

**The Municipal Solid Waste Landfill as a Source of
Montreal Protocol-restricted Halocarbons in the
United States and United Kingdom**

by

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B.A. in Chemistry
Cornell University, 1999

Submitted to the Dept. of Earth, Atmospheric and Planetary Sciences
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Abstract

Central to the study of stratospheric ozone recovery and climate change, is the ability to predict emissions of Montreal Protocol-restricted halocarbons (MPGs) over the coming decades. The prediction of emissions has become difficult as global production of MPGs has rapidly declined establishing “banks” (MPGs which have been produced but not yet released) as the main emission sources. Both the magnitude and release rate of global banks is quite uncertain. Very few field studies have been conducted to provide estimates of global bank emissions from individual sources within countries. This thesis provides the first known observation-based estimates of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 emissions in the United States (US) and United Kingdom (UK) from municipal solid waste (MSW) landfills.

With several hundred MSW landfills in both the US and UK, estimating emissions of MPGs from landfills required a targeted approach. Whole landfill mixing ratios and flow rates were sampled monthly at one landfill in southern Massachusetts to provide temporal coverage. Spatial coverage was achieved through one time sampling at seven landfills in Massachusetts and through data provided by nine UK landfills for CFC-12 and CFC-11. Only actively managed MSW landfills were sampled.

US and UK MPG landfill emissions were estimated and compared to recent observation-based estimates of total US and UK MPG emissions to determine the importance of the landfill source. US MPG landfill emissions were estimated to be 0.008 - 0.08 Gg year⁻¹. For all four MPGs, US landfill emissions were ~ 0.6% of total US emissions. The UK landfill emission estimates were 6% and 0.8% of total UK CFC-12 and CFC-11 emissions, respectively. All estimates were accurate to within a factor of 2. This indicates that landfills are not currently a significant source of lingering MPG emissions in the US and UK. The implications are that the majority of MPG emissions in industrialized countries are likely coming from faster emitting sources.

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Academic

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Landfills

Landfills are typically the realm of regulators, government studies, private companies, and municipal solid waste departments. They are incredibly difficult to gain access to, which made this study completely different than studies of natural environments. Individual access to every site in the United States had to be obtained one landfill at a time. Without the good will of many individuals within the landfill business, there would be no data for this thesis.

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Chapter 1

Introduction

1.1 Scientific Relevance

The Montreal Protocol has had great success in reducing the global burden of ozone-depleting gases in the atmosphere since it came into effect in 1996. Before 1996, the Montreal Protocol-restricted halocarbons present in the troposphere in the highest concentrations were three chlorofluorocarbons (CFCs); CFC-12 (CCl_2F_2 , dichlorodifluoromethane), CFC-11 (CCl_3F , trichlorofluoromethane), and CFC-113 ($\text{C}_2\text{Cl}_3\text{F}_3$, 1,1,2 trichloro- 1,2,2 trifluoroethane); and two chlorinated solvents, carbon tetrachloride (CCl_4 , tetrachloromethane) and methyl chloroform (CH_3CCl_3 , 1,1,1 trichloroethane). Since 1996, their production and consumption have been almost completely banned in industrialized countries with exceptions made for “essential uses” when no acceptable substitutes have been found (*UNEP*, 2002). Today, their rate of accumulation in the troposphere has declined to the point where tropospheric concentrations are now stable or decreasing (*WMO*, 2007; *AGAGE*, 2007).

The four Montreal Protocol-restricted gases (MPGs) in this study are CFC-12, CFC-11, CFC-113, and CH_3CCl_3 . They all continue to be important to the recovery of the stratospheric ozone layer, to climate change, and to the study of atmospheric chemistry. It is the combination of ozone depleting potential (ODP), the shear volume historically released to the atmosphere, and their long lifetimes which make CFCs still highly important to the study of ozone recovery. ODP is defined as the global ozone loss due to a unit mass of a compound compared to the ozone loss due to the same unit mass of CFC-11. The only MPGs with higher ODPs than the CFCs are the halons, which have a small fraction of the tropospheric concentration of CFCs (*WMO*, 2007). CFC-12 and CFC-11 have the highest global background concentration of any Montreal Protocol gas, and only HCFC-22 has surpassed CFC-113 (*AGAGE*, 2007;

WMO, 2007). The long lifetimes of the CFCs are due to their lack of hydrogen atoms, removing tropospheric OH scavenging and leaving only stratospheric photodissociation as the predominant sink. CH_3CCl_3 concentrations have decreased sharply in recent years so that it is no longer as important a factor in ozone recovery (AGAGE, 2007; WMO, 2007), but it remains important as a method of estimating OH mixing ratios (Prinn *et al.*, 2005; Bloss *et al.*, 2005; Bousquet *et al.*, 2005). The effect the CFCs and CH_3CCl_3 have on climate is two fold. Directly, they cause a positive radiative forcing of climate. In particular, CFCs have very high global warming potentials (GWPs), possessing $\sim 5,000 - 15,000$ times the effect which the same amount of added CO_2 would have on warming the atmosphere over 100 years. Indirectly, the MPGs also cause a small negative radiative forcing by reducing the amount of stratospheric ozone (IPCC/TEAP, 2005; WMO, 2007).

Central to the study of stratospheric ozone recovery and climate change, is the ability to predict the emission rate of MPGs over the coming decades. MPGs are anthropogenic in origin and have widespread use in consumer goods. If the products containing MPGs release them to the atmosphere within the first few years after production, MPG emissions closely approximate production. This was the case before the mid-1990s. The few companies in industrialized countries which produced MPGs released annual audited records of production and emissions (McCulloch and Midgley, 1998; AFEAS, 2006).

Today global emissions far outstrip global production (UNEP, 2005; AFEAS, 2006), which has fundamentally altered the calculation of future MPG emission rates. Over the decades, as the type of products shifted from those which release MPGs quickly to those which release MPGs over a longer time period, the amount of “banked” MPGs grew (UNEP, 2005; AFEAS, 2006; Daniel *et al.*, 2007). Banks are MPGs which have already been produced, but have not yet been emitted to the atmosphere. They are found in products still in use, stockpiled products in case of equipment replacement, or discarded products in landfills (e.g. refrigerators, air conditioners, aerosol cans, blown foam). It is the amount of MPGs in banks and the rate at which the banks release MPGs which now dominates MPG emission rate calculations.

Both the magnitude of the global bank and expected release rate are quite uncertain. The difference between the the two types of methods commonly used to estimate global banks differ by ~ 1100 Gg for CFC-11 and 711 Gg for CFC-12 in their 2002 global bank estimates (WMO, 2003; IPCC/TEAP, 2005; WMO, 2007). There is less uncertainty between methods for the emission rates. For example, global CFC-11

and CFC-12 emissions are forecast to either taper to zero by 2030 (*WMO*, 2003) or be $\sim 20 \text{ Gg y}^{-1}$ and 10 Gg y^{-1} , respectively (*WMO*, 2007). While the fractional differences are greater between the available global bank estimates compared to the forecast emission rates, *Daniel et al.* (2007) show that the bank emission rates are potentially just as important to stratospheric ozone recovery as the bank sizes. *Daniel et al.* (2007) estimate a reduction in cumulative stratospheric ozone loss of 6.2% at midlatitudes over the next 40 years by reducing the rate of CFC-11 emissions from banks.

1.2 Why Landfills?

This study is an effort to estimate an emission rate and characterize its variability from one potential MPG bank, the municipal solid waste (MSW) landfill. Many observation-based studies have estimated national emissions of MPGs in industrialized countries (*Ryall et al.*, 2001; *Barnes et al.*, 2003; *Gros et al.*, 2003; *Millet and Goldstein*, 2004; *Li et al.*, 2005; *Reimann et al.*, 2005; *Hurst et al.*, 2006). The estimates are consistent within countries and indicate that emissions of MPGs are slowly declining, but may persist for many decades. MSW landfills may be a significant potential source of MPGs. Certainly as more and more MPG products reach the end of their lifetime, characterizing the release rate of MPGs from landfills will become more important.

Landfills have the added interest of being a subject of some controversy in the atmospheric science community. Observation-based estimates of emission rates have suggested that landfill emissions account for a significant fraction of the total national emissions observed in industrialized countries (*Krol et al.*, 2003; *Manning*, 2007). Estimates comparing the effect of CFC-11 bank release rates or those who estimate CFC-11 bank release rates using bottom-up methods have used contradictory emission functions which assume either all of the remaining CFC-11 in the landfilled product is released immediately upon landfilling or only 20% of the remaining CFC-11 is released and the rest is landfilled (*McCulloch et al.*, 2001; *IPCC/TEAP*, 2005; *Daniel et al.*, 2007). CFC-11 is the only MPG where modelers have considered landfills to be a possible significant global source, because CFC-11 is largely found in products with longer release times (*Deipser et al.*, 1996; *McCulloch et al.*, 2001, 2003).

There are good, but competing, reasons to believe that landfills may or may not be significant sources of MPGs. Experiments measuring CFC-11 release times have suggested 50% of the CFC-11 content could take 9-300 years to be released (*Kjeldsen*

and Jensen, 2001). On the other hand, waste is typically crushed when landfilled. Thus, we would expect that much of the MPG content of the waste would be released before the waste had a chance to be covered and therefore part of the underground landfill gas system.

CFC-12, CFC-11, CFC-113, and CH_3CCl_3 have all been detected in landfill gas in significant amounts (Brookes and Young, 1983; Young and Heasman, 1985; Dent et al., 1986; Deipser et al., 1991; Rettenberger and Stegmann, 1996; Allen et al., 1997). CCl_4 has not been detected in landfill gas, including in this study. Major landfilled products include aerosol cans (propellant residue), refrigerant liquid, and foam blowing (mainly polystyrene) for CFC-12; aerosol cans, closed cell polyurethane foam (e.g. refrigeration insulation), soft foam plastics (e.g. furniture and mattresses) for CFC-11; solvent residues (e.g. dry-cleaning) for CFC-113; and solvent residues (e.g. stain removers, detergents, adhesives, lacquers) for CH_3CCl_3 (Deipser et al., 1996; McCulloch, 2007).

There are no previously published observation-based studies estimating emissions of MPGs from landfills in any rigorous manner. One study in the United Kingdom (UK) did an order of magnitude estimate for UK landfills based on incomplete data from 4 landfills (Allen et al., 1997). They estimated a maximum of 1 Gg/yr for the sum of all CFC emissions from UK landfills in 1995. The closest any other studies have come is measuring concentration ranges. The reported ranges, converted to mixing ratios, are n.d. - 121.7 parts per million (ppm) for CFC-12, 0.05 - 39.2 ppm for CFC-11, n.d. - 0.8 ppm for CFC-113, n.d. - 5.3 ppm for CH_3CCl_3 (Rettenberger, 1986; Brookes and Young, 1983; Young and Heasman, 1985; Dent et al., 1986; Schilling and Hinz, 1987; Laugwitz et al., 1988; Deipser and Stegmann, 1993; Allen et al., 1997), where n.d. stands for not detectable. These are large ranges, most without reference to individual sample sites and published over a decade ago. More recently, significant work has been done characterizing degradation rates of halogenated compounds under simulated landfill conditions (Denovan and Strand, 1992; Deipser and Stegmann, 1997; Scheutz et al., 2003; Balsiger et al., 2005; Scheutz and Kjeldsen, 2005; Scheutz et al., 2007). Scheutz et al. (2007) estimated that > 90% of CFC-11 and > 60% of CFC-12 are degraded in landfills. Kjeldsen and Scheutz (2003) estimate expected CFC-11 emissions from decommissioned refrigerators and freezers in the US (produced between 1985-2010) to be \sim between 3-8 Gg year(y)⁻¹ for 2006.

1.3 Approach

Estimating emissions of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 from landfills in industrialized countries required a targeted approach. The approach chosen for this thesis was a set of field studies intended to provide both temporal and spatial coverage for the emission rate calculations. The approach was intentionally data heavy with no modeling, since very few measurements have been made of MPGs in landfill gas. Ideally, one would be able to sample emissions from every landfill in the United States and the United Kingdom. With over 1600 open MSW landfills in 2005 in the US (*Simmonds et al.*, 2006), hundreds more in the UK, not to mention industrial and C&D (construction and demolition) landfills or closed MSW landfills, complete data was unobtainable within the time frame of a Ph.D. thesis. This thesis focuses on characterizing the emissions from MSW landfills in the US and UK by sampling at selected actively managed MSW landfills (see Box 1.1).

The experimental data collection consisted of the following:

1. *Monthly sampling at one US MSW landfill to provide temporal coverage (“One Landfill Study”)*
2. *One time field sampling at several US MSW landfills to provide spatial coverage (“Multi-landfill Study”)*
3. *Data made available by UK MSW landfills to provide a comparison with another industrialized country (“Multi-landfill Study”).*

The data from the One Landfill Study is discussed in Chapter 3, while the data from the Multi-landfill Study is in Chapter 4.

The decision to sample at MSW landfills vs. industrial or C&D landfills was made for several reasons. First, because the data sets from the One Landfill Study and Multi-landfill Study are the first available of their kind for CFC-12, CFC-11, CFC-113, and CH_3CCl_3 , it was important to be able to use comparative studies of different landfill gases, but from the same type of landfill. This was especially important for the Multi-landfill Study in Chapter 4. There is a wealth of peer-reviewed literature and annual technical reports which discuss MSW landfills, but hardly any literature studying industrial or C&D landfills. A second reason is there are more MSW landfills in the US than industrial or C&D sites. In 1994, there were 3558 MSW (*EPA*, 2007d), 1370 industrial, and 1889 C&D landfills in the US (*EPA*, 1994). Massachusetts has no

open industrial landfills (*DEP*, 2007). Moreover, CH_4 generated at industrial landfills is 7% of that at MSW landfills (*EPA*, 2007b).

Within MSW landfills, a further qualification was made; to sample only actively managed landfills and no passive landfills (see Box 1.1). This was done to increase the number of measurements. Measuring emissions at passive landfills is either incredibly time intensive, requiring hundreds of surface chamber samples or to accurately estimate one emission rate from one landfill, or requires specialized equipment, such as a mobile laboratory, which was not available for this study (*Czepiel et al.*, 1996; *Mosher et al.*, 1999). Even by sampling at actively managed sites, only data from 16 different sites in the US and UK were collected. A rigorous statistical analysis, as was used in this thesis, for estimating US and UK MPG landfill emissions would not have been possible by sampling at passive landfills.

Box 1.1 Important definitions used throughout the thesis

Municipal Solid Waste (MSW) - contains domestic and commercial waste

MSW landfill (US) - contains > 50% MSW, but also contains some industrial waste, construction and demolition (C&D) waste, recycling residue, sludge, ash, Department of Public Works (DPW) waste, as well as some other non-MSW special waste such as fish remains or tires

MSW landfill (UK)^a - contains > 50% MSW, but also some industrial waste, difficult waste (literally wastes which are problematical), sludge, and contaminated soils

Industrial landfill (US) - contains 100% industrial waste

Industrial landfill (UK)^a - contains > 50% combined commercial and industrial waste, but also some domestic waste, difficult waste, sludge, and contaminated soils

C&D landfill - accepts 100% of waste from construction and demolition projects

Actively managed landfill - a landfill with an underground pipe system that mechanically pumps the landfill gas out of the landfill for burning, electricity, or heat generation.

Passive landfill - a landfill which at most has vertical wells to allow easier diffusion of gas to the atmosphere from underground.

Open landfill - landfill which is currently accepting waste for disposal

Closed landfill - landfill which is no longer accepting waste for disposal

Flare - high temperature stack which burns landfill gas

Gas-to-energy plant - A reciprocating engine, gas turbine, fuel cell or similar which converts landfill gas into electricity or heat

Generated gas (actively managed landfill) - gas which is pumped out but may not be emitted to the atmosphere because of combustion at the flare or gas-to-energy plant

^aThe categories of waste (e.g. domestic, difficult, etc.) in the UK landfill definitions are used industry wide, but the division of UK MSW and Industrial landfills are definitions used only in this thesis.

Chapter 2

Instrumentation and Sampling Equipment

The following sections describe each set of data collected as well as the methodology used in the gas sampling and analysis. Section 2.1 describes the general flask evacuation and analysis routines which were used in the Prinn group laboratory at MIT, where all of the US gas samples were prepared and analyzed. Information specific to the two main field campaigns, the One Landfill Study and Multi-landfill Study, are presented in Sections 2.2 and 2.3, respectively.

