum cooking pots, under reported the fluxes compared to estimates using ambient air sampling methods (Waite, Cabalo, Chau, & Sproull, 2007). Conversely in a similar comparison study, the chambers, blue polycarbonate water-cooler bottles with the bottoms removed, were over reporting the fluxes (Matthews, St Louis, & Hasslein, 2003). The problem with comparing these two studies was they were carried out at different locations and different times. This makes comparing the difference between the different chambers' design and sampling biases difficult. In yet another study a more advanced chamber design was used. The chamber was a Teflon coated stainless steel cylinder open at one end and the other end was sealed by a flexible membrane of Tedlar film. Attached to the side of the chamber was a small air pump to re-circulate and mix the chamber air, as well as a series of carbon traps to absorb the desired compounds (Tillman Jr., 2003). The flexible membrane allows for the expansion and contraction of the chamber in relation to changes in atmospheric pressure and eliminates changes in the pressure gradients (Tillman Jr., 2003). The only issue with using a flexible membrane is the constant changing of the chambers headspace.

A dynamic open chamber has been found to have the potential to both over and under estimate fluxes in a number of different situations. Riechman and Rolston (2002) reported that on high permeability soil with a low airflow rate, an open chamber will underestimate the flux; if the air flow rate is high the chamber will overestimate the actual flux (Riechman & Rolston, 2002). There are several possible reasons for the mixed results including the sample not being well mixed within the headspace of the chamber and the over or under pressurization of the chamber. It is also possible that with a low flux, an open chamber will not allow the target gases to build up enough to be measured by the analyzer.

As a direct form of measure a flux chamber will impact the micro environment surrounding it. Often these impacts are related to temperature, moisture, and surface winds, that is the surface under the chamber will be protected from winds and to some degree the air temperature and air moisture. The combination of open and closed chamber sampling is attractive because it can minimize the bias caused by each type of chamber.

If the gas of interest has a different density than the ambient gases in the chamber, the gases can stagnate and stratify if not agitated. A sweep air system needs to be used within the chamber to keep the gases well mixed (Su & Su, 2003). This may either be a fan to mix the air in a closed chamber or the inlet gas from a cylinder that balances the sample being withdrawn in an open chamber. The sweep air system has another challenge in that it needs to flow parallel with the sampling surface in such a

way so as to minimize the alterations to the surface friction so that the results are representative of the surface's actual emission rates.

An additional consideration to flux sampling is the protection of the technician who sets up the sampling system, and who collects the sample, because the technician is exposed to the pollutants being released. The sample duration may also be long or the locations difficult to access so that automated systems may be required. Because of the number of different sampling chamber designs comparing studies is difficult (Murthy, 1993; Su & Su, 2003). Of the several variables considered (height, diameter, ratio of height to diameter), chamber height was found to be the most important variable influencing errors associated with closed chamber flux measurements. For most fluxes, the error increases significantly when the chamber height is less than 10 cm (Senevirathna, Achari, & Hettiaratchi, 2006). The flux also impacts the error: the higher the fluxes, the larger the error (Senevirathna, Achari, & Hettiaratchi, 2006). Senevirathna et al. show that the error in flux chamber measurement is controlled by three variables, namely chamber height, fluxes, and flux measurement duration. The resulting error could be controlled by selecting a chamber of suitable height provided the flux is approximately known and the sampling duration is kept short (Senevirathna, Achari, & Hettiaratchi, 2006, p. 243).

What this implies is that a variety of chamber sizes is needed to sample different fluxes. Senevirathna et al. (2006) discuss the variables that affect the error of a closed flux chamber and the factors to consider when sampling. The chambers need to be

sized appropriately to accurately measure the flux. The chamber needs to be large

enough to collect a measurable sample in a relatively short period of time. If the

chamber is too small or the duration too long the inherent errors of the flux chamber

system build and bias the results. As mentioned there are two different kinds of flux

chambers, open and closed. Used together they can eliminate each other's biases. In

large areas where multiple sampling locations are needed, closed chambers are

inexpensive allowing multiple chambers to be operating at the same time. The flux off

the surface and the pollution of interest will dictate the type of chamber to be used.

Closed flux are better suited for long deployments needed for low fluxes, open

chambers are better suited for yielding real time results on higher fluxes.

5   Using a Flux Chamber

Similar to isokinetic sampling in which the diameter of the sampling nozzle changes depending on the flow rate, the chamber size also changes according to the expected flux. A higher flux can use a smaller chamber, which requires a shorter sampling time than a bigger chamber. The larger chambers require longer sampling times for lower fluxes in order for enough gases to build up in the chamber to be sampled. The larger the flux chamber the smaller the detectable flux can be. The size of the chamber also plays a role in the amount of inherent errors found in the flux chamber. In lab tests, the smaller chambers build up errors quicker than larger chambers (Senevirathna, Achari, & Hettiaratchi, 2006). In smaller chambers, pressures build more rapidly thus distorting the air flow from the surface. As noted earlier by Senevirathna et al, chamber height has a greater effect on the error measurement than the chamber's volume.

The rim of the flux chamber is placed below the surface creating a seal. Thus the only gases in the chamber are the known gas and any gases percolating to the surface directly below the chamber. Given the gas concentration, sample duration and the area of the flux chamber, the flux can be determined using Equation 1 referenced earlier

Equation 1   Determination of Flux with a Chamber

$$F_c = \frac{\left(\frac{V_c}{A_c}\right) dC}{dt}$$

To determine the most appropriate volume for the flux chamber to accurately sample a given flux, a few assumptions can be made about the sampling duration, gas concentration and the expected flux rate. An experienced sampler can make these assumptions from historical results or a test flux chamber could be used to get a rough initial flux to work with.

For an open chamber, the volume needs to take into account the sample flow rate of the sweep air system and the desired time to cycle the headspace once. The volume of the chamber is determined by the following:

Equation 2   Determination of Chamber Volume

$$V_c = t * Q$$

Where

- V_c = the chamber volume,
- t = the desired time for the headspace to be filled, and
- Q = the flow rate of the gases into the chamber.

With the desired volume determined, Equation 3 gives the area needed for the chamber to meet the sampling criteria.

Equation 3   Determination of Chamber Area

$$A_c = \frac{V_c \left(\frac{dC}{dt}\right)}{F_c}$$

Where

- F_c =Surface flux rate (gm^{-2} *unit of time*$^{-1}$),

- V_c = volume of the chamber (m^3),

- A_c= Cross-sectional area of the chamber (m^2), and

- dC/dt = concentration gradient of the component gas (g/m^3/*unit of time*)

In theory a chamber could be made to meet every potential sampling flux rate and

sampling duration. What the equation gives is an idea of the area needed. A technician

can look at the areas of the available chambers and adjust the sampling time as

required. As the chamber area and the flux rate decrease the sampling time increases.