2.1 MIT Pre-sampling and Analysis

2.1.1 Gas Chromatography Instrumentation

The US gas samples were analyzed on an Agilent Gas Chromatograph 6890N (GC) with dual detectors: a micro electron capture detector and a flame ionization detector (μ ECD and FID). Each detector was part of an entirely separate set-up each consisting of a 6-port valve injection system, sample loop, column, and detector. CFC-12, CFC-11, CFC-113, and CH_3CCl_3 were all analyzed on the GC- μ ECD, while methane (CH_4) was analyzed on the GC-FID. All gas sample concentrations were calculated in mixing ratio units (parts per million (ppm) or parts per billion (ppb)).

Figure 2-1 provides a schematic of the MIT set-up. Two 6-port dual-position valves (Valco Instruments Inc.) formed the center of the injection systems. The valves were each connected to a sample loop, inlet, exhaust, column, and carrier gas flow. The set-up was intended to be as simple as possible. Landfill gas is already highly concentrated, which made pre-concentration unnecessary. However, it was

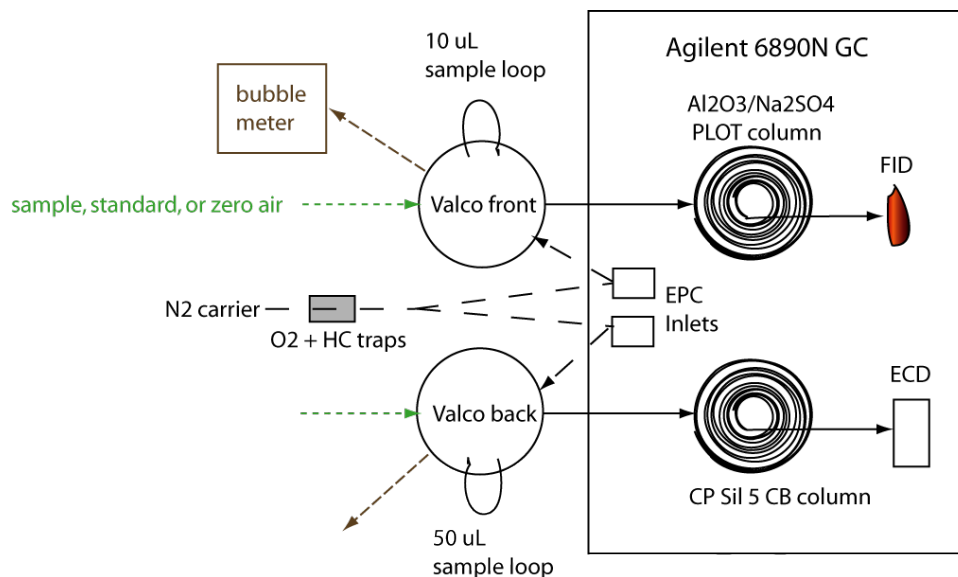


Figure 2-1: Schematic diagram of the MIT GC- μ ECD and -FID set-up. The unlabeled green and brown arrows connected to the back 6-port Valco valve indicate that the input gas and bubble meter were either connected to the front or back valves, but never both at the same time. See text for further explanation.

much more likely than with ambient sampling, that any part of the analysis line could become contaminated.

Sample, standard, or zero air was loaded onto the front or back sample loop through a 1/16" stainless steel inlet line by opening and quickly closing the cylinder or flask valve five times to limit gas loss. The carrier gas was plumbed through factory installed Electronic Pneumatic Control (EPC) Split/Splitless Inlets (Splitless mode, 150°C, flow rate 34.6 mL/min). A column nut welded to a 1/16" Swagelok fitting redirected the carrier gas (Ultra High purity (UHP) N₂, 99.999% pure research grade) to the front or back 6-port valves.

The gas to be analyzed was injected either onto a 50 m x 0.32 mm i.d. Chromopack PLOT fused silica column of Al₂O₃/Na₂SO₄ stationary phase (Model No., CP7565 Varian Inc.), which was connected to the FID; or onto a 25 m x 0.32 mm i.d. CP Sil 5 CB capillary column (Model No. CP7680, Varian Inc.), which was connected to the μ ECD. Only one column and detector was used for analysis during the same GC run. The columns were run in constant flow mode (flow rate = 2.3 mL/min for both columns). The μ ECD (300°C, column + make-up: UHP N₂ 30 mL/min), FID (220°C, flame gases: UHP H₂ 45 mL/min + UHP zero-air 400 mL/min, column + make-up: UHP N₂ 45 mL/min), and EPC inlets were run at the same settings regardless of

whether the gas was being analyzed using the FID or μ ECD. For the GC-FID set-up, the front 6-port valve injected the gas onto the $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ PLOT column at 0.2 minutes and remained in the inject position until the end of the program at 5 minutes because CH_4 had a long tail at high mixing ratios. Returning the valve to load prematurely cut off the peak. The oven was run isothermally at 45°C during the program. For the GC- μ ECD system, the back 6-port valve injected the gas onto the CP Sil fused silica capillary column at 0.2 minutes and returned to the load position at 0.7 minutes (inject time = 30 s). The oven remained at 45°C for 1 minute while the valve switching was happening. Then the temperature was ramped $10^\circ\text{C}/\text{min}$ to 100°C , held at 100°C for 0.5 minutes, and finally ramped $30^\circ\text{C}/\text{min}$ to 200°C and held there for 1 minute. The compounds of interest eluted during the initial ramping, while the final ramping flushed most of the heavy compounds out of the column. If this final ramping was not done during each run, the next run would see ghost peaks.

To limit analysis error, it was important that: (1) the sample canisters and standard and zero air cylinders were all regulated to approximately the same pressure, and (2) each sample or standard was injected onto the column at atmospheric pressure. All sample gas cylinders were pressurized to ~ 30 psig during field sampling, so the standard and zero air cylinders were regulated to match this pressure. The pressure in the sample loop was monitored through a bubble meter connected to the exhaust port of the 6-port valve.

Supelco Oxygen and Hydrocarbon traps were used for the makeup gas, where impurities might affect the measurement. None of the gas samples ever seemed to contain a significant amount of water, so no traps were used for the standard or sample gas. A discussion of detector precision and accuracy can be found in Section 2.1.4

2.1.2 Preparation of the Sampling Flasks

All US gas samples were collected in either 0.8 L cylindrical or 2.9 L spherical stainless steel flasks (Biospherics Research Corporation, Hillsboro, Oregon). All of the canisters were previously purchased by former Prinn group graduate students, and were electropolished (Electromatic, Inc.) upon purchase as described in Dr. Michele Sprengnether's Ph.D. thesis (*Sprengnether*, 1992). From April 2006 onwards, the cylindrical flasks were used exclusively for sampling to allow long term gas storage for standards in the newer spherical flasks. To compensate for switching to the older cylindrical flasks, the number of repetitive samples taken for each data point was also

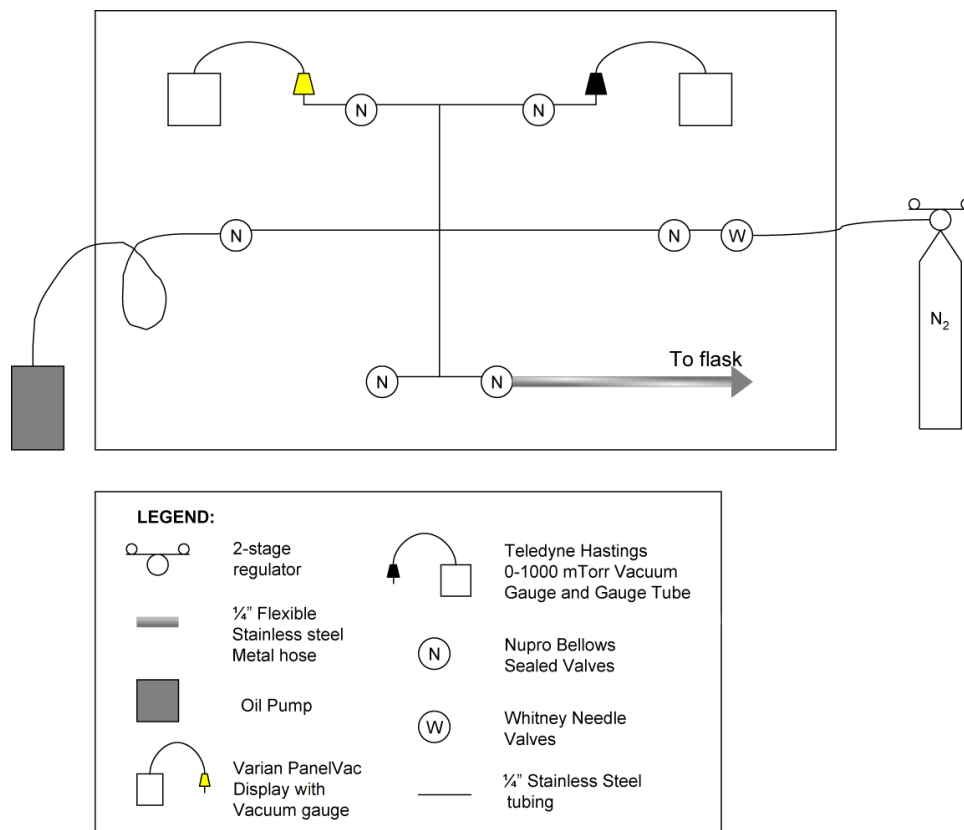


Figure 2-2: Schematic diagram of the set-up for evacuating canisters

increased from two to three in June of 2006. For all data points, there are at least two consistent mixing ratio measurements from two separate flasks.

The canisters were evacuated using a vacuum line constructed as shown in Figure 2-2 the day before they were used in order to minimize the loss of vacuum. They were first evacuated with an Edwards High Vacuum pump (Model No. E2M2, Serial No. 58195) to get rid of any landfill gas before being filled to 30 psig with ultra high purity (UHP, 99.999% pure) N_2 and then evacuated. A Varian PanelVac ConvecTorr (Serial No. LIB020877) connected to a Varian ConvecTorr P-type vacuum gauge was used to measure the vacuum to 1 Torr. Once the vacuum reached below 1 Torr, a Teledyne Hastings Instruments Vacuum Gauge with a range of 0-1000 mTorr (Model No. VT-6, Serial No. 2676700015) combined with a Teledyne Hastings Instruments Vacuum Gauge Tube (Type: DV-6M) was used for the final pressure reading which was between 10-200 mTorr. This was repeated two more times. If it was necessary to test a set of canisters for cleanliness, one of the two or three canisters from each previous set of repetitive samples was filled once more with N_2 and then tested in

this pressurized state. After testing according to the procedure described above, the canister was once more evacuated to ~ 100 mTorr. Canisters which had landfill gas from Crapo Hill landfill, the study site for the One Landfill Study (see Chapter 3), never showed any residual chlorine signature after the 3 cleanings. There was usually a residual CH_4 signature of ~ 20 Hz, but this was less than 0.1%. For this reason, only canisters which had just been used for landfill gas from landfills other than Crapo Hill were checked for cleanliness.

The samples were almost always analyzed within 24 hours after collection. However longer-term storage was also possible. Under exceptional circumstances such as a 6-port valve malfunction, flasks were reanalyzed or analyzed for the first time up to two months after initial sampling. Because the compounds under investigation are essentially inert in the cylinders, reanalysis of flasks 79 days after the original sampling and analysis showed no detectable change in mixing ratio.

2.1.3 Identification and Quantification

Chromatography is not an absolute method of identification. Chromatograms of sample gas are compared to chromatograms of a standard with known mole fractions of the compounds of interest. The standard for the four halocarbons in this study, named the “CFC standard”, was bought from Scott Specialty Gases (expiration date 7/26/06, cylinder no. ALM059493, Project No.: 01-13427). It contained a mixture of compounds with the ratio (and blend tolerances), HCFC-22 10.2 ppm (2%), CFC-12 10.1 ppm (1%), CFC-11 1.05 ppm (5%), CFC-113 1.04 ppm (4%), CH_3CCl_3 1.05 ppm (5%), CCl_4 1.04 ppm (4%), CH_4 802 ppm (0.3%), and N_2 as the balance gas. The certified accuracy is 5% for all compounds, although the indicated blend tolerances were often lower as shown above. The CFC standard was used until December 2006 although it was only certified until the end of July 2006. The standard did not show any strange trends after July (see Section 2.1.4), so it was considered better to use the same standard throughout the analysis. Even though CH_4 was not quantitatively measured by using the CFC standard, it was added to the mixture as a way to compare the CFC standard to other standards. CH_4 was quantified using a pure CH_4 standard (research grade, 99.999% pure, BOC gases) because landfill gas is $\sim 50\%$ CH_4 .

A typical set of runs for one day started with one or two blank runs of UHP zero-air until a clean blank run was achieved, followed by two standard runs to check whether the detectors were functioning properly. Often another blank run was done

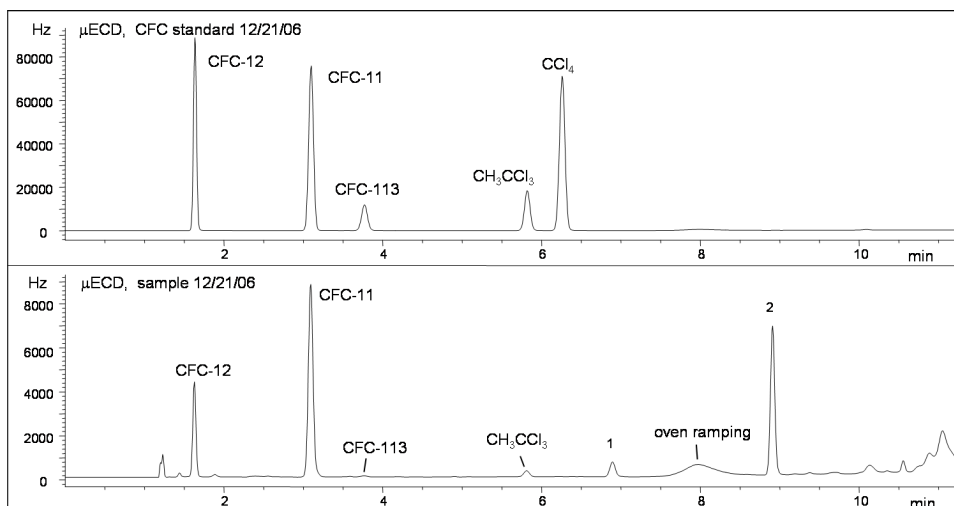


Figure 2-3: Typical MIT GC- μ ECD chromatogram of the CFC standard (top) and landfill gas sample (bottom). The sample peaks labeled by number were identified, but were not present in the CFC standard. Peak 1 is trichloroethylene (TCE) and peak 2 is perchloroethylene (PCE). The three smaller sample peaks which eluted about the same time as CFC-12 were not positively identified, but are likely Halon 1301 (co-eluted), Halon 1211, and CFC-114.

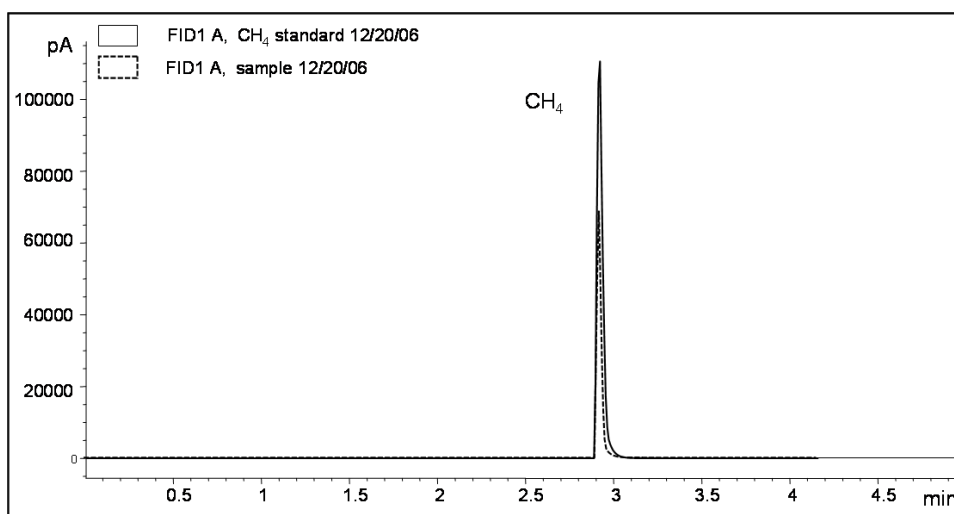


Figure 2-4: Typical MIT GC-FID chromatogram of the CH₄ standard (solid line) and landfill gas (dashed line)

after the first two standards to check that the inlet line was being flushed properly by the zero air. This was especially important for the pure CH₄ standard. For the MIT GC- μ ECD, one sample was then run three times in succession followed by another standard run. This was repeated until all the sample canisters had been run. Sets of repetitive samples taken for each landfill measurement were always run one after another on the same day. Zero air was flushed through the inlet line and sample loop for at least 10 minutes between standard and sample runs and visa versa. The CH₄ analysis was identical to that of the halocarbons until November 20, 2006, when the intensive field sampling made it necessary to run the CH₄ standard every 6 runs or 2 sample flasks. This had no effect on the mixing ratio calculation, because detector drift was not an issue for the FID with runs of 5 minutes each. Detector precision calculation continued to be possible by adding extra CH₄ standard runs to the beginning and end of the analysis period.

Figure 2-3 and Figure 2-4 show typical standard and sample chromatograms from the MIT GC- μ ECD and GC-FID, respectively. The chromatograms demonstrate the separation, resolution, and identification capabilities. Peak identification of the CFC standard was made by comparing my chromatograms to published chromatograms. The CFC standard had only 5 compounds which the MIT GC- μ ECD could detect, namely CFC-12, CFC-11, CFC-113, CCl₄, and CH₃CCl₃. Integration of peaks to determine peak area and peak height was done using Chemstation 10.02 Revision A. The peak baseline was drawn manually, always as close to the detector baseline as could be determined. Blank subtraction was not found to be necessary (see Section 2.1.4).

The mole fraction of the compounds under study was calculated by a simple ratio between the sample peak and the standard peak according to the following equation:

$$X_{sample} = \sum_{i=1}^N (A_{sample,i} \times X_{standard} / A_{standard,i}) / N \quad (2.1)$$

where X = mixing ratio and A = peak area, and N = 6 or 9 depending on whether 2 or 3 flask samples were collected (see Figure 2-8). Peak height was calculated in the same way by substituting peak height for peak area. Only peak area was used for the quantitative analysis. Peak height was used as a quality assurance check for peak area. In Equation 2.1, the sample peak height or area was measured on the MIT GC, the mixing ratio of the standard was a constant, but the peak height or area of the standard was interpolated according to Equation 2.2 because the standard was analyzed only once every fourth run.

$$A_{standard,i} \Big|_{i=1}^N = \Big|_{k=1}^3 k(A_{standard,after} - A_{standard,before})/4 + A_{standard,before} \quad (2.2)$$

where $A_{standard,before}$ and $A_{standard,after}$ represent the peak area (or peak height) of the last standard run before $A_{sample,i}$ and the next standard run after $A_{sample,i}$, respectively. The peak area and height of the first two standards of the day were averaged and used as if only one standard had been run.

2.1.4 Accuracy, Precision, and Calibration

MIT GC- μ ECD

To characterize the MIT GC- μ ECD response to the range of typical sample mixing ratios shown in Table 2.1, three sets of dilutions of the CFC standard, at the factors indicated in Table 2.2, were created. August 30 was a reanalysis of the same dilutions created on July 21. The balance gas was UHP N₂. The dilutions were prepared using the vacuum system described in Section 2.1.2, a highly accurate pressure transducer (Keller AG, Type PAA-33X, range 0-30 bar absolute, accuracy 0.05% of full scale for 10 - 40°C, resolution 0.002% of full scale) powered by a 12 V battery (Yuasa Corporation, No.NP7-12), and Read 30 software (Keller).

Figures 2-5 and Figure 2-6 present the drift corrected calibration curves for the four MPGs present in the CFC standard, which were also detected in the landfill gas samples. HCFC-22 and CCl₄ were not analyzed in the samples, so no calibration curves were generated. The curves were corrected for detector drift over the analysis period, but not for drift from one day to the next. All fits were done by using the reduced Chi Square method with the dilution accuracy errors from the Keller pressure transducer as weights. All of the data from all 3 sets of dilutions plus the August 2006 reanalysis were included. For CFC-12 and CFC-11, the residual plots show the goodness of fit, while for CFC-113 and CH₃CCl₃, the low range plots provide visual verification. Error bars are plotted for all dilutions, but the dilutions were so accurate that the error bars are not visible. The accuracy of the dilutions allowed for very precise fitting. All R² values are above 0.9999. The fact that the detector response of the reanalyzed dilutions in August 2006 was indistinguishable from the detector response of the same dilutions in July 2006 provides evidence that the calibration curves are unlikely to have drifted much over the 1.5 years of sampling. Further evidence of the lack of drift of the calibration curves is their goodness of fit

Table 2.1: Average and Maximum Ratios Between the Landfill Gas Samples and Gas Standards

	Average ratio to standard ^a	Maximum ratio to standard ^b
CFC-12	1:15 (0.0667)	1:20 (0.05)
CFC-11	1:8 (0.125)	1:12 (0.08333)
CFC-113	1:110 (0.00909)	1:150 (0.006666)
CH ₃ CCl ₃	1:30 (0.0333)	1:50 (0.02)
CH ₄	1:2(0.5)	1:2 (0.5)

^aThe ratio is 1:(mixing ratio of standard/average mixing ratio of sample) while the numbers in parentheses are the inverse of the ratio and are equal to (average mixing ratio of sample/mixing ratio of standard.)

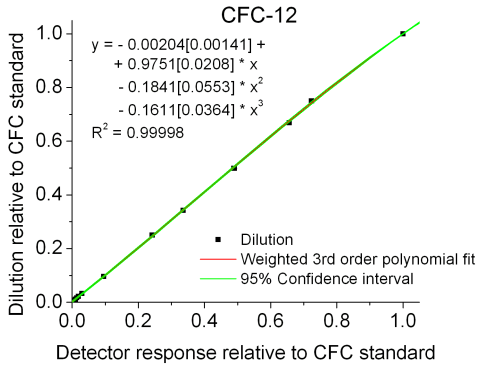
^bThe ratio is 1:(mixing ratio of standard/minimum mixing ratio of sample) while the numbers in parentheses are the inverse of the ratio and are equal to (minimum mixing ratio of sample/mixing ratio of standard.)

Table 2.2: Three Sets of Dilutions Run on the MIT GC- μ ECD on the Dates Indicated^a

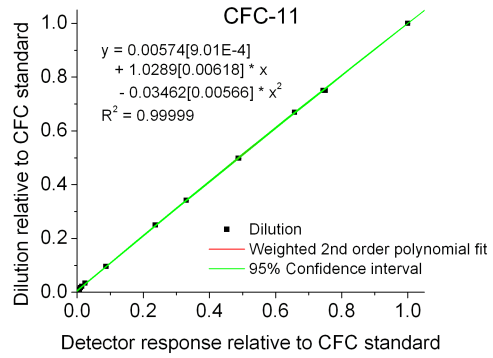
July 18, 2006	July 21, 2006	August 30, 2006 ^b	September 29, 2006
1:120	1:90	1:90	1:144
1:90	1:10	1:10	1:45
1:60	1:4	1:4	1:3
1:30	1:2	1:2	1:1.5
	1:1.3	1:1.3	

^aDilution ratios are relative to CFC standard.

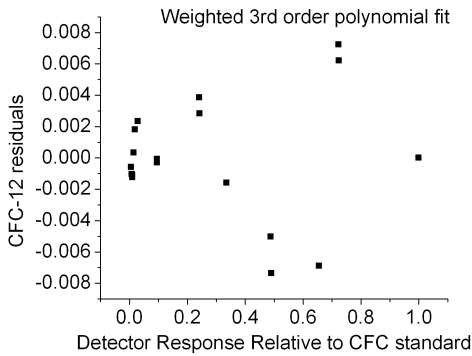
^bThe same dilutions from July 21 were reanalyzed on August 30.



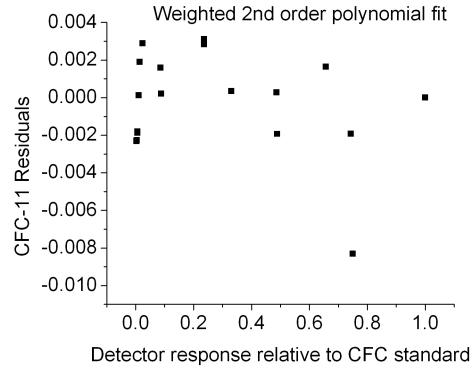
(a) CFC-12 calibration curve with third order polynomial fit



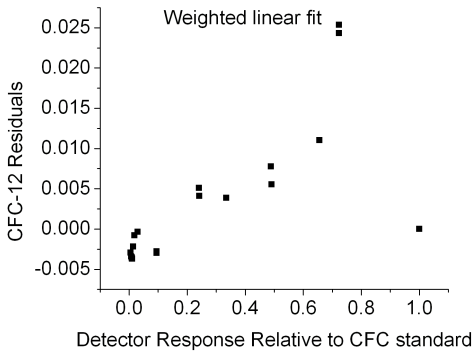
(b) CFC-11 calibration curve with second order polynomial fit



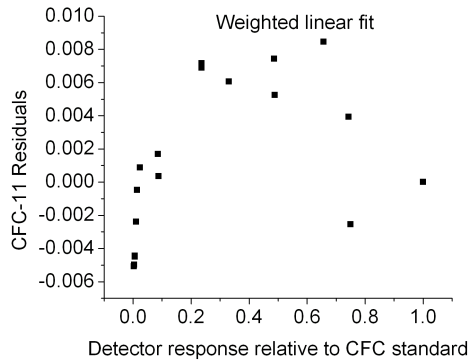
(c) Residuals from CFC-12 third order polynomial fit



(d) Residuals from CFC-11 second order polynomial fit

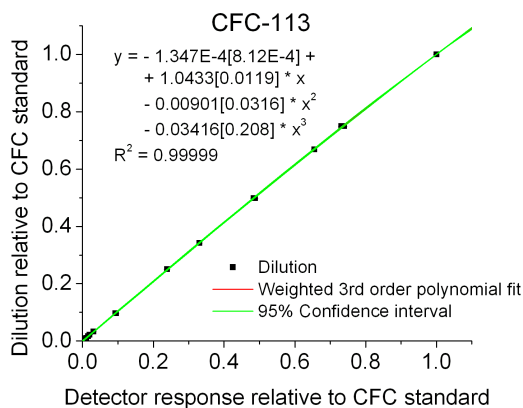


(e) Residuals from CFC-12 linear fit

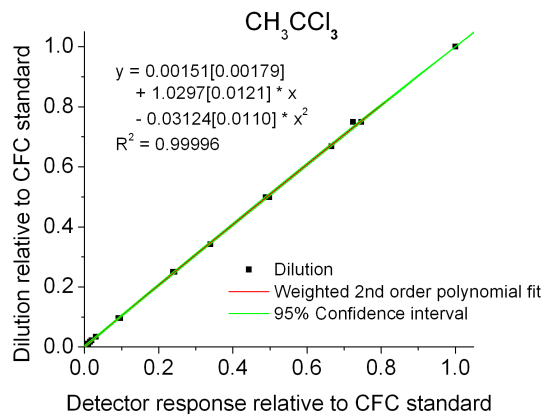


(f) Residuals from CFC-11 linear fit

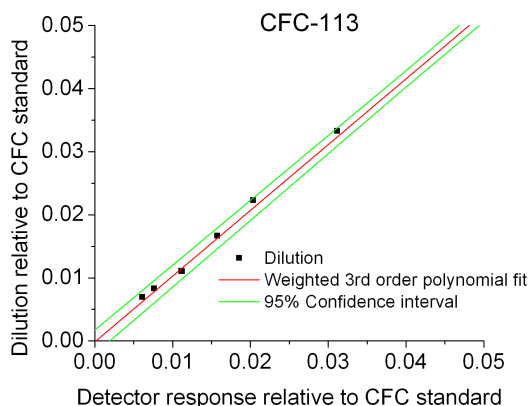
Figure 2-5: CFC-12 and CFC-11 drift corrected calibration curves and their associated fits and 95% confidence intervals. All three sets of dilutions and the August reanalysis were used for the fits (see Table 2.2). The dilutions of the CFC standard and their detector responses are normalized against the original CFC standard so that both x and y axes scale from 0 to 1.



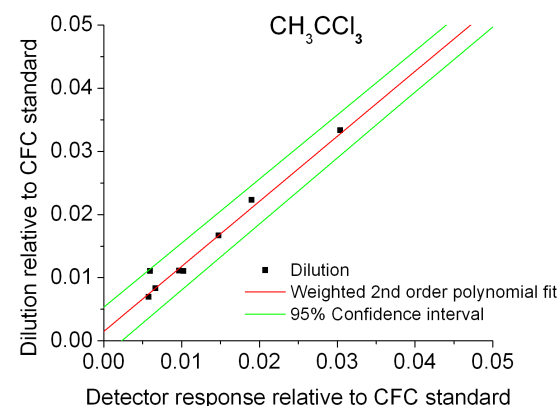
(a) CFC-113 calibration curve with third order polynomial fit, full scale



(b) CH₃CCl₃ calibration curve with second order polynomial fit, full scale



(c) CFC-113 calibration curve with third order polynomial fit, low range



(d) CH₃CCl₃ calibration curve with second order polynomial fit, low range

Figure 2-6: CFC-113 and CH₃CCl₃ drift corrected calibration curves and their associated fits and 95% confidence intervals represented as in Figure 2-5. The full scale is the entire range from 0 - 1, while the low range is only those dilutions in the 0 - 0.05 range.

Table 2.3: Calculated Percent Difference Between the Weighted Polynomial Fit Equations in Figures 2-5 and 2-6 and a Linear Fit Through Zero for Dilutions of the CFC Standard

	Dilution ratio	% difference between polynomial fit and $y = x$
CFC-12	1:15	1.69%
	1:20	2.41%
CFC-11	1:8	6.58%
	1:12	8.67%
CFC-113	1:110	2.76%
	1:150	2.25%
CH ₃ CCl ₃	1:30	6.89%
	1:50	9.47%

throughout the low to high range of dilutions.

Table 2.3 shows the percent difference between the calibration curve polynomial fit equations and a linear fit to the calibration curves with zero intercept ($y = x$) at typical and maximum standard to sample ratios taken from Table 2.1. For CFC-12 and CFC-113, which had less than a 5% difference between the polynomial fit equations vs. $y = x$, no correction was made for detector non-linearity. The mixing ratios were calculated as described in Section 2.1.3. For CFC-11 and CH₃CCl₃, which had > 5% difference between their polynomial fit equations and $y = x$, the mixing ratios were calculated using the polynomial fit equations presented in Figures 2-5 and 2-6.

MIT GC-FID

The MIT GC-FID was also checked for linearity because the detector is not intended for use at such high CH₄ mixing ratios. Using the same dilution method as for the MIT GC- μ ECD linearity check, two dilutions in ratios of 1:1.5 and 1:3 were made of the pure CH₄ standard with UHP N₂ as the balance gas. The CFC standard contained 802 ppm CH₄, so it was used as the lower end point in the calibration curve. From Figure 2-7, we see that a sample which is 50% CH₄ would have 1% error if $y = x$ was used to calculate sample mixing ratios instead of the linear fit equation in Figure 2-7. Thus, no correction for non-linearity was made for the MIT GC-FID measurements.

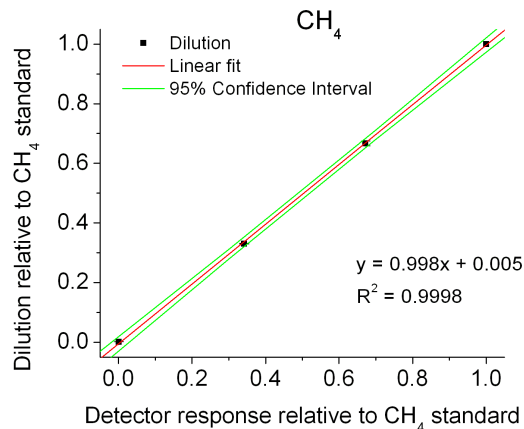


Figure 2-7: CH_4 drift corrected calibration curve including a linear fit and 95% confidence intervals. The CFC standard and the dilutions of the pure CH_4 standard and their detector responses are normalized against the pure CH_4 standard so that both x and y axes scale from 0 to 1.

2.1.5 Detection Limits

Detection limits were calculated using the International Union of Pure and Applied Chemistry (IUPAC) definition as outlined in *Thomsen et al.* (2003). In this definition, the detection limit is 3 times and the limit of quantitation is 10 times the standard deviation of blank responses. Blanks run during analyses in 2006 were used to calculate the standard deviation in the CH_4 peak area. For CFC-12, CFC-11, CFC-113, and CH_3CCl_3 ; 10 successive sets of CFC standard and blanks were run. The sample line was flushed for 13 minutes after each standard injection just as it was done in the analytical method described in Section 2.1.3. The conversion from measurement units to mixing ratio was calculated by

$$c = ks_dS \quad (2.3)$$

where c = limit of detection or quantitation in ppb or ppm, $k = 3$ or 10 for the limit of detection or quantitation, respectively, s_d = the standard deviation of the mean peak area for blank runs, and $S = \Delta\text{concentration}/\Delta\text{intensity}$ which was calculated through repeated CFC standard runs done at the time of the blank runs. The results are shown in Table 2.4. All sample mixing ratios well exceeded the minimum quantitation limits.