The size of the chamber is dictated by the sampling requirements and the practicality of

the sampling device. The biggest challenge is having a methodology that is practical for

a variety of different surfaces under a variety of different flux rates.

5.1 Different Measurement Methods

There are other ways of indirectly measuring emissions from a large surface such

as a wastewater settling pond or a landfill. For example there is ambient air testing also

known as the aerodynamic method of sampling, micrometeorological testing, or eddy

covariance method (Riechman & Rolston, 2002). These methods typically incorporate

a series of sensors placed on a tower and rely on the wind to carry the pollution over

the sensors. The micrometeorological-based measurements, for example, are

frequently used to measure pesticide volatilization rates and concentrations at different

heights in the air (Riechman & Rolston, 2002). The micrometeorological method also

requires a large area to achieve a reasonable fetch which is also true of the ambient air

testing (Riechman & Rolston, 2002). The fetch is the distance upstream of a

measurement site, receptor site, or region of meteorological interest that is relatively

uniform. The method relies upon knowledge of the wind conditions and the buoyancy of

the plume. A large fetch area means that a large area can be sampled with a single

micrometeorological station if the winds are blowing in the stations favour. In marginal

wind conditions, micrometeorological methods tend to under report flux rates (Werner,

et al., 2003). The flux is determined by back calculating the measured concentration

and the assumed diffusion of the target gas. Micrometeorology stations are usually

combined with a Bowen ratio-energy balance (BREB) (Wywail, 2008). There is also vent

sampling, concentration-profiles, mass balance and transecting techniques (Murthy,

1993). Vent sampling and flux chambers are the only direct measure. When the

emissions are intermittent vent sampling is not suitable for soils (Murthy, 1993). Vent

sampling also does not work for water bodies as the vent is a perforated pipe driven into

the soil. Concentration-profiles and transecting techniques are variations of ambient

monitoring.

5.2 Flux Chamber Sampling on Water

Much of the work around flux chambers is based on their use on solid surfaces.

US EPA Method 600/8-86/008 *Measurement of Gaseous Emissions Rates from Land*

Surfaces using an Emission Isolation Flux Chamber: User's Guide, describes the basic

operations of flux chamber sampling on a solid surface as a single point of sampling

(Kienbusch, 1986). Flux chamber sampling on water is adapted from the use of flux

chambers on solid landfill surfaces. Applying the method to water bodies is relatively

simple if the principles of operation are remembered. For the chambers to work they

need to create a seal between the inside of the chamber and the surface. On water that

seal is created via the surface tension between the water and the chamber. On soil the

rim of the flux chamber needs to penetrate into the surface roughly 2.5 cm. If the seal

on the soil is ineffective the chamber could potentially be drawing gases in from outside

of the column directly below the chamber thus biasing the sample. Theoretically

pollutants are from the column directly below the chamber and not drawn in from the

surrounding area. Sampling from a liquid surface presents a few additional design

considerations for the sampling system. The placement and anchoring of the chamber

now becomes a factor, as does withdrawing a sample. If the anchor is placed directly

below the chamber, it may agitate the sediments at the bottom of the water body,

releasing an excess of the pollutant and biasing the sample high.

A flux chamber is buoyant partly due to the air trapped within the chamber. Most

chambers used on water have added floatation devices more for stability than for

buoyancy. To draw a sample from a closed land based chamber, the sample gas is

withdrawn from the chamber into a sampling medium outside the chamber. Examples of

these media are SUMAS canisters, Tedlar bags, and sorbent tubes.

The withdrawal of the gas from the chamber creates a negative pressure within the chamber. When the chamber is on a matrix of soil, the chamber remains in place and depending on the density of the soil matrix, air may get drawn in from the soil. On a liquid surface, withdrawing the sample to a media outside the chamber reduces the pressure inside the chamber causing the liquid to rise within the chamber. That rise of liquid alters the headspace within the chamber. Depending on the volume of gas being removed, the liquid could overcome the buoyancy and sink the chamber. The solution is to maintain a constant volume of air within the chamber. One way to do this is to add replacement air at the same rate as the sample air is being withdrawn. Alternatively the sample media could be placed within the chamber. Placing a Tedlar bag inside the chamber at the start of the test means that the volume inside the chamber remains constant throughout the test even after the bag is filled.

5.3   Edge Effects

The water level in a pond fluctuates, changing the surface area of the pond. Hence, edge effects refer to the changing total area of a pond, which results in the boundary area not being clearly defined. In sewage ponds with large amounts of suspended solids, what defines the shore and what is just floating solids in the shallows along the shore is often difficult to determine. The assumptions that the test operators make about the area of a fluctuating surface area need to be explained and reported when reporting the emission rates of the test area. This is where experience and understanding of the forces generating the targeted emission are needed. If anaerobic

digestion processes create the target pollutant and the boundary area is a hard exposed

lining, then measurements close to that edge will be of limited value. If the edge is a soft

soil matrix consistent with what would be expected at the bottom of the pond, the edge

measurements become more important. In other cases, the question is whether the

addition or subtraction of the edge areas affects the reported emission results. By not

taking the edge effects into account, the emissions from a body of water could be

misrepresenting the emission rates.

6   Flux Chamber Field Studies

As already discussed methane is a greenhouse gas created by the decomposition of organic matter (Draper, 2002).The first of the two case studies that will be discussed in this chapter is a survey of methane emissions from an anaerobic lagoon in the BC interior which was conducted as part of a larger project. This anaerobic lagoon is part of a municipal sewage treatment plant. The lagoon is used to settle out large solids as the first stage of the waste water treatment process. Thus the lagoon has a lot of organic material to decompose, which generates methane. The impetus for the project was to cap the lagoon and capture the methane. The emission survey was to determine the volume of methane being released and whether the best use of that methane would be either to flare it off or use it as part of a small co-generation unit. Determining the best use for the methane required knowing how much methane was available.

6.1   First Flux Chamber Study

The study was intended to measure the amount of methane being released from the water to the atmosphere. Water samples indicated that dissolved methane was in the water but not how much was being released to the atmosphere. Several other sewage lagoons in the sewage treatment plant, which neighbours the municipal landfill, surround the lagoon. All are potential sources of methane making ambient monitoring of a specific lagoon difficult. This is the kind of situation where flux measurements are important as a method of direct measurement of the movement of the target gas.

There was so much digestion occurring within the lagoon that gas bubbles were visible on the surface. An open floating flux chamber was used to avoid contamination from the surrounding sources and to get real time emission data. The sampling train operated in a relatively simple manner. Like a CEM system, this train was made up of the following components (Jahnky, 2000):

- from the source there was an extractive probe with

- a set of sample lines leading to a sample conditioner then to

- a pump, and

- an analyzer

The flux chamber was the extractive probe in the system. The rest of the system was very much identical to any other CEMS. The analyzer was kept on shore while the flux chamber was moved around the lagoon. The flux chamber that was used is referred to

as the PT minnow and is shown in Figure 6.1.