Table 2.4: Limit of Detection for the MIT GC-FID and μ ECD Detection Systems

Compound	Limit of Detection (ppb)	Limit of Quantitation (ppb)
	n=10	n=10
CFC-12	0.48	1.6
CFC-11	0.042	0.14
CFC-113	0.13	0.42
CH ₃ CCl ₃	0.17	0.57
CH ₄	400.	1330

2.2 One Landfill Study

Monthly Gas Sampling

Gas samples were taken approximately monthly from July 12, 2005 - December 16, 2006 at Crapo Hill landfill in New Bedford, Massachusetts. One last sample was taken on June 12, 2007. A full description of the site can be found in Chapter 3 along with a schematic of the gas collection system (see Figure 3-2). For each sample either two or three flasks were filled in succession to 30 psig as shown in Figure 2-8. All samples were taken between 11:00 EST - 13:00 EST at sample ports located on the main gas line directly before either the flare or the gas-to-energy plant. The flasks were filled using a AC metal bellows pump (Senior Aerospace Metal Bellows, Sharon, MA, Model MB-158, P/N 28950) from July 2005 - October 2006 and a KNF Neuberger 12V DC battery operated pump (6.5 L/min, Model UN86 KNDC, S/N 1/829383) from November - December 2006. The sample line was flushed 3 times with landfill gas before filling the flasks. Line pressure was monitored using a stainless steel line gauge (McDaniel Controls Inc., Luling, LA). All fittings and tubing were stainless steel or Teflon PFA.

The flasks were analyzed for CFC-12, CFC-11, CFC-113, and CH₃CCl₃ on the MIT GC- μ ECD for the entire length of the study and for CH₄ on the MIT GC-FID from October 20, 2005 onwards as described in Section 2.1. CH₄ measurements before October 20, 2005 were provided by Paul Pease, technical supervisor at Crapo Hill landfill, who used a CES LandTec GEM500 Landfill Gas Monitor. From 2001 - 2005, before the gas-to-energy plant was installed, Mr. Pease analyzed landfill gas from the flare port on a weekly basis using a CES LandTec GEM500 Landfill Gas Monitor (accuracy $\pm 3\%$) for CH₄, CO₂, O₂, and N₂ in units of volume percentage of total gas stream. The LandTec was calibrated or checked against span (50% CH₄, 30% CO₂) and zero (4% O₂) calibration gas mixtures provided by LandTec each time

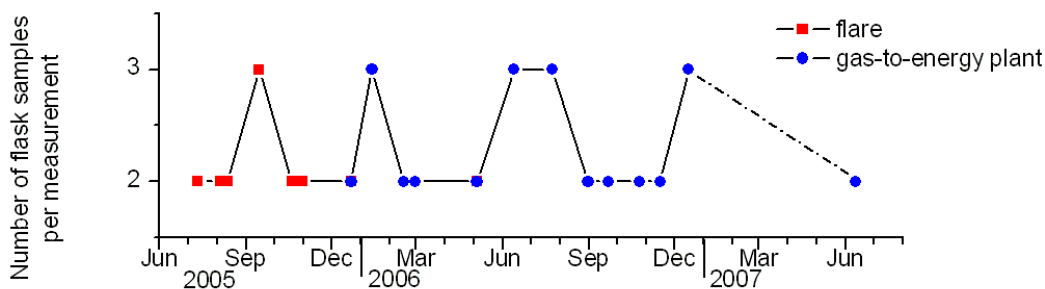


Figure 2-8: Number of flask samples averaged for each measurement in the One Landfill Study

the landfill gas was sampled.

The calculation of CFC-12, CFC-11, CFC-113, CH_3CCl_3 , and CH_4 mixing ratios was complicated by the discovery of a sample line leak in mid 2006. The leak was discovered by comparing the MIT GC-FID CH_4 mixing ratios and the CH_4 mixing ratios from an in-situ instrument at Crapo Hill. Since October 2005, Robert Whalley, operator of the Commonwealth New Bedford Energy gas-to-energy plant at Crapo Hill, has maintained a continuous in-situ 602P Non-Dispersive Infrared (NDIR) Analyzer (linearity > 0.5% full scale) from California Analytical Instruments at the gas-to-energy plant. The detector measures CH_4 , CO_2 , O_2 , and N_2 several times a minute. Mr. Whalley calibrated the NDIR analyzer weekly starting in November 2005 using pure CH_4 (Praxair, Slatersville, RI, accuracy $\pm 1\%$) and N_2 (Praxair, accuracy $\pm 1\%$) as the span and zero gases, respectively. The detector drifted no more than 0.5% in % CH_4 by volume between calibrations except between October 16 - November 3, 2006 where the detector drifted 2.7% in % CH_4 by volume.

To correct the samples which had already been taken at the plant port, the measured MIT GC- μECD and -FID halocarbon mixing ratios were multiplied by a correction factor equal to the ratio of the daily average CH_4 from the NDIR \div the MIT GC-FID measured CH_4 . This not only corrected for the sampling error, but also yielded daily average mixing ratios. For CH_4 , this effectively means the reported % CH_4 by volume from December 2005 - October 2006 is that from the NDIR. A test using the leaky vs. new shut-off valve indicates that the corrected value is likely $\pm 1\%$ of the true value for CFC-12, CFC-11, and CH_3CCl_3 . For CFC-113 the corrected value was 2.5% smaller than the true value.

To correct the July - September 2005, December 2005, and May 2006 flare measurements, all mixing ratios were multiplied by the average of the LandTec GEM500 CH₄ mixing ratio for October 20 and 31, 2005 and then divided by the average MIT GC-FID CH₄ mixing ratio for the same dates. The individual LandTec GEM500 to MIT GC-FID ratios were used for the October 20 and 31, 2005 samples. These were the only dates for which both sets of CH₄ measurements were available. The LandTec GEM500 measurements were point-in-time measurements, so the final corrected mixing ratio for samples taken from the flare port were not daily averages like the plant samples. That created a bit of a mismatch when comparing the flare measurements to the plant measurements, but it could not be helped. The same test of the corrected vs. true value was not done for the flare samples, because the flare corrections were much smaller (correction < 5%). The difference in correction factor was because the flare port was at positive atmospheric pressure, while the plant port was under vacuum. The correction factors are shown in Figure 2-9.

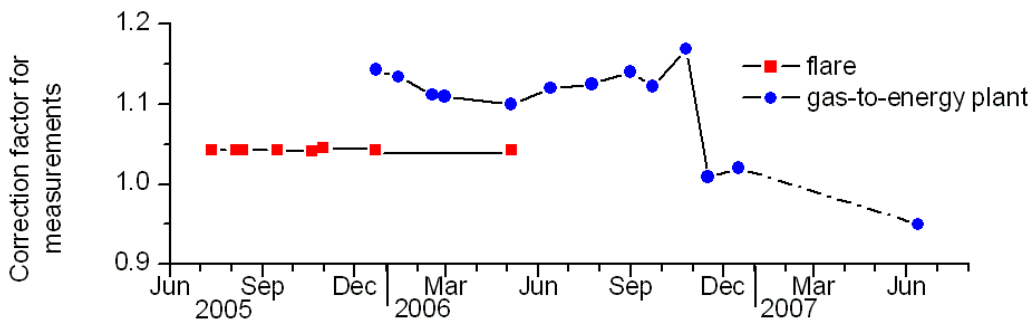


Figure 2-9: Correction factor used for all measurements made on the MIT GC-FID and GC- μ ECD systems during the One Landfill Study

Flow Measurements

Daily averaged gas pipeline flow rates standardized to 1 atm and 20°C were provided by Thomas Yeransian of Commonwealth Resource Management Corporation, who co-owns and manages the gas-to-energy plant at Crapo Hill. Commonwealth Resource Management Corporation maintains an in-situ, continuous monitoring orifice plate (accuracy $\pm 0.6\%$ of flow, Oripac Model, Lambda Square Inc., Bay Shore, NY). The

validity of the provided flow rates was checked by comparing instantaneous flow rate readings from the orifice plate and a traverse with a Dwyer 166 T Telescoping Pitot Tube (Dwyer Instruments Inc, Michigan City, IN) combined with a Dwyer 477A-1 Handheld Digital Manometer (scale 0"-20" water column, accuracy is 0.1% full scale). Both readings were found to be within 4% of each other which is well within the systematic errors associated with manual pitot tube traverses.

2.3 Multi-landfill Study

2.3.1 US Gas Sampling

Seven US MSW landfills were sampled between October - December 2006. A summary of the types of sites sampled can be found in Table 4.1. For each site three 0.8 L cylindrical flasks (see Section 2.1.2) were filled in succession to 30 psig. All samples were taken between 9:00 EST - 14:00 EST at sample ports located on the main gas line directly before either the flare or the gas-to-energy plant. The flasks were filled using a KNF Neuberger 12V DC battery-operated pump (6.5 L/min, Model UN86 KNDC, S/N 1/829383). The sample line was flushed 3 times with landfill gas before filling the flasks. Line pressure was monitored using a stainless steel line gauge (McDaniel Controls Inc., Luling, LA). All fittings and tubing were stainless steel or Teflon PFA. The flasks were analyzed for CFC-12, CFC-11, CFC-113, CH_3CCl_3 , and CH_4 mixing ratios on the MIT GC- μ ECD/FID as described in Section 2.1. All three flasks were analyzed in triplicate. The whole landfill mixing ratio used for the analysis in Chapter 4 is the average of all 9 analysis runs as described in Equation 2.1. Percent standard deviations (standard deviation of all 9 analyses \div average of all 9 analyses \times 100) for each sample site are $< 1.5\%$ for CFC-12 and CFC-11. CFC-113 mixing ratios have percent standard deviations $< 4.6\%$ for all sites. CH_3CCl_3 mixing ratios have percent standard deviations of $< 2.5\%$ except for one closed landfill with percent standard deviations of 5.5% . CH_4 mixing ratios have percent standard deviations of $< 1.05\%$.

2.3.2 UK Gas Sampling

A summary of the sampling techniques and resulting mixing ratios for each landfill is presented in Table 2.5. The landfills are labeled by number from 1-9. Viridor Waste Management (Exeter, Devon, UK) explicitly requested that the landfill names be kept confidential. All 9 sampled landfills are owned by and all but landfill No. 4 are operated by Viridor. All have gas-to-energy plants with one or multiple reciprocating

Table 2.5: Description of UK Landfill Gas Samples

	sample date	sample point ^a	sample type ^b	collection ^c	analysis ^d	N ^e	CFC-11 (ppm)	CFC-12 (ppm)	N ^f	CH ₄ %
1	3/21/06	plant	bags	Viridor	CERAM	1	0.36	2.3	1	52.8
	5/1/07	main	tubes ^g	C&P	Harwell	2	0.37		6	49.6
2	2004	flare	bags	Viridor	CERAM	1		1.8		
	5/3/07	main	bags	C&P	C&P	1		1.8	1	47.8
3	1/10/07	flare	bags	Viridor	CERAM	1	0.30	2.8	1	56.2
	3/22/07	main	tubes ^g	C&P	Harwell	2	0.68		6	59.1
4	4/7/06	main	bags	Viridor	CERAM	1		2.8	1	40.4
5	4/23/04	main	bags	Viridor	CERAM	1	0.32	2.5		
	5/3/07	main	bags	C&P	C&P	1	0.53	2.2	1	46.6
6	4/7/06	main	bags	Viridor	CERAM	1	0.78	2.2	1	49.6
	6/28/04	main	bags	Viridor	CERAM	1	0.94	2.3		
7	4/7/06	main	bags	Viridor	CERAM	1	0.59	2.3	1	39.5
8	4/7/06	main	bags	Viridor	CERAM	1	0.20	1.2	1	51.3
9	3/21/06	plant	bags	Viridor	CERAM	1	0.25	1.6	1	55.6

^aSample point is the location on the landfill gas line where the gas sample was collected. Main refers to a sample port on the main line somewhere before the flare or gas-to-energy plant (see Figure 3-2 for a visual example). Plant and flare are sample ports on the main line directly before the gas-to-energy plant or flare, respectively.

^bSample type refers to the type of material used to collect the gas sample. The material is the same for CFC-12, CFC-11, and CH₄ unless otherwise indicated. bags = Tedlar bags, tubes = sorbent tubes.

^cRefers to the company who collected the gas sample(s). See text.

^dRefers to the company who analyzed the gas sample(s). See text.

^eNumber of samples analyzed and averaged together to yield each displayed CFC-11 and CFC-12 mixing ratio

^fNumber of points recorded or samples analyzed and averaged together to yield each displayed CH₄ mixing ratio.

^gFor the C & P Environmental samples, sorbent tubes refer only to the CFC sample methodology. CH₄ mixing ratios were measured with a GA2000+ Infrared Gas Analyzer (Geotechnical Instruments) 3 times before and after sorbent tubes were filled. The displayed CH₄ mixing ratio is an average of all 6 measurements.

engines. Each landfill has 1-2 flares, a few of which operate continuously at the sites which produce more gas than can be used by the engines.

Table 2.5 presents the average mixing ratio of either CFC-12, CFC-11, or CH₄ for the listed number of measurements made on each sample date. Mixing ratios were reported to two significant figures for the CFCs and three for CH₄ by the two different analysis companies. For each landfill, the average mixing ratio of the 1-2 sample days was used for the emission estimates in Chapter 4. All of the data from 2004, 2006, and 2007 were used. The only time a measurement was removed was if it was from 2004 and no more recent measurements in 2006 or 2007 existed to see that the landfill mixing ratio had not drastically changed over the 2-3 years.

One concern did arise with the 2007 data. Prof. Peter Simmonds at the University of Bristol visited the Harwell labs and expressed concern that their sorbent tube sampling and analysis would result in artificially high CFC-11 mixing ratios. This affected one sorbent tube sample from landfill No. 3 and one from landfill No. 1. Because both sorbent tube samples did not have higher CFC-11 mixing ratios than the Tedlar bag samples at the same landfill, it was unclear whether it would be better to keep or discard the sorbent tube samples. The final estimates were very similar with or without the sorbent tube samples, so a decision was made to include the sorbent tube samples.

The gas samples were collected by Viridor themselves or by C & P Environmental (Bedford, Bedfordshire, UK) in either Tedlar bags or sorbent tubes. The gas analysis was done by C & P Environmental, CERAM (Stoke-on-Trent, Staffordshire, UK), or Harwell Scientifics Laboratory (Didcot, Oxon, UK). The three possibilities for gas sampling and analysis are presented in the following sections.

Viridor Collection and CERAM Analysis

For all of the CERAM analyses, Viridor did the sample collection themselves. They filled one or more Tedlar bags using a GA2000 Infrared Gas Analyzer (Geotechnical Instruments, Chelmsford, England), which has an internal pump. The bags were filled via the following method. First, a water filter was fitted to the gas analyzer sample tube. The analyzer was purged with ambient air. Next the analyzer was connected to the sample port and gas was pumped through the analyzer. When the CH₄ mixing ratio reached a stable level as reach on the GA2000, the Tedlar bag was connect to the analyzer outlet. The bags were filled to ~ 3 cm thick and shipped to CERAM.

CERAM is an UKAS ISO 17025:2005 accredited testing laboratory specializing in landfill gas analysis. The gas samples were analyzed for CFCs and CH₄ using

CERAM's UKAS in-house method BCRL-C51 or BCRL-C72, respectively. Both methods were accredited in 1999. All of the gas samples were analyzed on a GC-MS at most two weeks after sampling.

C & P Environmental Sampling and Analysis

In 2007, Viridor switched analysis companies from CERAM to C & P Environmental, who offers the additional service of sample collection by a technician. C & P were more conscientious than Viridor with their quality control documentation. C & P used a GA2000+ analyzer to fill and evacuate their Tedlar bags two or more times before filling the final sample. They always filled two Tedlar bags in case one leaked before the gas analysis. Bags were kept at ambient temperature in a dark, cool box during transportation after sampling and before analysis. Analysis was done one week after sampling on a GC-MS at C & P which is a UKAS accredited testing laboratory No. 2125.