Figure 6-1 PT Minnow (Image taken by G, Rutgers. 2009)

The PT Minnow was made from a plastic bucket, originally used for creating

small garden water features. Modifications included adding a thermocouple, a sample

line in with sweep air system, a sample gas line out, and some foam for floatation and

balance. The air trapped in the chamber maintained the buoyancy while the foam kept

the chamber from overturning and sinking. Zero air was a nonreactive gas, which was

not read by the analyzer and was thus used to set the zero during calibrations. The flow

rate of zero air was matched to the flow rate of the sample gas line. If the two were not

matched the chamber would not maintain the pressure equilibrium between the inside

and outside of the chamber. The analyzer pump would either suck out all the air in the

chamber, creating a vacuum and sinking the chamber or alternatively, the sweep air

would over pressure the chamber and force gas out of the chamber, biasing the sample to low values. The zero air was supplied from a compressed gas cylinder.

The sweep air ensured the gas in the chamber was well mixed and in the case of floating chambers maintained the pressure equilibrium between the chamber and the outside environment, keeping a constant headspace within the chamber. There were four equally spaced nozzles placed above the waterline inside the chamber. The nozzles directed the flow of the zero air into a cyclonic pattern across the surface of the water. The sample line extracted the gases via a Teflon probe extending 2.5 centimeters below the top of the chamber. The sample line ran back to the shore where the sampled air was drawn through an analyzer.

It was realized that there was no established sampling pattern for conducting this kind of emission sampling. The lagoon was roughly a 2 ha triangle. The original sampling plan was to sample at the centroid of three equal-area polygons (see Figure 6-2). The flux chamber had a 45.7 centimeter diameter; this would mean that each sample point would represent roughly 0.7 ha. To put that in perspective 0.7 ha is nearly 1 ½ football fields which is being represented by a single large pizza in the center. That comparison is the heart of the issue that is being discussed. Are those three points representative of the 44,276,323 possible sampling points of 45.7 cm that can fit into 2 ha?
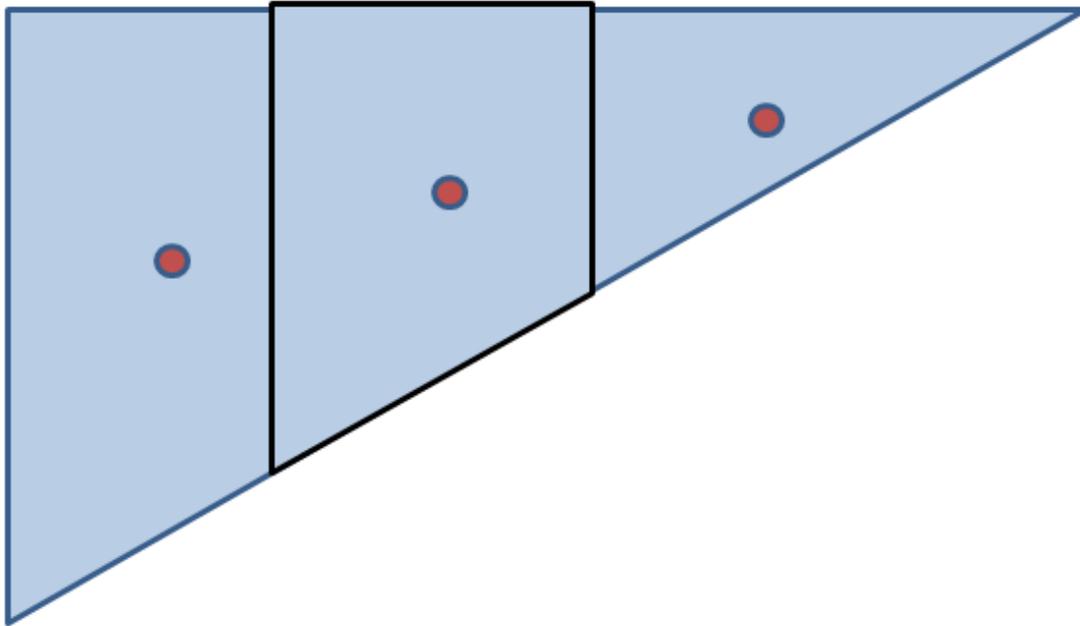
Figure 6-2 Planned Sampling Pattern, (Figure created by G, Rutgers. 2013)

Due to some logistical concerns that arose while on site, the planned sampling pattern

was revised. The modified sampling pattern is illustrated in Figure 6-3.
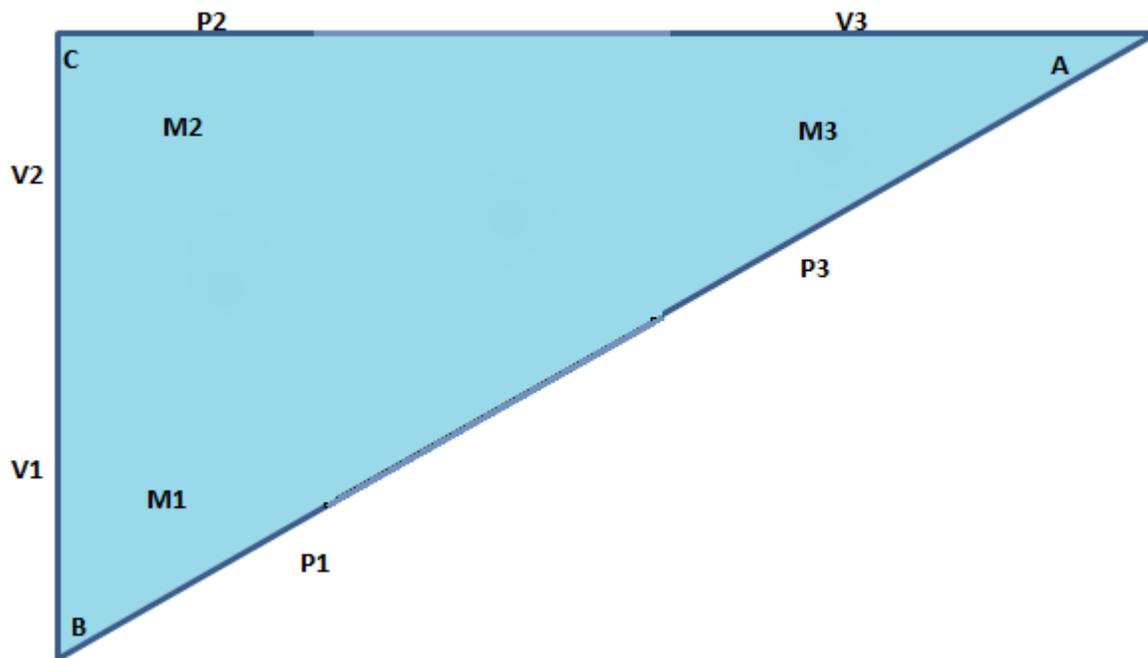
Figure 6-3 Actual Sampling locations (Figure created by G, Rutgers. 2013)

The M labels indicate flux chamber locations, V labels indicate analyzer location, and P labels indicate the anchor locations. The inflow pipe is located just above corner A. The outflow pipe is located between corner B and P1. In Figure 6-3 the distance between the flux chamber locations and the corresponding analyzer locations is 91.4 meters. The sampling pattern was used to place each flux chamber as far out into the pond as possible with the available equipment. Location M1 was close to the outflow pipe and location M3 was close to the agitation from the inflow pipe.