C & P Environmental Sampling and Harwell Scientifics Analysis

C & P filled two dual sorbent Automated Thermal Desorption (ATD) tubes coated with Sulphinert and sealed the tubes with a PVC cap. Sample tubing was purged for a few minutes before filling the sorbent tubes by passing 100 mL of gas through the tubes. The sorbent ATD tubes were then sent to Harwell Scientifics along with a blank ATD tube to make sure no contamination occurred during transport. At Harwell, the samples were analyzed by ATD-GC-MS using a Perkin Elmer TurboMatrix ATD connected to an Agilent 6890/5973N GC-MS operating in scan mode. Before the tubes were analyzed they were purged with 1.5 L of dry nitrogen gas. Harwell is a UKAS accredited testing laboratory.

Chapter 3

The One Landfill Study: Variability in Mixing Ratios and Generation Rates

The main focus of the “One Landfill Study” is to provide insight into the variability of CFC-12, CFC-11, CFC-113, CH_3CCl_3 (called Montreal Protocol-restricted gases or MPGs); and CH_4 mixing ratios and generation rates (flow rate \times mixing ratio) at actively managed MSW landfills. Because we visited landfills only once for the emission estimation sampling in Chapter 4, a longer study at one landfill was needed to quantify landfill gas variability and thus correct any sampling biases. This chapter presents data collected during a 17 month long field campaign from July 2005 - December 2006 at a landfill in Southern Massachusetts. The data analysis is exploratory by nature, since this is a first analysis of a time series of MPG mixing ratios and generation rates in landfill gas. By the end of the chapter, we aim to be able to answer the following questions.

1. What is the total variability in landfill gas mixing ratios and generation rates over one year?
2. Is there strong seasonal variability?
3. How does the variability differ between different types of landfill gas technologies?

This chapter also introduces a concept used throughout the rest of the thesis; that of generated landfill gas. For this thesis, we sampled bulk landfill gas at actively

managed landfills to increase the number of sample measurements. Since the gas at actively managed landfills flows first to either a flare or gas-to-energy plant where it is combusted before being emitted to the atmosphere, the bulk gas we are sampling cannot be called emissions. Here we name it generated gas or generation rate.

3.1 Background

There are different factors, both natural and engineered, which might affect MPG variability within a landfill system. These factors create complex responses in the MPG mixing ratio and generation rates, which we attempt to piece apart in this analysis. Previous studies have shown landfill CH_4 surface emissions to vary with the following environmental factors: ambient pressure, soil moisture, soil temperature, precipitation, ambient temperature, wind speed, and the pressure gradient between ambient pressure and landfill pressure (*Young, 1990; Bogner et al., 1995, 1997, 1999; Czepiel et al., 1996; Borjesson and Svensson, 1997; Christophersen et al., 2001; Czepiel et al., 2003; Poulsen et al., 2003; McBain et al., 2005*). It is important to note that all of these studies were done on surface emissions, many at passive landfills where the main gas escape route is through the landfill surface cover or passive gas vents. The surface emission studies done at actively managed landfills show greatly curtailed emissions and can even be CH_4 sinks (*Bogner et al., 1995; Mosher et al., 1999; Czepiel et al., 2003*). *Chanton and Liptay (2000)* found little seasonal variation in CH_4 production within landfills because of the interior's constant temperature.

Some of these environmental factors may not only affect the generation and emission rates of the bulk gas, defined as CH_4 (~ 55%), CO_2 (~ 45%), and < 1% other compounds which are present in the pore space of a landfill (*Deipser et al., 1996*), but also of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 . For example, CFCs have been shown to biologically degrade under anaerobic conditions such as those found in landfills (*Denovan and Strand, 1992; Deipser and Stegmann, 1997; Scheutz et al., 2003; Balsiger et al., 2005; Scheutz and Kjeldsen, 2005; Scheutz et al., 2007*). Microbial degradation is temperature dependent, as is a second parameter, the diffusion rate of MPGs from the waste into the bulk gas.

Lastly, modern landfills are not only governed by natural processes, but are also engineered systems. The study site for this variability study is actively managed, meaning the landfill gas produced underground is pumped to a flare or gas-to-energy plant (see Box 1.1) where it is combusted before final release to the atmosphere. During the study, we had the opportunity to collect data on both of these major landfill



Figure 3-1: Top left: Google Maps image of southern New England. Blue arrow indicates location of Boston. Yellow arrow indicates location of Crapo Hill landfill; Top right: Aerial view of Crapo Hill landfill taken on February 22, 2006 ©Thomas Yeransian; Bottom left: Crapo Hill landfill leachate tank on left and gas to energy plant on right; Bottom right: Crapo Hill landfill flare

gas technologies. The interaction between the natural and engineered variability is one of the main foci in this chapter.

3.2 Methods

3.2.1 Study Site

All samples for the One Landfill Study were taken at Crapo Hill landfill in New Bedford, Massachusetts. Figure 3-1 shows the location, an aerial photograph, and the gas-to-energy plant and flare at Crapo Hill landfill. The landfill is about 70 miles south of Boston, Massachusetts. It is one of 17 open MSW landfills in Massachusetts, 8 of which are actively managed (*DEP*, 2007).

Crapo Hill is typical of most of the modern landfills in the US and other industrialized countries. It opened in 1995, which puts it in the middle of the youngest 25% nationally and the newest in Massachusetts by 20 years, which has older and smaller landfills than the national average. It accepts about 115,000 tons annually

which places it in the middle percentile of Massachusetts landfills based on annual waste input but in the small (defined as smallest 25%) to medium (defined as middle 50%) range nationally. Crapo Hill accepts on average 93.6% MSW, 5.5% C&D waste, 0.4% recycling residue, 0.3% other non-MSW, and 0.2% DPW waste (see Box 1.1 for waste definitions). This is the highest MSW percentage of the 18 Massachusetts landfills which have active gas collection systems, but it is not an outlier.

Like all MSW facilities nationally, Crapo Hill does not accept toxic waste. It was permitted for the first few years it was open to accept white goods (e.g. refrigerators and air conditioning units), but has not for close to a decade. White good disposal in MSW facilities has been restricted in Massachusetts since 1992.

Crapo Hill's engineering design and environmental control measures are representative of all of the newer sections in landfills nationally and in other industrialized countries. These include a leachate tank to collect liquid run-off, geomembrane liner on 100% of the landfill to trap liquids and gases, synthetic cap on sections which are closed to dumping, and a gas collection system to actively pump out landfill gas. Crapo Hill estimates that it is able to capture between 80-95% of its landfill gas. Nationally about 25% of the US MSW landfills convert landfill methane to electricity (*EPA*, 2007a), while many more have active gas collection systems combined with flares (*EPA*, 2007c; *DEP*, 2007).

A schematic of the gas collection system is depicted in Figure 3-2. A flare system (2000 cubic ft/min, Organics, Ltd., Coventry, UK) was in place by 1999. During our study in the fall of 2005, a gas-to-energy plant (four reciprocating engines, maximum output 825 kW each, Caterpillar) was installed. Once the gas-to-energy plant, hereinafter called the "plant", was fully operational in January of 2006, the flare was only turned on less than once a month when one or more plant engines had mechanical problems. Both the flare and plant are optimized to pull as much gas out of the landfill as is possible with the number of wells in place without causing ambient air infiltration into the landfill.

3.2.2 Data Collection

The data collected, which is used for the analysis in this chapter, included: whole landfill CFC-12, CFC-11, CFC-113, CH_3CCl_3 , and CH_4 bulk gas mixing ratios; daily average pipe flow rates; and the ambient climate parameters, temperature (daily high, low, and average), humidity (daily high, low, and average), sea level pressure (daily average), and precipitation (daily total).

Crapo Hill Landfill

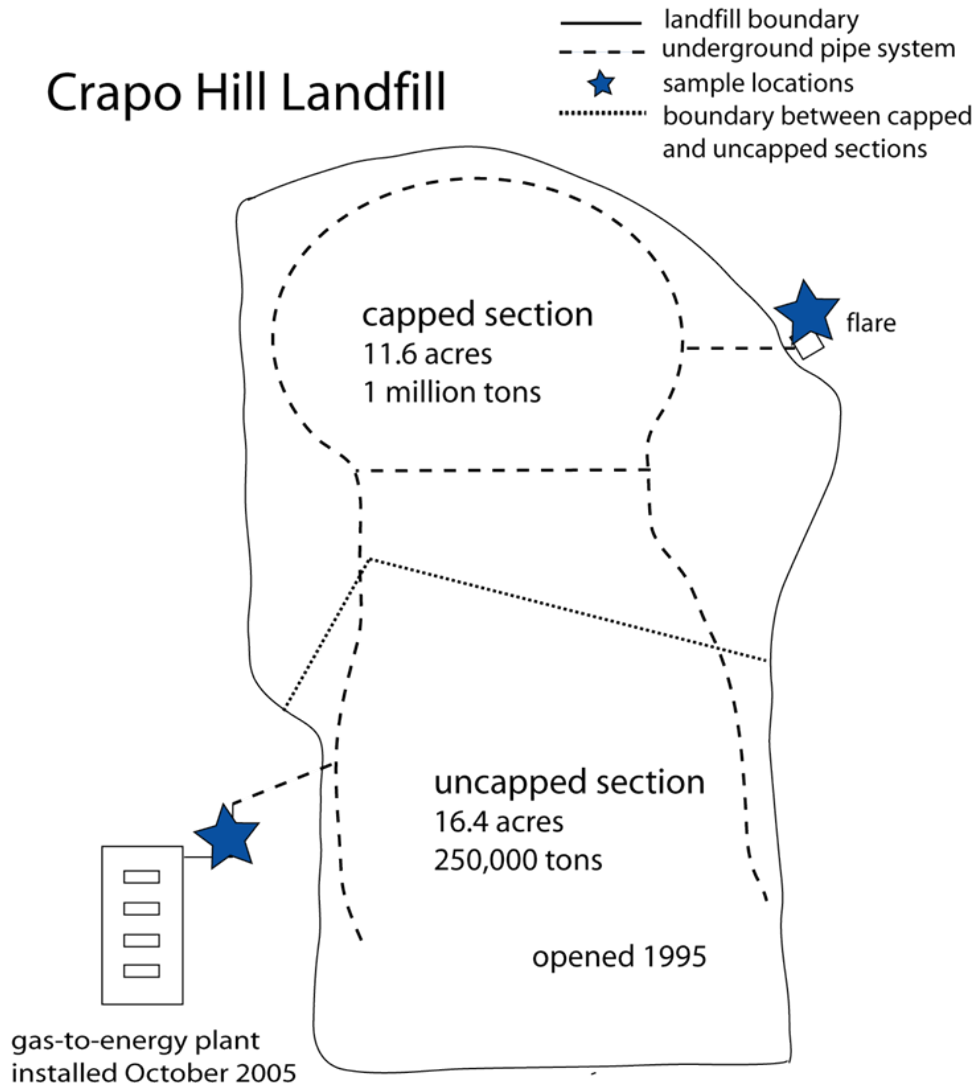


Figure 3-2: Schematic drawing of the underground gas piping system at Crapo Hill landfill

The bulk gas mixing ratios were sampled on a monthly basis from July 12, 2005 - December 16, 2006. One last sample was taken on June 12, 2007. The sample port locations are depicted by a blue star in Figure 3-2. From July - December 2005, samples were taken from the flare port. When the plant began operation, the sample port switched to one directly before the plant. This plant port was sampled from December 2005 - December 2006 and again in June 2007. Both ports were sampled during December 2005 and May 2006. The details of the gas sampling are described in Section 2.2.

Daily averaged gas pipeline flow rates standardized to 1 atm and 20°C were provided by Thomas Yeransian of Commonwealth Resource Management Corporation, who owns and manages the gas-to-energy plant at Crapo Hill landfill. Details of the flow instrumentation are in Section 2.2.

The climate data was obtained from the New Bedford airport weather station, which is approximately 10 miles from Crapo Hill landfill. The weather station is part of the US Automated Surface Observing System, which is a joint effort of the National Weather Service, the Federal Aviation Administration, and the Department of Defense.

3.3 Trends

The full time series of mixing ratios and generation rates are shown in Figures 3-3 and 3-4. MPG mixing ratios are in parts per million (ppm), while CH₄ mixing ratios are in fraction of total landfill gas volume. Generation rates are in g/day and were calculated by converting mixing ratio to mass concentration and multiplying by pipe flow rate. The red squares are samples which were taken at the flare port, while the blue circles are samples which were taken at the plant port. The error bars represent standard deviations of the mean, which include instrument precision error and variability from averaging across flasks. The July - September, 2006 CH₄ mixing ratios were measured by Paul Pease at Crapo Hill and do not have error bars (see Section 2.2). The dotted lines show the two breaks between data sets: 1) the switch from sampling at the flare to the plant port and 2) the break from December 2006 to June 2007.

There are several obvious trends from the mixing ratio time series. CFC-11 and CH₃CCl₃ both increase strongly from the beginning to the end of the flare measurements. CFC-113 is the only one of the compounds which peaks and begins to decrease during the flare measurements. The CFC-12 and CH₄ flare measurements

seem to show no obvious trend, hovering around 1 ppm and 57% of the landfill gas by volume, respectively. After the plant begins operation, MPG mixing ratios and generation rates all seem to follow a similar pattern. They decrease for a few months and then appear to oscillate around a constant value. That constant value appears to remain relatively unchanged even 6 months after the monthly sampling ended. CH₄ seems to have a different response than the MPGs once the plant begins operation. The CH₄ plant mixing ratios increase instead of decrease. In general, the CH₄ mixing ratio variability is much less than that for the MPGs. It is the only one of the compounds where the measurement error begins to approach the variability in the mixing ratios over the study period.

The generation rate and mixing ratio time series for both the flare and plant time series are very similar for each MPG. There is a slight perceivable difference between the flare trends of the two time series, where the generation rates have more of an upward trend than the mixing ratios, especially for CFC-12. For the plant time series, MPG mixing ratios and generation rates will be used interchangeably for the rest of the analysis presented in this chapter, because they are well correlated. Using a standard measure for calculating the linear relationship between two numerical quantities, the Pearson product-moment correlation coefficient, it is possible to calculate a R² value for the degree of correlation between the plant mixing ratio and generation rate time series. The R² values are CFC-12 = 0.93, CFC-11 = 0.98, CFC-113 = 0.99, and CH₃CCl₃ = 0.96. The degree of similarity between the mixing ratios and generation rates for each MPG indicates that most of the variability in the plant MPG generation rates is due to the variability in mixing ratios not flow rates.

The CH₄ mixing ratios and generation rates are much more dissimilar than was observed with the MPGs. When compared to the pipe flow rates in Figure 3-5, the generation rate variability more closely resembles the flow rate variability. The pipe flow rate should have more of an effect on CH₄ than the MPGs. CH₄ is ~ 55% of the total gas volume while the MPGs combined are much less than 1% (*Deipser et al.*, 1996).