The sample rate and volume of the chamber was such that once the chamber was in place, it took 12 minutes to fully exchange the air in the chamber. The first two air exchanges were disregarded to eliminate any added methane resulting from

agitation while setting up the chamber. The concentration of the next following three air exchanges was used to determine the flux for each point. The flux was determined by the concentration of methane times the sample rate divided by the volume of the chamber. The field work required to set up and sample the three points took three people 12 hours to gather the 90 minutes of CEM data or 36 man hours for 30 minutes of readings per point. This does not include the equipment and field preparations or the analysis of the data. This is a large investment of time for this kind of emission sampling. It does demonstrate that these kinds of testing are time consuming and need some refinement before being widely adopted.

6.2   The Problem

Reflecting on the sampling, lessons can be drawn from the experience. The problems can be broken down into a few different sections; equipment, planning, and analysis. Factors in all these sections combine to make the testing just too labour intensive to make it viable as a widely used test method.

6.2.1 The Equipment

In the case of the anaerobic lagoon the major limiting factor was the equipment. The analyzer, sample conditioner, calibration and analyzer fuel gases and the generator all needed to stay on shore because the small row boat that was available could not safely support the weight of all that equipment. The benefit of leaving the equipment on shore is that it provided one end of an anchor line for the flux chamber thus preventing it

from drifting. The sample lines limited the distance that the chamber could be placed

from shore. As the length of the sample line increases, the line resistance increases

slowing the air exchange rate and increasing the vacuum the pump has to generate,

which thus limits the maximum distance of the sample lines to the size of the pump. The

analyzer used to detect methane was a J.U.M. 3-300A flame ionization detector (FID),

fuelled by ultra-high purity hydrogen gas. The FID is a hot/wet system, which means

that the sample gas arrives heated and moist. Unlike a cool/dry analyzer, which uses a

chiller close to the sample location to remove the moisture; a hot/wet system uses

heated lines to keep condensation from forming in the sample lines. The advantage of

the hot/wet system over a cool/dry system is that a separate system to measure the

moisture content of the sample gas is not needed. The disadvantage is the cost of the

heated lines versus the cost of Teflon sample lines. Either way, sample lines heated or

unheated will always limit the distance between an open chamber and the analyzer.

A flux chamber is a direct measurement method, so it has an effect on the

location it is sampling. The analyzer adds to the area affected by flux chamber, unless it

is separated from the chamber by a sample line. The sample lines allow the analyzer to

be moved far enough away from the sample location that the analyzer and all its

supporting equipment is not impacting the sample location. The most expensive single

piece of equipment is the analyzer. Due to the expense it is impractical to have multiple

analyzers of high accuracy. Smaller inexpensive analyzers are available but have

limited ranges and accuracy. An analyzer is not the only means of detecting a gas.

6.2.2 The Analysis

Once the raw data is collected, it needs to be processed into a usable form. The raw data from the CEMS can show average parts per million (ppm) for a programmed unit of time, often between 5 to 60 seconds. The calibration bias needs to be added to the raw date. The calibration bias is the difference between a known calibration standard such as an EPA Protocol 1 gas and what the analyzers measured. To be considered calibrated, bias difference must be less than +/- 2% or 5 ppm (Jahnky, 2000; Environment Canada, 2005). The average ppm of methane for a given sampling period was multiplied by the volume and area of the chamber to determine the flux in the chamber using the Equation 1 referenced earlier.

Equation 1   Determination of flux in a Chamber

$$F_c = \frac{\left(\frac{V_c}{A_c}\right) dC}{dt}$$

The fluxes from each sample point are averaged then multiplied by the surface area to create a mass emission rate for the entire surface using Equation 4.

Equation 4   Determination of Total Flux of a Surface

$$F_{total} = \left(\frac{1}{n} \sum_{i=1}^{n} F_{ci}\right) \times A_{total}$$

Where

- F_{total} = Total surface flux (gm^{-2} *unit of time*$^{-1}$)

- F_{ci} = Surface flux rate iterations (gm^{-2} *unit of time*$^{-1}$),

- A_{total} = Total surface area (m^2)

- *n* = Equals a given sample size

- *i* = iteration

The issue was how to most accurately estimate the mass emission rate for the surface. One question is whether any of the sample points should be weighted, and if so by how much? The original sampling plan divided the pond into three equal area quadrants running north-south across the pond (Figure 6-2). Since the equipment could not accommodate that plan, new sampling locations were chosen to accommodate the equipment constraints (Figure 6-3). The question is how representative those points were of the whole surface. Because this was only a scoping study, the required level of accuracy is less than it would be if it were a pollution release survey.

To deal with similar issues in industrial smoke stacks, the sources sampling method is considered. Alberta source testing code Method 1 divides a stack into 12 to 24 equal-area sections (Alberta Environmental Protection Services, 1996). Samples from those equal area sections are measured using a nozzle that's diameter does not get much bigger than 1.3 cm. At the small side, in a 40.6 cm diameter stack, the areas are between 21.3 to 42.6 cm^2 depending, on the number of sample points as dictated by Method 1. The single 1.3 cm sample point thus represents 41 to 82 other potential sample points within the 12 to 24 equal-area sample areas or 15% to 60% of the total

stack area. Whereas the three flux chamber points on the anaerobic lagoon represented only 0.000006% of the total area. On the large stack size of say 4.3 meter diameter, the sample area is 0.1% of the total stack area.

An anaerobic lagoon does not follow the same laminar flow pattern as a smoke stack. The gases being emitted by a lagoon or a field are dictated by a number of different factors that are not in an industrial smoke stack and the areas considered are very different. Still many of the factors that make the sample points of a stack test representative would also make flux chamber testing representative.

The velocity of a stack gas is an arithmetic average of the samples. With the different discharge pattern in lagoons, the arithmetic average may not be the most representative way of determining the average mass emission rate for the entire surface. In the case of the anaerobic lagoon weighting factors were investigated but in the end the arithmetic average total emission rate was taken to be the best fit for the scope of the study and the number of sample points available.

6.3   Second Flux Chamber Study

6.3.1   The Plan

An emission survey was planned for a second set of sewage lagoons as part of a GHG study. The survey was developed in order to measure and track the emissions from the lagoons on an on-going basis. Three plans were developed that incorporated many of the data quality and sampling objectives developed from the previous study.