3.4 Gas-to-energy Plant

Variability Due to Technology (December 2005 - May 2006)

For the variability analysis, the flare and plant measurements are analyzed independently, as are the MPGs and CH₄. This section discusses MPG plant trends, Section

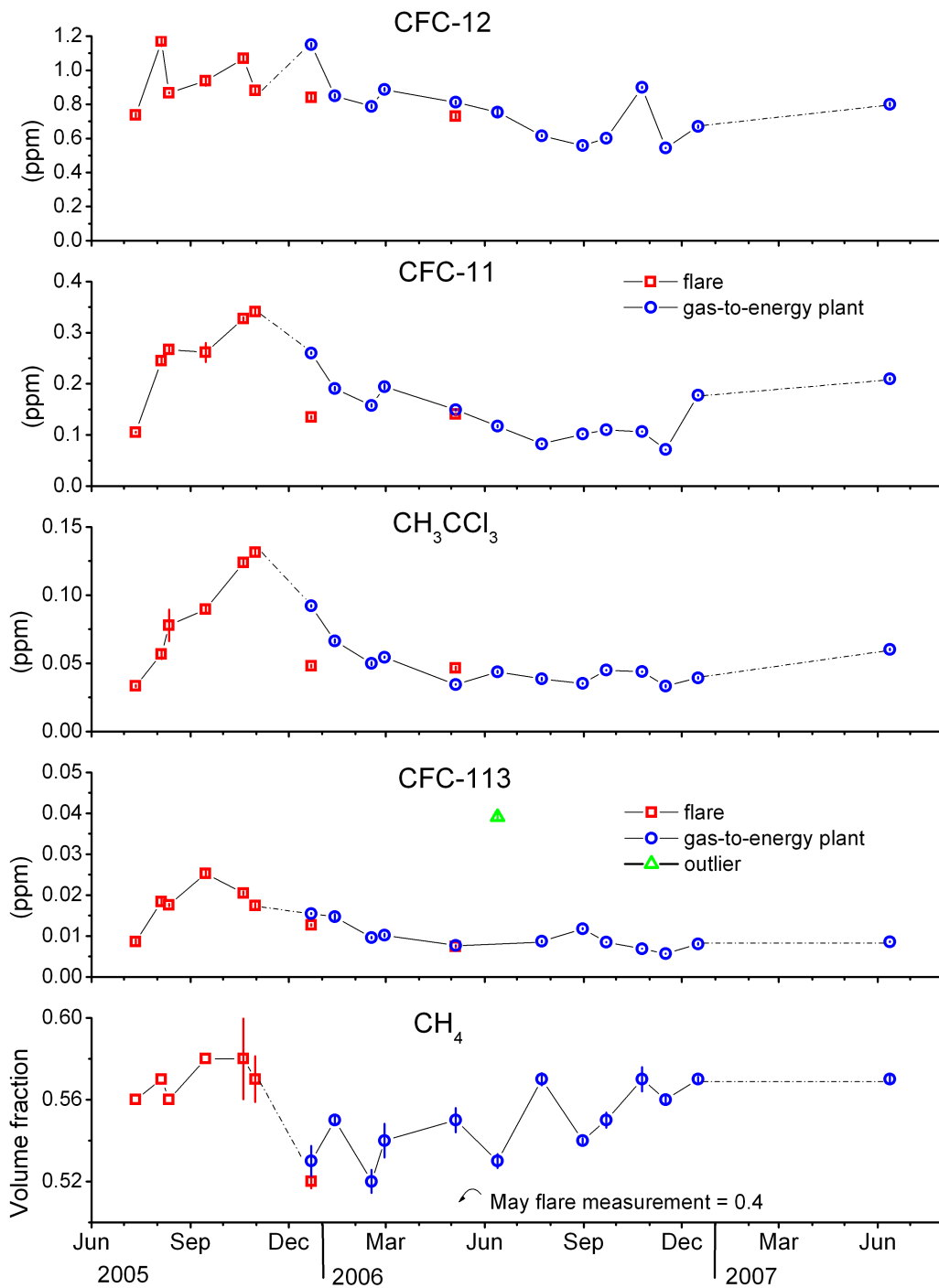


Figure 3-3: Mixing ratio time series of Crapo Hill landfill gas. Red squares are samples taken at the flare port, while blue circles indicate samples taken at the gas-to-energy plant port. All samples were taken before combustion. Vertical lines represent one standard deviation of the mean, which is due to flask averaging and detector imprecision. X-axis labels mark the first of each month. Dashed lines indicate a break or change in the monthly sampling routine.

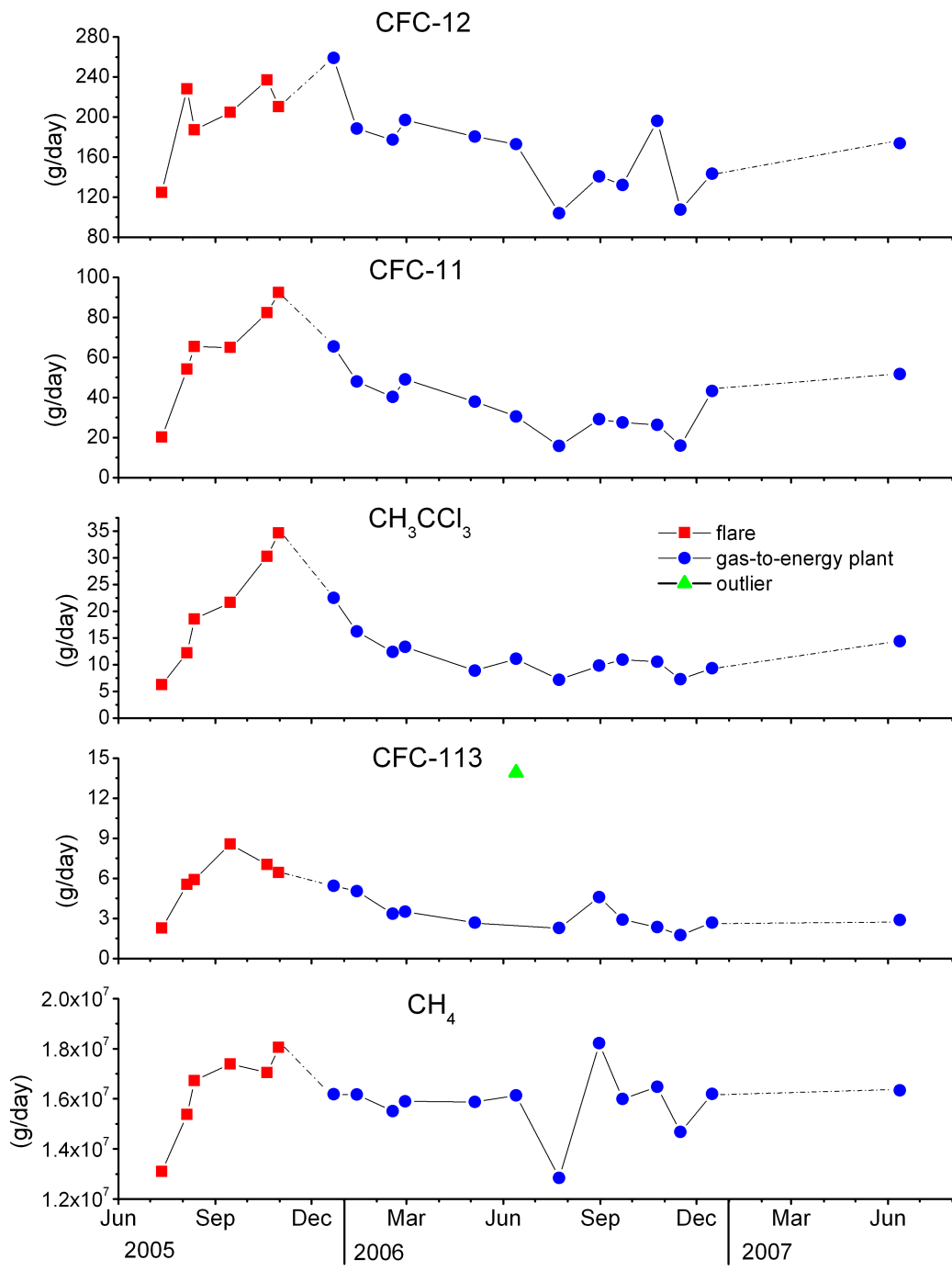


Figure 3-4: Generation rate time series of Crapo Hill landfill gas. The data symbol (square or circle) refers to the main gas technology used at the time of measurement. X-axis labels mark the first of each month. Dashed lines indicate a break or change in the monthly sampling routine.

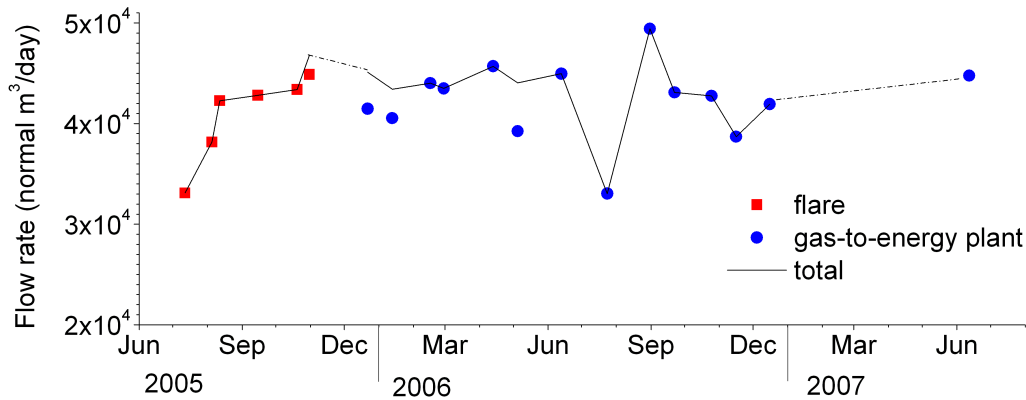


Figure 3-5: The pipe flow rate to the flare or plant and the total flow rate (flare + plant flow rate) on the days when samples were taken. The flow rate is standardized to 0°C and 1 atm.

3.5 discusses the MPG flare trends, and Section 3.6 discusses the CH₄ measurements.

One of the most obvious trends mentioned in the previous section is the strong decrease in both concentrations and generation rates observed at the beginning of the plant MPG time series. This corresponds to a time when the gas recovery technology first switched from the flare to the plant. In order to investigate the effect this technology switch may have on the variability, correlations among the MPGs are compared using the whole (December 2005 - December 2006), the first half (December 2005 - July 2006), and the second half (May - December 2006) of the plant time series. The first and second half of the plant time series overlap slightly to maintain as many data points as possible for the correlations.

The correlations of MPG generation rates using the whole plant data set are shown in Figure 3-6. Significant correlations (p-value < 0.05) are shown with regression lines and Pearson R² values. All MPGs correlate with one another when the complete plant data set is used, but some of the correlations are weak.

The comparison between the whole and first half of the data set is shown in Table 3.1. December 2005 - July 2006 produce much stronger correlations than those for the whole plant data set. The second half of the plant time series (May - December 2006) does not have any significant correlations. This has important implications for the estimation of MPG mixing ratios and generation rates at landfills with gas-to-energy plants. For example, if we have a mixing ratio or generation rate of CFC-12 at a landfill where a gas-to-energy plant has been installed for longer than 6 months,

	R^2 (Dec 05 - Dec 06) ^a	R^2 (Dec 05 - Jul 06) ^a
CFC-11 vs. CFC-12	0.72	0.93
CFC-113 vs. CFC-12	0.41	N/A
CFC-113 vs. CFC-11	0.56	0.74
CH ₃ CCl ₃ vs. CFC-12	0.74	0.79
CH ₃ CCl ₃ vs. CFC-11	0.75	0.84
CH ₃ CCl ₃ vs. CFC-113	0.70	0.92

^aDec = December, Jul = July, 05 = 2005, N/A = no correlation. The R^2 values are calculated by taking the square of the Pearson product-moment correlation coefficient. The length of the time series used for each correlation is shown in the column headings.

we could estimate mixing ratios and generation rates for CFC-11, CFC-113, and CH₃CCl₃ within a 10-30% error depending on the MPG (see Tables 3.3 and 3.4).

The fact that MPG generation rates are more highly correlated in the first half of the plant time series than those for the whole time series is consistent with the idea that the switch in gas technology is the main cause of MPG variability for the first half of the plant data set. Further evidence of this comes from samples collected from the flare and plants ports during December 2005 and May 2006. The percent difference between flare and plant mixing ratios is shown in Table 3.2. In December 2005, there is a significant difference between mixing ratios at the two ports. By May 2006, CFC mixing ratios reach consistency. However, CH₃CCl₃ mixing ratios continue to show significant differences. This is consistent with the idea that CFC mixing ratios and generation rates are influenced by the switch from one gas recovery system to another during the first few months of 2006, but that influence disappears by May 2006. Because there is no data from both ports between December 2005 - May 2006, it is unclear how soon after December 2005, the two sample ports become consistent with respect to CFC mixing ratios.

Table 3.2: Percent Difference Between Flare and Plant Mixing Ratios in December 2005 and May 2006

	December 2005	May 2006
CFC-12	20%	4%
CFC-11	43%	0%
CFC-113	10%	0%
CH ₃ CCl ₃	43%	28%

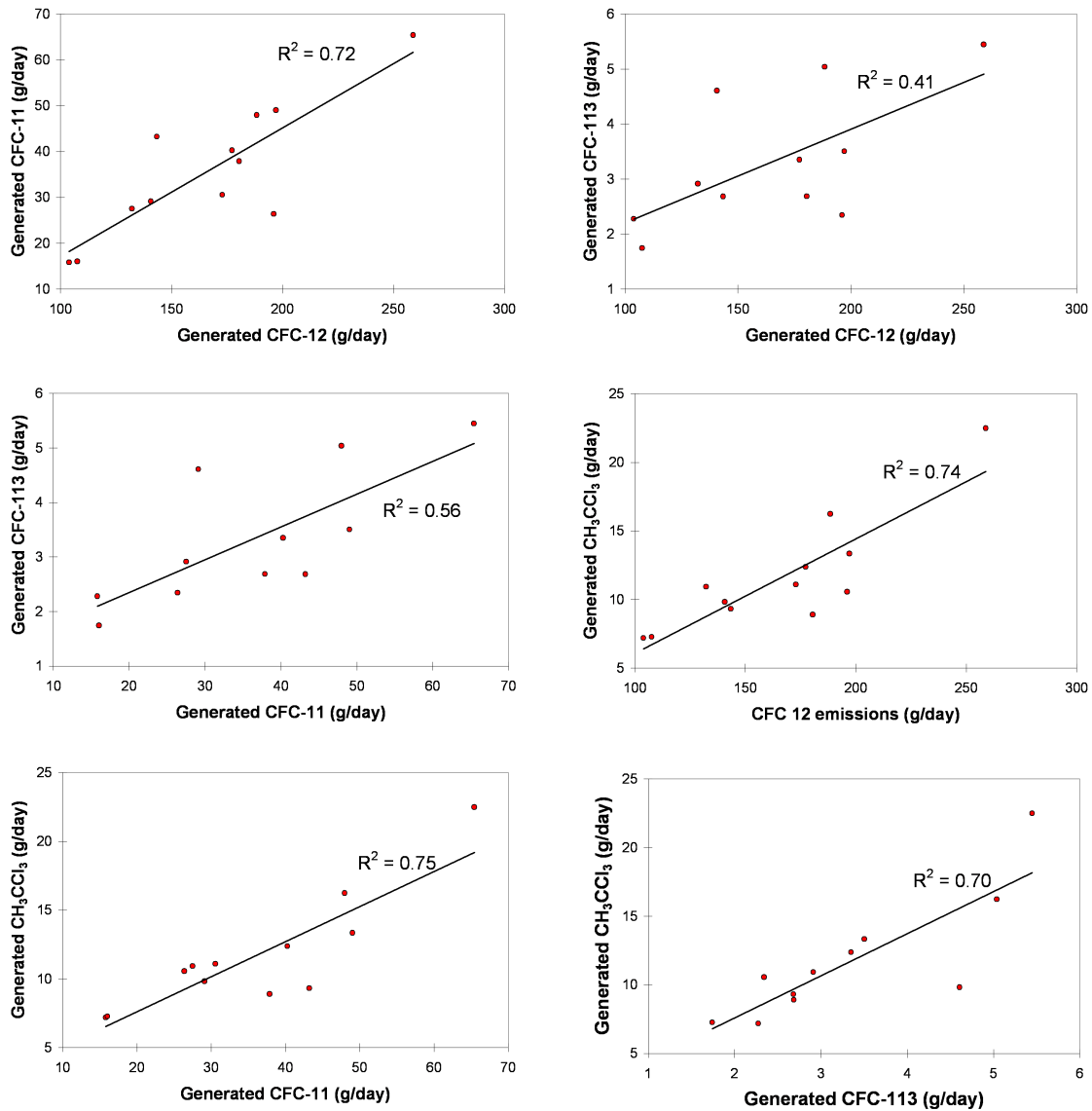


Figure 3-6: Correlations between plant generation rates using all plant data from December 2005 - December 2006. R^2 values, calculated by taking the square of the Pearson product-moment correlation coefficient, are shown on each plot.

Variability Due to Seasonality (May 2006 - December 2006)

Thus far, we have attributed the variability in the MPG time series from December 2005 - May 2006 to a switch in gas recovery technology. After May 2006, there is certainly less of an obvious trend in the MPG data sets, implying a more random forcing. To investigate possible explanations of this smaller variability, the MPG plant generation rates are correlated against several common natural variability indicators including: daily high, daily low, and daily average temperature; daily high, daily low, and daily average humidity; daily average sea level pressure; total precipitation in previous 5, 10, and 30 days; and previous 5, 10, and 30 day average temperature, humidity, and sea level pressure. The previous 5, 10, and 30 day averaged parameters are calculated by taking the mean of the average daily values for the prior 4, 9, or 29 days plus the day of the MPG measurement. The ambient climate data is from the New Bedford airport weather station approximately 10 miles from Crapo Hill landfill as described in Section 3.2. No correlations could be done with landfill climate data, because only partial records were available.