One major difference was the temporal component: sampling would be conducted at various times of the year to capture seasonal variations.

The study area consisted of four settling ponds and a stockpile of solids from the settling ponds. The first part was a scoping survey similar to the previously mentioned study. A single chamber would be used to measure a single point in each of the ponds and four locations in the solids stockpile. Ultimately the single point sampling plan would result in a single point representing a much larger area. In this case, if the same sized chamber was used a 374,000 m^2 area would be represented by only four 0.013 m^2 points. This would provide very rough estimates of the emissions.

Two other sampling plans were prepared, which followed similar temporal timelines but required statistical tests to verify the accuracy of the results. The number of sample locations was determined by meeting a minimum confidence level. The number of locations was calculated by taking the area of each pond and dividing by the area of the flux chamber. This gave a population or a number of possible sample points from which a statistically representative sample was drawn. A grid pattern with the number of cells needed for a representative sample was then superimposed on the individual lagoons. The sample locations were then located at the centroid of each of the grid cells. Given the size of the lagoons and the targeted statistical confidence of 90% or 95% for the respective sampling plans, the number of sampling locations on each lagoon was 16 and 32, respectively.

The number of sampling locations presented the challenge of how to conduct the

sampling in a relatively short time period to minimize diurnal variations. If it took 12

hours to sample 3 locations it would take 384 hours to sample the 32 locations of a

single pond using the open flux measuring system described in the first flux chamber

study above.

In this case closed flux chamber systems would be used with samples collected

in Tedlar bags and analyzed on-shore with mobile CEMS. The closed chambers were

chosen because they are relatively inexpensive and thus several chambers could be

used simultaneously. The logistics of controlling the sweep air systems on multiple

chambers plus the sample air systems and the time it takes to set up the system, meant

a closed chamber system was the best option. A shared CEMS has many draw backs

namely every time the system is switched between sampling locations this must be

logged and the lines need to be purged before a reliable reading can be done (Jahnky,

2000). Given the multiple sampling locations, it becomes very difficult to proof the

system with a calibration or to trouble shoot for leaks.

Regardless of the system complexity, it needs to be proofed and calibrated. In

the case of closed chambers, a lab spike would have to be done. The lab spike, also

known as the matrix spike, would be conducted by placing the floating chamber in a

small pool and releasing a known concentration of gas into the chamber over the course

of the predicted sample duration. Once the lab spike has been collected at the end of

the sample duration, the sample would be analyzed. The spike should fall within the

expected range of the pollutant. The reason for the lab spike is to prove that each chamber is working, leak free and that any biases that may be caused by the chamber or the analytical system are identified.

The closed flux chambers for this study would have the Tedlar bag mounted inside the chamber with a small circulation fan and air sampling pump. The sampling pump would suck the air out of the chamber and back into the Tedlar bag. With the bag inside the chamber there would be no change in the volume of air inside the chamber, hence the chamber's buoyancy would not change. The chambers would be held in place either by a line of rope from shore to shore or by a three point off-set anchor system. The off-setting of the anchor would prevent the anchor from disturbing the sediments directly below the chamber and biasing the sample on the high side.

While the study was not conducted, the plans demonstrated how minor changes to the sampling plan could create statistically significant results similar to those found for existing point source sampling methods and provide a level of reliability in the results. A flux chamber is a method of determining the gases present at a single point. The issue however, is whether that point is representative of the entire area since there are numerous subsurface factors that may affect gas emission rates across the entire area. Thus, the solution is to sample in multiple locations. The simplest sampling pattern is a grid pattern. Researchers must also answer questions about the size of the cells in the grid and the number of cells to use in the sample.

7   Reporting of Data

Flux chambers are simple devices that measure fluxes of gases released across a surface. They only sample one point at a time and each sample point is used to represent a wider area. Without a detailed subsurface study to ensure homogenized subsurface conditions, the flux is only truly applicable to the sample location. However, it is impractical to measure the entire surface of a large area source. To determine the flux of a large area source, it is assumed that the area surrounding the flux chamber has a similar flux to that measured by the chamber. Several sample points need to be collected to make up an image of the whole area.

There are two approaches for deriving a total emission rate from the surface area based on the sample points. Either each of the points could be summed up and the arithmetic mean calculated or the points could be mapped out and peaks and ridges of flux could be identified and a weighted average determined. Both methods will provide an estimate of the flux for the entire surface and both have advantages and disadvantages. While the arithmetic mean is a simple calculation, the use of weighted averages can provide additional useful information.

In the first approach, using the arithmetic mean is similar to Alberta Stack Sampling Method 2 "Determining flow rate (S-type pitot)",where between 12 to 25 points are measured and a total emission rate is given (Alberta Environmental Protection Services, 1996). This approach is good for a regulatory framework.

The second approach which involves mapping the isopleths of flux provides a total flux

for an area and also identifies peaks and valleys of emission. In this way this direct

measure of flux can be used to interpret the subsurface conditions.

Sampling using a flux chamber is a simple inexpensive way to gather emissions

data and subsurface data without having to do extensive studies such as sonar

mapping coupled with detailed water sampling. Flux mapping takes advantage of spatial

autocorrelation methods that have already been developed for other types of

georeferenced data (Griffith, 2008). As with other georeferenced data and statistical

data, a number of sample points are needed to produce reliable results. The question is

how many points should be sampled to get the level of detail that is required for the

survey.

7.1   Number of Sample Points and Where

There are several ways to determine the number of sample points required to

meet the level of statistical reliability that is needed for a study. This paper will look at

two options for determining the number of samples depending on the Acceptable

Quality Level (AQL). Option one is to determine a total emission rate, while option two is

to map out the peaks and valleys of flux over an area. What is being created is a

statistical sampling matrix. Regardless of the size or number of sampling locations, a

level of statistical confidence needs to be given with each study (Kienbusch, 1986). In

Kienbusch's study, it is suggested that with a target of 95% confidence the emission

range is within 20% of the true mean (Kienbusch, 1986). Using simple statistical

analyses of the results, a confidence in the result representing the whole population can

be assigned. To determine the sampling size for a given level of confidence, a standard

deviation is determined. If the Kienbusch's example is used then 95% of the sampled

concentrations need to fall within 1 standard deviation within 20% of the mean.

If the results of the sample do not provide the required level of confidence, then there is

a high degree of variation within the area of interest and more sample locations are

required. The variation is an indication of changes within the subsurface environment.

Potentially this type of variation would be seen in a landfill. Since the composition of the

subsurface is unknown and it is often too costly to survey a flux chamber can be used to

indicate the variability.

The sampling pattern for a flux chamber is essentially the same as any

geographic sampling pattern. There has been extensive debate and research

conducted on sample size and scheme (Lo & Yeung, 2002). There are two basic

sampling approaches: a simple random sample pattern, in which points are chosen at

random; and a systematic sample where the sample points are laid out according to a

system (Lo & Yeung, 2002). All the schemes have their drawbacks and merits (Lo &

Yeung, 2002). Some are more difficult to apply while being statistically acceptable. Rigid

systematic sampling schemes have been shown to suffer from periodicity (Lo & Yeung,

2002). Common offshoots of rigid systematic sampling which account for periodicity are

stratified sampling and stratified systematic unaligned sampling. The latter divides the

area into strata and a random number of points are sampled from within each strata.

The former divides the area into a grid pattern and a single random point within each cell is sampled (Lo & Yeung, 2002).

There are several different approaches for partitioning a surface into a grid of sample cells. A simple grid pattern can be used to divide up the surface. Another example is a tessellation, which uses hexagonal polygons. The reason for the hexagons is the relative equal distances between the centroid and the sides without getting overly complex. The surface area is divided up into a series of hexagons and a sample is taken randomly or from the centroid of the cell to represent the total for a given cell. The size of the hexagons is determined by the following equation:

Equation 5   Determination of Size for Hexagons

$$b \approx \sqrt{\frac{a}{n} * \frac{2}{3\sqrt{3}}}$$

Where

- b = The Side of the Hexagon,

- a = The Area of Study

- n = Equals a Given Sample Size

Regardless of the shape of the cells the centroids need to be mapped out before getting to the sample area. The reason for mapping out the sampling locations before reaching the sampling site is because that will minimize time on-site. Another reason for mapping out the centroids before reaching the sampling location is setting out a hexagonal pattern on the surface of a water body could prove difficult. The more difficult the

testing, the more likely the errors will be introduced by technicians carrying out the sampling.

7.2   Mapping the Results

Depending on what kind of analyses the operators want to conduct, the displaying of the results will change. A study by the Smithsonian Global Volcanism Program, measured the CO_2 emissions coming from the crater lake of Mount Kelut (Smithsonian National Museum of Natural History, 2008). The sampling was conducted using a small open floating chamber that was towed behind a small boat. The boat was run in a basic grid pattern across the lake. The boat paused at 230 points and the chamber collected a sample (Smithsonian National Museum of Natural History, 2008). The location and flux of each point was recorded. The recorded fluxes were used to create a digital elevation model (DEM) of the fluxes of the lakes surface. The resulting map generated showed the uneven distribution of the fluxes, creating ridges and valleys of flux (Smithsonian National Museum of Natural History, 2008). This study with a large sampling size showed the complexity of the pattern of emissions released from a surface; at the edges of the lake, outside of the sampling grid and further away from the measured fluxes, the mapped flux was very homogenous (Smithsonian National Museum of Natural History, 2008). As with any mapping, the lack of sample locations reduces the level of detail and increases the level of uncertainty.

When mapping fluxes, the surface from which the samples are drawn is considered to be a flat homogeneous plane. If the surface is a water body such as a settling pond, this assumption holds true.

Because each sampling situation is different, the flux chamber method needs to be versatile and adaptable to the changing situations, as does the grid pattern used to determine the sample locations. Random sampling and stratified sampling schemes have been generally considered suitable in most situations. Stratified sampling schemes have been shown to be most suitable when a minimum number of samples are selected (Lo & Yeung, 2002). Keeping the sample size small does induce potential spatial errors but those possible errors need to be weighed against the errors created by the variables that affect the flux in the first place. If sampling takes too long then changes in the conditions within the subsurface may occur. In a large area the duration of the sample may not be an issue as the conditions in a large area may be slower to change than small areas. Sampling for fluxes is very much geographic dependent. Instead of sampling topography one is sampling fluxes, which are as variable as the weather conditions. A map of a surfaces flux is very much like that of a weather map. Unlike meteorologists who have developed techniques (e.g., Doppler radar, weather satellites, and hundreds of years of observations) measuring fluxes off of surfaces is relatively new.

For flux chamber sampling methodologies to be applicable and comparable, there needs to be a common thread. The shape of the sample areas will never be

consistent. The common thread that allows different sampling locations to be compared

is the relationship between the sampling points within the respective area. If the

confidence level is the same, then the fluxes from different sources should be

comparable between two different locations.

8   An Alternative Method

8.1   Proposed Method and Derivation of a Sampling Plan

This thesis concludes with suggesting an alternative and somewhat more refined approach to sampling fugitive gases from a liquid non-point source surface. The discussion in the prior sections of this report has highlighted a number of issues with the existing testing methods including:

- Lack of statistically represented sample sizes for an area

- Different Chamber construction

- Different operating conditions

- Difficulties of other methods in achieving similar results

Using the US EPA sampling methods as a guide the following is a refinement of all that was previously discussed to provide a method to conduct a successful emissions test of a liquid non-point source surface (United States Goverment , 1990).

8.1.1   Method Summary

A series of open or enclosed flux chambers are placed upon a designated sampling surface in a pattern and quantity which provides a statistically representative sample of the emissions being released from the surface. The closed chamber allows the gases to build up within the chamber and to be collected. The collected gases are withdrawn and analyzed with a method that depends on the sampling medium used to collect the

targeted pollutant. The open chamber allows continues monitoring of a flux. The total emission rate as well as variations across the sample area can be reported.

8.1.2 Scope and Applicability

8.1.2.1 Scope

The methods described in this thesis are applicable for measuring the flux emissions from liquid non-point sources. The methods as written may not be applicable for solid surfaces or semi-solid surfaces. A flux chamber is a sample collection system. The closed chamber allows the gases to build within the chamber in order to collect a measureable sample. The open chamber allows the gases to collect in the chamber and be measured continuously. The total area of the source used to calculate total emission rate is reported. If there is variation in the total area as the water level changes then the reasoning for choosing a given area also needs to be reported. The area of each flux chamber is determined and recorded. The number of sample points required is calculated to meet the statistical relevance required by the test administrator. An appropriate sample pattern is laid out in the sampling plan locating the sampling points. The sampling pattern used is at the discretion of the tester who considers the following criteria:

- What the results of the sampling will be used for

- The shape of the sampling pattern compared to the shape of the sample area.

8.1.2.2 Analytics

Depending on the type of flux chamber used and the proposed collection method, the analytics can vary greatly. A flux chamber can collect samples using thermal desorption tubes, Sorbent tubes, grab samples (SUMMA canisters or Tedlar bags, evacuated glass bombs) or electrochemical analyzers. Prior to sampling, appropriate field spikes and lab spikes will need to be collected to verify the performance of each chamber.

8.1.3 Method range and sensitivity

The sensitivity of the methods described depends on a combination of the chamber size and sampling duration, and ultimately the detection limit of analysis of the target pollutant. In order to determine small fluxes, the size of the flux chamber and the sampling duration must increase. The magnitude of the measurable flux depends on the sensitivity of the analytical method used. Care must be taken that the reported detection limit of the analytical method is not greater than the source's emission limits. If the reported detection limit is greater, a different analytical method should be chosen or a re-test should be conducted using a greater sampling time and chamber size.