For the seasonal correlations, we want to remove the effect of the technology switch, while preserving as much of the plant data set as possible. This means we want to remove the measurements closest to when the gas-to-energy plant began operation, specifically, December 2005 and January 2006. April 2006 was previously removed due to sampling errors, which leaves only February and March 2006 as data which is included in the correlations before May 2006. All climate parameters with significant correlations with respect to MPG generation rates (p -value < 0.05) are normal distributions with no autocorrelation. As for the previous correlations, we will use R^2 , which is calculated by taking the square of the Pearson product-moment correlation coefficient, as a quantitative measure of the degree of correlation.

Select scatter plots are shown in Figure 3-7. CFC-12 has significant correlations with previous 5 ($R^2 = 0.44$), 10 ($R^2 = 0.47$), and 30 day ($R^2 = 0.41$) average temperature. CFC-11 correlates with daily low temperature ($R^2 = 0.71$), and previous 5 ($R^2 = 0.68$), 10 ($R^2 = 0.70$), and 30 day ($R^2 = 0.62$) average temperature. A correlation of CH_3CCl_3 with previous 5 day relative humidity only occurs if the February data point is used. Because February is so close to the flare to plant switch, the CH_3CCl_3 correlation with humidity can not be separated sufficiently from the overall technology switch to be an independent correlation with ambient climate data. CFC-113 has no significant correlations. Several of the climate indicators correlate with each other including: daily high, daily average, and daily low temperature; previous 5, 10, and 30 day average temperature; and previous 5 day relative humidity. Previous 5, 10,

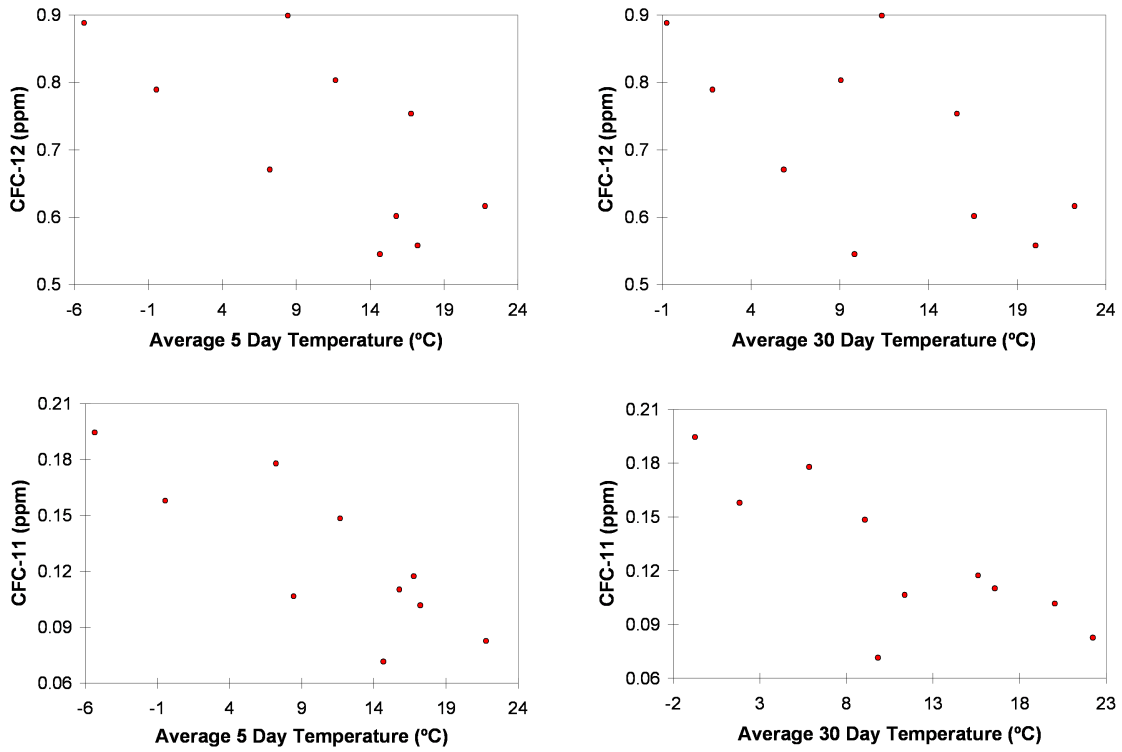


Figure 3-7: Selected scatter plots of mixing ratios vs. ambient temperature. 5 and 30 day temperature refer to the average of the 4 or 29 days previous plus the day on which the gas sample was collected.

and 30 day average temperature also correlates with previous 10 and 30 day average relative humidity.

The scatter plots and R^2 values are consistent with the conclusion that CFC-11 and CFC-12 mixing ratios are inversely proportional and very weakly linearly related to ambient temperature, while CH_3CCl_3 and CFC-113 mixing ratios have no attributable seasonal effects. Most likely CFC-11 and CFC-12 correlate more strongly with ambient temperature than CFC-113 and CH_3CCl_3 because CFC-12 and CFC-11 landfill mixing ratios are significantly higher than those for CFC-113 and CH_3CCl_3 . The magnitude of a 20% variation in CFC-12 is much larger than that for CFC-113, which means that any variation in the CFC-113 and CH_3CCl_3 plant mixing ratios is lost in the noise. In general, it seems that once the gas-to-energy plant begins operation, the month-to-month variability in MPG mixing ratio greatly decreases to the point where only very weak trends can be detected.

3.5 Flare

While the flare data set is too short to do the same type of quantitative analysis as was done for the plant data set, there are a few interesting differences between the two data sets. From Figures 3-3 and 3-4 it appears that CFC-11 and CH_3CCl_3 strongly correlate during July - October 2005, while CFC-12 and CFC-113 exhibit very different behaviors. This is in contrast to the plant data set where all four MPGs exhibit much more similarity in their time series.

The strong correlation between CFC-11 and CH_3CCl_3 and lack of correlation between CFC-12 and CFC-113 is consistent with the idea that the gas recovery technology has less of a dominant effect on mixing ratios and generation rates in the case of the flare than for the gas-to-energy plant. Figure 3-8 shows an extended time series of landfill pipe flow. The gas flow to the flare has a regular seasonal cycle where it is high in the fall and low in the spring. For 2005, the maximum, average, and minimum flow rates are $4.45\text{E}5$, $3.69\text{E}5$, $3.06\text{E}5$ and normal $\text{m}^3 \text{day}^{-1}$, respectively. This closely approximates a normal distribution. On the other hand, the gas flow to the plant is much more like a maximum extreme distribution, where the flow rate is heavily skewed towards the maximum value of the distribution with a few low outliers. For 2006, the maximum, average, and minimum flow rates are $4.93\text{E}5$, $4.14\text{E}5$, and $2.31\text{E}5$ normal $\text{m}^3 \text{day}^{-1}$, respectively. The difference between the flow to the flare and plant, as observed from the many US and UK landfills visited for this thesis, is caused by the system management. Gas-to-energy plants have full time operators who optimize

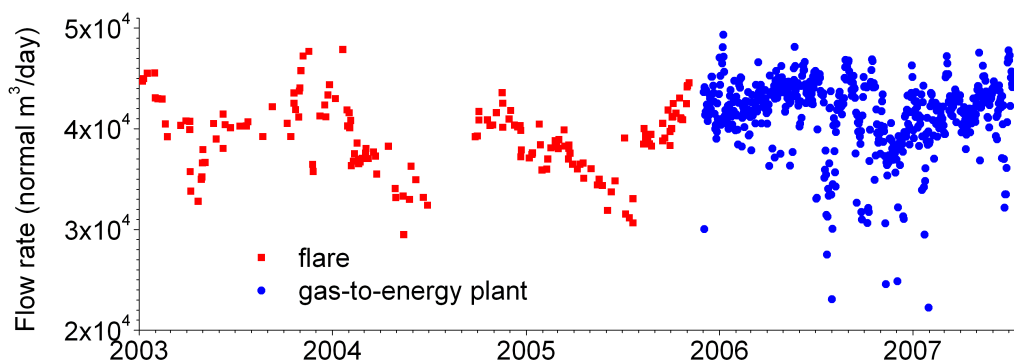


Figure 3-8: Pipe flow recorded at Crapo Hill landfill from 2003 - 2007 standardized to 0°C and 1 atm. The flow rate shown is for the total pipe flow (gas flow to the flare and plant). The majority of the days with both technologies in operation occurs in December 2005. The gas recovery technology receiving > 65% of the flow is marked by either a red square (flare) or blue circle (plant). The year on the x-axis marks January 1.

the flow 24 hours a day to pull as much bulk landfill gas as possible without pulling in outside air. Flare flow rates are generally optimized once every few days. Judging from Figure 3-8, these management practices cause the flare flow rate to more closely approximate the natural gas generation rate under no mechanical forcing.

Both CFC-11 and CH_3CCl_3 mixing ratios correlate strongly with all the ambient temperature parameters used in the previous section. They also correlate with the flow rate, unlike the plant data set where MPG mixing ratios and flow rate showed no relationship. While we can not say whether the seasonal temperature change or the flow rate or both is the cause of the flare MPG variability, we can point out a curious similarity with the expected variability based on microbial degradation rates. Microbial degradation of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 has been observed in simulated landfill conditions in several studies (*Denovan and Strand, 1992; Deipser and Stegmann, 1997; Scheutz et al., 2003; Balsiger et al., 2005; Scheutz and Kjeldsen, 2005; Scheutz et al., 2007*). Under anaerobic conditions, *Balsiger et al. (2005)* and *Scheutz et al. (2007)* found the metabolism rate of CFCs to follow the sequence: CFC-11 > CFC-113 > CFC-12. CFC-12 has been reported to metabolize 10 - 100 times slower than CFC-11 in anaerobic environments (*Denovan and Strand, 1992; Oster et al., 1996; Deipser and Stegmann, 1997; Scheutz et al., 2007*). *Deipser and Stegmann (1997)* reported CH_3CCl_3 and CFC-11 to be more easily degradable than

CFC-12 and CFC-113 under anaerobic conditions. Because biological degradation is temperature dependent, we might expect CH_3CCl_3 and CFC-11 to be the most easily degradable and thus show the most seasonal variability; CFC-113 to show a less obvious correlation with temperature; and CFC-12 to show the most random variation. The flare time series follows this trend. The increased flow, during the period of the flare measurements, may have further amplified the microbial effect by allowing the bacteria less time to act on the generated MPG, which would decrease preferential degradation of CFC-11 and CH_3CCl_3 .

3.6 Methane

For CH_4 , the variability in the mixing ratio and generation rates must be analyzed separately. Variability in the CH_4 generation rates is closely tied to the flow rate variability. The Pearson R^2 value for the correlation of CH_4 generation rate with flow rate (not shown) is 0.89. The monthly samples analyzed on the GC-FID and shown in Figures 3-3 and 3-4 are capable of capturing this strong correlation between CH_4 generation rates and flow rates. However, to see how the generation rates differ between the flare and gas-to-energy plant, we need to look at the higher frequency flow rate data in Figure 3-8 which closely approximates the CH_4 generation rates. We can discern a seasonal effect in the plant time series, but it is less pronounced than that for the flare time series. The same is true of the CH_4 generation rates (higher frequency data not shown).

The mixing ratios suggest a different story. The CH_4 flare mixing ratios are relatively constant. Then, when the plant begins operation, the mixing ratios drop quickly, but rise steadily over 2006 until reaching the 2005 flare mixing ratios (see Figure 3-3). This is the opposite response which the MPG mixing ratios exhibited at the beginning of the plant operation. What appears to have happened is the methanogenic bacteria reoptimized their CH_4 production within the landfill. When the technology switched from the flare to a gas-to-energy plant, the pump which pulls the bulk landfill gas also switched location from one side of the landfill to the other (see Figure 3-2). Most likely the new location of the pump also changed the distribution of vacuum pressure on the underground pipe system. It is interesting to note that for the biologically active gas, i.e. CH_4 , the landfill gas mixing ratios rebound to the flare mixing ratios which we observe at the beginning of the study. For the MPGs, a similar return to starting mixing ratios does not occur.

The only significant correlations, which CH_4 has with the MPGs, are between the

flare CH_4 , CFC-11, and CH_3CCl_3 generation rates, because they all correlate with flow rate. This is similar to what was observed by *Allen et al.* (1997). They measured total halogenated compounds and CH_4 monthly over a 15 month period at one gas well within a landfill with a gas-to-energy plant. It is important to emphasize that their study was at one gas well, which is more likely to approximate the seasonal variability and flow rate changes which we see in the flare data set. They found that the mixing ratio of CH_4 and total halogenated compounds were directly related, which they attributed to changes in the flow rate at their sample well.

3.7 Conclusions

Returning to the questions posed at the beginning of the chapter, Tables 3.3 and 3.4 summarize the mixing ratio and generation rate variability for the study period. The measurements are divided into three time periods: 1) before the plant was installed and only the flare was operating (July - November 2005), 2) from the time the plant was installed to the end of the study (December 2005 - December 2006), and 3) from the time the landfill gas system reached an equilibrium after plant installation until the end of the study (May - December 2006).

CH_4 mixing ratios have a percent standard deviation (mean \div standard deviation \times 100) of $\sim 3\%$ regardless of the gas technology. MPG mixing ratios vary between 12% - 44% depending on the compound and gas recovery technology. Except for CFC-12, which does not have a flare trend, there is less variability in MPG mixing ratios with the plant as the main operating gas capture technology compared to the flare. This is especially true for CFC-11 and CH_3CCl_3 which do have a large flare trend. All of the mixing ratios vary by far less than 100%, which means that single samples taken once during a year would be reasonably good estimators of annual mixing ratio averages.

Because CFC-12, CFC-11, CFC-113, and CH_3CCl_3 mixing ratios are effectively constant from May - December 2006, we can estimate concentration ratios. The ratios for landfill gas at Crapo Hill are 85:14:5:1 for CFC-12:CFC-11: CH_3CCl_3 :CFC-113 with a gas-to-energy plant installed. In other words, CFC-12 is 6x more concentrated than CFC-11, 17.5x more concentrated than CH_3CCl_3 , and 85x more concentrated than CFC-113 in the landfill gas flowing to the plant.

Variability in plant MPG generation rates is mostly controlled by variability in the mixing ratios with a percent standard deviation between 16% - 34% for the May - December 2006 time period. This is a $\sim 4\%$ increase in variability compared to MPG

mixing ratios. During the same time period, the variability in the CH₄ generation rates is heavily dependent on the flow rate which means that CH₄ generation rates increase 7% over CH₄ mixing ratios. For the flare time series, the generation rate variability of all three compounds which correlated with flow rate, namely CFC-11, CH₃CCl₃, and CH₄, increase 7-8% over their mixing ratio variability.

In summary, the flare seems to exhibit a large seasonal effect for CFC-11 and CH₃CCl₃, but not for CFC-12 and CFC-113. This effect is tied to the increase in bulk gas flow rate in the late summer. The strong MPG trend seen at the beginning of the plant data set is mostly due to an adjustment phase within the landfill as the gas recovery technology switched from a flare to gas-to-energy plant. Once the gas system re-adjusts (production = outflow), the MPG mixing ratios become effectively constant with a very slight attributable seasonal effect. The seasonal effect is so small, that it can be considered negligible. The variability in the MPG generation rate is closely tied to the variability in mixing ratios. CH₄ mixing ratios are almost constant for the entire time period of the study, while CH₄ generation rates show some seasonal effects throughout the study period. Variability in the CH₄ generation rate is closely tied to variability in the flow rate.

Table 3.3: Summary of Mixing Ratios for the One Landfill Study^a

	Maximum	Minimum	Mean	Std dev	% Std dev	N
Flare [July - November 2005]^b						
CFC-12	1171	737	944	155	16%	6
CFC-11	341	105	258	84	33%	6
CFC-113	25	9	18	5	30%	6
CH ₃ CCl ₃	132	33	86	38	44%	6
CH ₄ (flare) ^f	59	53	57	1	2%	31
Gas-to-energy plant [December 2005 - December 2006]^c						
CFC-12	1150	544	761	176	23%	13
CFC-11	260	71	143	55	39%	13
CFC-113	16	6	10	3	32%	12
CH ₃ CCl ₃	92	33	48	17	35%	13
CH ₄ (MIT) ^e	57.4	52.0	54.9	1.7	3.1%	13
CH ₄ (plant) ^f	61	48	54	2	4%	365
Gas-to-energy plant [May - December 2006]^d						
CFC-12	899	544	682	128	19%	8
CFC-11	178	71	115	35	30%	8
CFC-113	12	6	8	2	23%	7
CH ₃ CCl ₃	45	33	39	5	12%	8
CH ₄ (MIT) ^e	57.4	53.0	55.5	1.5	2.8%	8
CH ₄ (plant) ^f	61	51	55	2	3%	241

^aUnits are ppb for CFC-12, CFC-11, CFC-113 and CH₃CCl₃ and % of total gas stream for CH₄. Std dev = Standard deviation, % Std dev = standard deviation ÷ mean × 100, N = number of data points used for each statistic

^bIncludes measurements from July 6 - November 5, 2005.