8.1.3.1 Data Quality

The quality of the data produced from the test methods described is determined by the execution of all the test protocols including the pre and post-test protocols. The records of the data collected need to be reported. Those records must include the concentrations measurements, the volume of the chambers used, the area and sample

location, sample duration, sample start and end time/date, the ambient temperature and

pressure outside the chamber, the temperature and pressure inside the chamber,

calibration records and the flow rate in and out of an open chamber. A sample field

sheet is included in Appendix A.

8.1.3.2   Interference

Background interferences can result from components within the sampling

system that may react with the targeted compound. Interferences can also include other

release non-target gases that can be highly reactive to the target compound or the

sampling media.

Analytical interferences from compounds that mask or react with the sampling

media can create false positives. Knowledge of the sampling media, possible

interference compounds to that media, and what compounds are expected at the

sample location should be considered.

8.1.3.3   Safety

The hazards of performing the methods described are those associated with any

sampling method, such as operation of a small watercraft, working in and around

contaminated water bodies, and handling analytical reagents. For each site the possible

hazards should be identified and the proper precautions then followed. Many hazardous

air pollutants are suspected carcinogens or present other serious health risks thus

appropriate personal protective equipment should be used (US Envirnomental

Protection Agency, 07).

8.1.3.4 Equipment and Sampling Supplies

A Flux chamber should be constructed according to the specifications below.

Closed chamber

A closed flux chamber system should be constructed of a vessel of non-reactive material, see Figure 8-1. The height of the inside of the chamber should be at least ½ the diameter of the chamber or greater. The system needs to be able to measure temperature and pressure inside the chamber. The system needs to have a way to extract the sample without evacuating the inside of the chamber. The chamber must have a mechanism to agitate the gases within the chamber without direct air pressure being applied to the surface. A flotation device is required to allow the rim of the chamber to sit a minimum of 0.64 cm below the waterline.
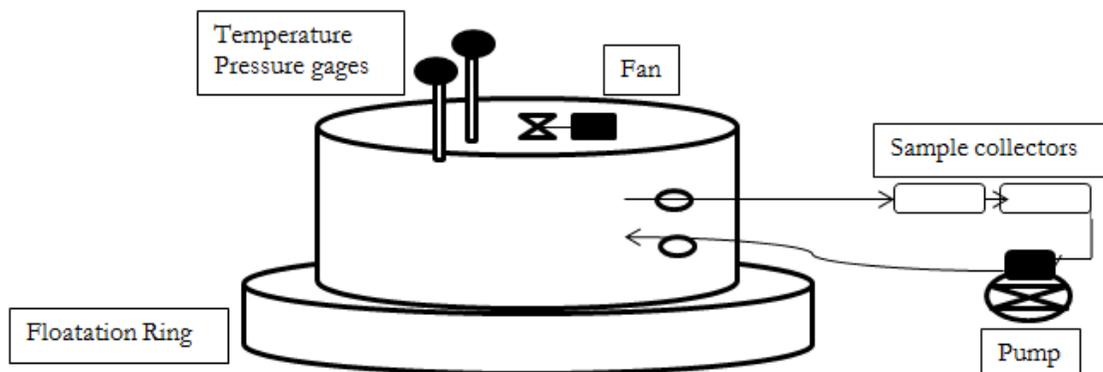

Figure 8-1 Closed Chamber, (Figure created by G, Rutgers. 2013)

Open chamber

An open flux chamber system should be constructed of a vessel of non-reactive material, see Figure 8-2. The height of the inside of the chamber should be at least ½ the diameter of the chamber or greater. The system needs to be able to measure temperature and pressure inside the chamber. The chamber needs to have an inflow airline and a sample line out. The lines in and out need to have flow controllers capable of ensuring the flow in and out of the chamber is equal. The chamber must have a mechanism to agitate the gases within the chamber without direct air pressure being applied to or agitating the surface. Often the sweep gas is plumbed in a fashion to facilitate this. A flotation device is required to allow the rim of the chamber to sit a minimum of 0.64 centimeter below the waterline.
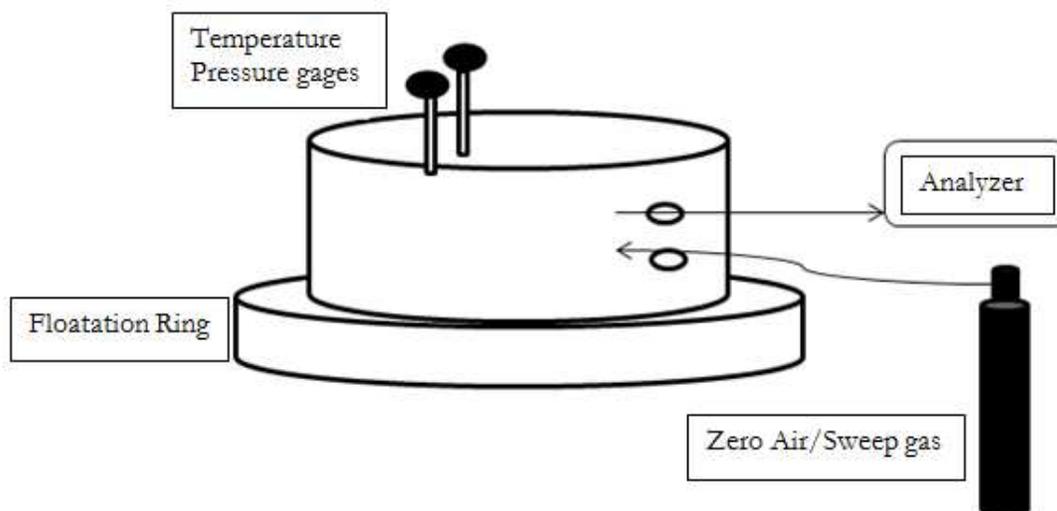
Figure 8-2 Open Flux Chamber, (Figure created by G, Rutgers. 2013)

8.1.3.5   Reagents and Standards

Reagents needed for the pre-survey sampling procedure depend on the sampling media and the target compound (US Environmental Protection Agency, 2007).

8.1.3.6   Sampling and Analysis procedures

In preparation for sampling, all exposed surfaces should be cleaned and contaminant free. The sampling system should be inspected for damage and tested for leaks.

The flux chamber should be placed at the identified sampling locations and the anchors set in place in such a manner to not disturb the area directly below the sampling chamber. The location, time, temperature and pressure both inside and outside the chamber should be recorded.

In the case of an open system the sweep air flow rates and the sample flow rates should also be recorded. The air within the headspace of the chamber should be cycled prior to commencing the sampling duration.

Once the chosen sampling duration has been reached, the sample within chambers should be collected. Note the end time of the sample duration as well as the temperature and pressure, both inside and outside the chamber. The sample container should be labeled appropriately with the sample time, sample location. Many gas samples degrade in light and heat. Sample containers should therefore be placed in a light-proof cool container and maintained in such a manner until analysis is conducted.

8.1.3.7   Calculations

Calculations of parameters of interest are determined as follows. The

determination of a surface area flux should be calculated by the equations below:

Determination of Total Surface Flux

$$F_{total} = \left(\frac{1}{n} \sum_{i=1}^{n} F_{ci} \right) \times A_{total}$$

Where

- F_{total} = Total Surface Flux (gm^{-2} *unit of time*$^{-1}$)

- F_{ci} = Surface flux Rate Iterations (gm^{-2} *unit of time*$^{-1}$),

- A_{total} = Total Surface area (m^2)

- n = Equals a Given Sample Size

- i = iteration

Determination of Chamber Flux

$$F_c = \frac{\left(\frac{V_c}{A_c} \right) dC}{dt}$$

Where

- F_c = Surface flux rate (gm^{-2} *unit of time*$^{-1}$),

- V_c = volume of the chamber (m^3),

- A_c = Cross-sectional area of the chamber (m^2), and

- dC/dt = concentration gradient of the component gas (g/m³/*unit of time)*

  (Senevirathna, Achari, & Hettiaratchi, 2007)*.*

Determination of Chamber Area

$$A_c = \frac{V_c \left(\frac{dC}{dt}\right)}{F_c}$$

Where

- F_c =Surface flux rate (gm⁻² *unit of time⁻¹*),

- V_c = volume of the chamber (m³),

- A_c= Cross-sectional area of the chamber (m²), and

- dC/dt = concentration gradient of the component gas (g/m³/*unit of time)*

Determination of Chamber Volume

$$V_c = t * Q$$

Where

- V_c = the chamber volume,

- t = the desired time to for the headspace to be filled, and

- Q = the flow rate of the gases into the chamber.

Determination of Number of Sampling Points

$$n^* = [TR(V)/1^T V1]n$$

Where

- n^* = Effective Sample Size,

- n = Equals a Given Sample Size

- TR = Denotes the Matrix Algebra Trace Operator

- 1^TV1 = Redundant Statistical Information

8.1.3.8   Quality Control

Depending on the sample collection media, a spike sample or an audit gas should be used. A system spike is a sample of a known concentration of the component introduced to the system. The difference between the known concentration and the spike results is the bias introduced by the sampling system. An audit gas is introduced into the system to prove the linearity of the electrochemical analyzer and indicate any bias in the sampling system. The audit gas or spike is introduced as close as practical to the front end of the sampling system. Ideally the spike should be introduced within the chamber in a clean environment.

8.1.3.9   Calibration and Standardization

Performance tests should be performed on each flux chamber to determine each individual chamber's error bias. The calibration of each chamber should be performed by placing the chamber on a shallow pool of contaminant free water and bubbling in a known volume and concentration of the desired pollutant. Protocol gases should be used. The difference between input and the collected results form the error bias which should be less than 5%.

$$Error(\%) = \frac{predicted\ flux - calculated\ flux}{predicted\ flux} * 100$$

Where

- *Error(%) = Percentage of Error*

- *Predicted flux = The Expected Flux*

- *Calculated flux= The Measured Flux*

8.1.3.10 Method Validation Procedure

The validation procedure for the methods described is based on EPA Method 301 (40 CFR Part 63, appendix A), (US Environmental Protection Agency, 2011). Bias (or systemic error) is established by comparing test results against a reference value. A correction factor is employed to account for bias (US Environmental Protection Agency, 2011).

8.2   Sampling Size and Pattern

The major factor that will affect the sampling size and pattern choice is time. Unlike geographic sampling where time is not a major factor, flux changes throughout the course of the day. The sampling may be carried out over a long period of time. Sampling durations of the fluxes can extend over the diurnal range in order to capture a measurable sample. The sample size should be large enough to meet the statistical confidence level laid out by the test administrator.

A simple sampling pattern that applies to all sites is not feasible due to the large variety in locations subsurface conditions and sampling equipment. This paper has

hopefully shown that the location of the sampling point is less important than the relation

each sample location has with each other and the entire surface area.

9 Conclusion

Public pressure in the 1960's and 70s significantly increased requirements to measure a wide variety of pollutants in order to better understand and mitigate the negative effects of urbanisation and industrialisation on the environment and human health. Air, water, and soil pollution became subject to considerable regulation and measurement.

The focus of this thesis is on the measurement of fugitive gas emissions associated with sewage lagoons, tailings ponds, and settling ponds. Gases such as methane, carbon dioxide, and volatile organic compounds are typically generated within these sources. The effect these gases have on the environment and human health requires measurement of the discharge rates for regulatory and management purposes.

The thesis reviews the theoretical and practical aspects of methodologies and instruments used in measuring fugitive gasses released from non-point sources. The principal sampling device, the flux chamber, and its two variants, open and closed are described and evaluated. The quality and effectiveness of the analysers, that measure the presence of pollutants in the samples is also considered.

The issues around sample size and pattern are also explored and the thesis concludes that the significant factors in achieving representativeness is the length of sampling time, the volume of the chamber and the number of samples taken.
The thesis reviews the technical, logistical and practical aspects in two of case studies and concludes with a description of sampling methods and protocols.

The approach refines existing practises, such as documented by the US EPA and it is

based on the research conducted for this thesis as well as the author's personal

experience with measuring fugitive gases.

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11 Appendix A   Field Data Sheet

Flux Chamber Field Sample Sheet

CLIENT: _____	DATE: _____
SOURCE: _____	TESTER(S): _____
SOURCE AREA: _____	BAROMETRIC PRESSURE: _____
NO. SAMPLE POINTS: _____	STATIC PRESSURE: _____
SAMPLE DURATION: _____	TEMP (^{o}F db): _____
CHAMBERS ID'S: _____	(^{o}F wb): _____
ABSORBING SOLUTION: _____	GAS COMPOSITION: _____

TEST NO. Location	TIME	(hhmm)	LEAK TEST cfm	LEAK TEST @ "Hg	METER VOL (ft^3)	METER TEMP (^{o}F) IN	METER TEMP (^{o}F) OUT	Test Run	Initial Values System Response (ppm)	Initial Values System Cal Bias (% of Span)	Final Values System Response (ppm)	Final Values System Cal Bias (% of Span)	Flow Rate Inlet	Flow Rate Outlet
								1. Zero						
								Upscale						
								2. Zero						
								Upscale						
								3. Zero						
								Upscale						
								4. Zero						
								Upscale						
								5. Zero						
								Upscale						
								6. Zero						
								Upscale						

1. Analyzer Calibration Error

Cal. Gas Conc.	Analyzer Response	Absolute Difference	Difference (% of