^cIncludes measurements from December 22, 2005 - December 16, 2006 including a period until May 2006 which was heavily influenced by the change in gas recovery technology from the flare to the gas-to-energy plant.

^dIncluded measurements from May 5 - December 16, 2006 which is the period most likely to approximate normal operation conditions (e.g. no new installation, no special maintenance, etc.)

^eCH₄ (MIT) refers to the gas samples analyzed at MIT.

^fCH₄ (flare) or (plant) refers to the in-situ monitoring done at the landfill.

Table 3.4: Summary of Generation Rates for the One Landfill Study^a

	Maximum	Minimum	Mean	Std dev	% Std dev	N
Flare [July - November 2005]^b						
CFC-12	230	120	200	40.	20.%	6
CFC-11	90.	20.	62	25	40%	6
CFC-113	8.4	2.2	5.9	2.1	35%	6
CH ₃ CCl ₃	34	6.1	20.	11	52%	6
CH ₄ (flare) ^c	1.8E7	1.2E7	1.6E7	1.5E6	9.8%	31
Gas-to-energy plant [December 2005 - December 2006]^c						
CFC-12	250	100	160	43	26%	13
CFC-11	64	16	35	14	40%	13
CFC-113	5.4	1.7	3.2	1.2	36%	12
CH ₃ CCl ₃	22	7.1	11	4.2	37%	13
CH ₄ (MIT) ^f	1.8E7	1.3E7	1.6E7	1.2E6	7.8%	13
Gas-to-energy plant [May - December 2006]^d						
CFC-12	190	100	140	33	23%	8
CFC-11	43	16	28	9.4	34%	8
CFC-113	4.5	1.7	2.7	0.89	33%	7
CH ₃ CCl ₃	11	7.1	9.2	1.5	16%	8
CH ₄ (MIT) ^f	1.8E7	1.3E7	1.6E7	1.5E6	9.8%	8

^aCFC-12, CFC-11, CFC-113, CH₃CCl₃, and CH₄ generation rates in g y⁻¹. All descriptive statistics are rounded to two significant digits. Std dev = Standard deviation, % Std dev = standard deviation ÷ mean × 100, N = number of data points used for each statistic

^bIncludes measurements from July 6 - November 5, 2005.

^cIncludes measurements from December 22, 2005 - December 16, 2006 including a period until May 2006 which was heavily influenced by the change in gas recovery technology from the flare to the gas-to-energy plant.

^dIncluded measurements from May 5 - December 16, 2006 which is the period most likely to approximate normal operation conditions (e.g. no new installation, no special maintenance, etc.)

^eCH₄ (flare) refers to the in-situ monitoring done at the landfill.

^fCH₄ (MIT) refers to the gas samples analyzed at MIT.

Chapter 4

The Multi-landfill Study: Emission Estimates

This chapter describes the emission estimates of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 (called Montreal Protocol-restricted gases or MPGs) from municipal solid waste (MSW) landfills in the US and UK which are the major goal of this thesis. It is a synthesis of the ideas regarding variability from Chapter 3 and a new data set consisting of measurements from many different landfills in the US and UK. The initial focus of this chapter is on finding a suitable methodology for these new measurements to provide accurate estimates of total MSW landfill emissions of MPGs for the US and UK. Once the methodology is chosen and discussed, the focus moves to the resulting estimates. By comparing the estimates of MPG landfill emissions to total MPG emission estimates from all sources in the US and UK, it is possible to test the hypothesis, that

1. Landfill emissions account for a significant fraction of the lingering MPG emissions observed in industrialized countries.

Lastly, sensitivity studies are presented testing the robustness of the MPG landfill estimates to the assumptions of the methodology.

4.1 Regression Methodology

The approach used in this thesis for estimating emissions of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 from US and UK MSW landfills involves relating MPG generation rates from individual landfills to a national scaling parameter. The national scaling

parameter is used to create linear regressions with the data from the Multi-landfill Study. These regressions are then combined with national estimates of the scaling parameter to calculate estimates of landfill MPG emissions in the US and UK.

The national parameter fulfills several criteria in order to be useful for the estimates. Most importantly, it has a linear relationship with the MPG measurements from the US and UK landfills. It is either estimated annually, preferably by a national statistics agency, or is in a national database which is frequently updated and preferably audited. If the national parameter is estimated, rather than measured directly, the methodology is published and accessible. Error reporting either by the agency itself or in the published literature is a bonus. The best parameter is one which can relate generation rates of MPGs to an emission rate. Not all generated landfill gas is emitted to the atmosphere, especially at landfills with gas recovery systems. Although it would still be possible to estimate total US or UK landfill emissions of MPGs from generation rates, this would lead to an overestimate of MPG emissions from landfills.

The national scaling parameter chosen for this thesis and described in this chapter is annual CH_4 emissions from landfills. It has all the necessary and desirable criteria. The ratio of MPG generation rates to CH_4 generation rates can be approximated as linear. In the US and UK, annual estimates with error analyses are provided by national statistical agencies to fulfill both countries' commitment to the United Nations Framework Convention on Climate Change (UNFCCC). The reporting agencies in both countries already include an estimate of the amount of recovered CH_4 , allowing the conversion from generated MPGs to emitted MPGs, as well as publish their estimate methodologies.

Several other parameters were considered such as total and annual landfilled waste, landfill age, megawatt capacity of gas-to-energy plants at each landfill, and total landfill surface area. Estimates made using landfilled waste are discussed at the end of the chapter. Their major disadvantage is that they do not allow the conversion from generation rates to emission rates. Landfill age does not have a linear relationship with MPG generation rates and it is reported in an unaudited database (*EPA*, 2007c). It is possible that landfill age might be useful as a secondary parameter in a multiple linear regression, but the small sample size for this thesis does not support anything more complicated than using a single linear relationship for the emission estimates. Megawatt capacity is also reported in the same unaudited database as landfill age. There is no annual estimate of total landfill surface area.

The regression method used in this chapter is weighted linear least squares. χ^2 is

minimized according to the following equation

$$\chi^2 = \sum_{i=1}^N \omega_i [y_i - (a + bx_i)]^2 \quad (4.1)$$

where ω = weighting term, a = y-intercept, and b = slope. The 95% confidence interval around the mean is calculated by $s_e \times t$ -value (0.975, DOF) where s_e = standard error of the mean and DOF = degrees of freedom. Linear least squares only takes into account error on the y-axis, which in the case of the regressions is error in generated MPG. We will use this technique instead of another, such as orthogonal distance regression, which incorporates error in both X and Y, because the purpose of the regressions is the prediction of Y (MPG emissions) given X (CH₄ emissions). Linear least squares is considered the most appropriate even if its assumptions are violated if the goal is the prediction of a dependent variable (Y) given an independent variable (X) (*Isobe et al.*, 1990). It is not a symmetrical technique, so that regressing X against Y will give a different relationship than if Y is regressed against X.

The total approach used to produce the national MPG estimates of landfill emissions is named the “Methane Regression Method”. The method assumes that generated MPG and generated CH₄ are linearly related because the total mass of landfilled waste is proportional both to the amount of landfilled waste containing MPGs and to the amount of CH₄ generated from anaerobic metabolism. Moreover, it assumes that the relationship between generated MPG and generated CH₄ is the same as the relationship between emitted MPG and emitted CH₄. The impacts, which all of the major assumptions are expected to have on the final estimates, are discussed in Section 4.7.

4.2 Experimental Methods

4.2.1 Study Sites

The sample sites consisted of seven US and nine UK actively managed municipal solid waste (MSW) landfills. A summary of the types of landfills sampled is shown in Table 4.1. The UK sites all belong to one landfill company, Viridor Waste Management, while the US sites are partly municipal and partly privately owned landfills. The UK sites are scattered throughout the UK and the US sites are all in Massachusetts.

Efforts were made to sample a representative cross section of US and UK landfills. The most important parameters affecting the sample representativeness are age, size,

Table 4.1: Summary of Sample Sites in the US and UK

Country	Total	Corporate ^a	Municipal ^a	Open ^a	Closed ^a
US	7	3	4	5	2
UK	9	9	0	7	2

^aSee Box 1.1 for definitions

type of waste accepted, gas collection system/engineering design, and climate. In order to narrow the study already we sampled only actively managed MSW landfills. For the US, practical concerns dictated that the sample sites be within a day's drive of Boston. The UK sites had to belong to Viridor, since this was the only landfill access we had in the UK.

This left only age and size which needed to be considered when selecting sample sites. The distribution of sampled US and UK landfills with respect to US landfills with operational gas-to-energy projects are indicated by black and red arrows in Figure 4-1, respectively. The US Landfill Methane Outreach Program (LMOP) maintains a database of all operational, potential, and shutdown gas-to-energy projects at landfills in the US (*EPA, 2007c*). Duplicate entries in the Landfill Methane Outreach Program database were deleted. Landfills with operational projects account for $\sim 25\%$ of total open landfills in the US using 1654 for the total number of open landfills (*Simmonds et al., 2006*). The intention was to sample a cross-section of small, medium, and large landfills covering a range of ages. On average, the sampled US landfills are older and smaller than the national average, because Massachusetts landfills are older and smaller than the national average. The sampled UK landfills are better at covering the range of sizes, but are younger than the US landfills. A sensitivity study discussing possible effects of these data biases can be found in Section 4.7

4.2.2 Data Collection

US Data

For the 7 US landfills, the data collected, which is used directly for the analysis in this chapter, included: whole landfill CFC-12, CFC-11, CFC-113, CH_3CCl_3 , and CH_4 mixing ratios; instantaneous pipe flow rates; and annual landfilled tons of MSW, commercial and demolition waste, industrial waste, recycling residue, sludge, ash, other (non-MSW), department of public works waste, and special waste for each landfill.

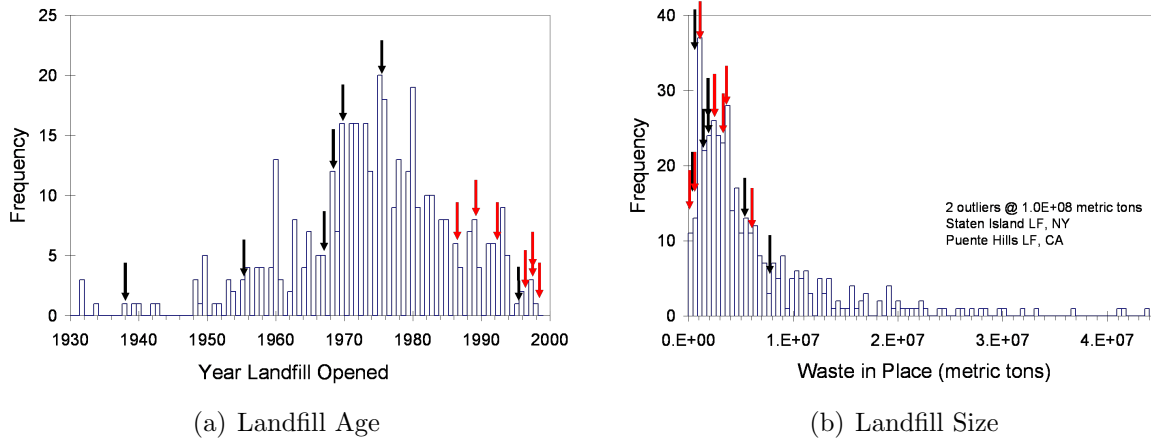


Figure 4-1: Relative age and size of sampled landfills in US (black arrows) and UK (red arrows) compared to all of the landfills in the US with operational gas-to-energy projects (*EPA, 2007c*). Similar data for all UK landfills was not available.

Qualitative informational surveys were also conducted at each landfill site. Questions included total capped and uncapped acres, number of wells installed, estimated percentage of gas capture, yearly CH_4 production, number of reciprocating engines and flares, megawatts of energy generated, percentage of landfill which is lined, etc.

The gas samples were collected and analyzed the same way as for the One Landfill Study in Chapter 3. The details are described in Section 2.3.

Six of the seven Massachusetts sites have gas-to-energy plants. All of the gas-to-energy plants have reciprocating engines, all with either the exact same technology as used for Crapo Hill (4 Caterpillar engines) or slightly older versions. For these sites, the instantaneous flow rates were obtained from the plant operators. These flow rates are considered to be as accurate as current technology allows. The same technology to measure pipe flow rates as used at Crapo Hill was used at the other five sampled Massachusetts landfills with gas-to-energy plants (see Section 2.2).

One Massachusetts landfill only has a flare. The instantaneous flow rate at this site was measured with a Dwyer 166 T Telescoping Pitot Tube (Dwyer Instruments Inc, Michigan City, IN) combined with a Dwyer 477A-1 Handheld Digital Manometer (scale 0"-20" water column, accuracy is 0.1% full scale). The accuracy of the pitot tube was checked against the in-situ Crapo Hill orifice plate. The two flow rate measurements were within 4% of one another.

The instantaneous flow rates were converted from standard cubic feet per minute (1 atm and 20°C) to normal meters cubed per day (1 atm and 0°C) by assuming that the instantaneous pipe flow rates were the same over the whole day. Because all the

measurements were taken at the same time of day, this should have a very minimal effect on the emission calculations.

Data on the annual landfilled tons of waste from 1994 - 2005 for each Massachusetts landfill was provided by Brian Holdridge at the Massachusetts Department of Environmental Protection (MA DEP), Bureau of Waste Prevention, Division of Planning and Evaluation. The MA DEP maintains a large publicly available database on waste statistics which is updated annually through mandatory reporting by the individual landfills.

UK Data

The UK data collection was considerably different than for the US. All of the data for the 9 UK landfills was obtained from Stuart James at Viridor Waste Management. The data obtained, which is used directly for the analysis in this chapter, included: whole landfill CFC-12, CFC-11, and CH₄ mixing ratios; annual average pipe flow rates; and annual landfilled tons of industrial/commercial waste, domestic waste, difficult waste, contaminated soils, and sludge. Additional qualitative data obtained included information on the percentage and type of cap on each landfill section, total landfill area, number of engines and flares, megawatts of energy generated, and landfill liner.

Although the gas mixing ratios were not sampled by me personally, the sampling and analysis methodologies used standard techniques and are well documented. The details are described in Section 2.3.

Viridor supplied the pipe flow rates and waste information. The flow rates were given in units of normal meters cubed per year (1 atm and 0°C). Viridor does not measure daily flow rates, but rather uses a model to calculate annual emissions based on landfill size, depth, age of waste, type of waste in landfill, etc.

4.2.3 Data Corrections Based on the One Landfill Study

It was necessary to standardize the US and UK data sets by calculating 2006 annual averages of mixing ratios and flow rates for each landfill. Table 4.2 lists the data collected from each country. Since the US field sampling was done during late 2006, average annual generation rates were calculated for 2006. The data which needed to be corrected for seasonal bias, according to the One Landfill Study, were flow rates for the US and CFC-11 and CH₃CCl₃ flare mixing ratios, which affected only one US landfill. To correct the US flow rates and CFC-11 and CH₃CCl₃ mixing ratios, flow

rates were averaged in the Crapo Hill data set for 10 days before and after the sample date of the flow rate to be corrected. The ratio between the 21 days and the annual average for flow rate in the Crapo Hill data set was then applied to the data set to be corrected. For the CFC-11 and CH_3CCl_3 flare mixing ratios, this exploited the correlation between flare mixing ratios and flow rate. No UK landfills were corrected for seasonal sampling biases, because all of the UK landfills have gas-to-energy plants.

The flow rate and CH_4 mixing ratios were non-normal distributions in the One Landfill Study. For this reason, we used a Monte Carlo approach to calculate a mean generation rate and standard deviation for each landfill. 10,000 Monte Carlo simulations were run using Crystal Ball 7.3.1. Each data point was assigned a probability density function (pdf) based on the One Landfill Study. Flow rate had a maximum extreme distribution (input parameters: maximum likely value, scale = $\sqrt{6\frac{s^2}{\pi}}$), CH_4 mixing ratio had a beta distribution (input parameters: minimum = $\bar{x} + 6.35$, maximum = $\bar{x} - 6.35$, beta = 4, alpha = 4), and all MPG mixing ratios had normal distributions (input parameters: \bar{x} , s) where \bar{x} = mean and s = standard deviation of the mean. The maximum likely value was corrected for sampling bias as described previously. The standard deviation was scaled by the mean or maximum likely value for MPG mixing ratio and flow rate, respectively. The exact distribution from the One Landfill Study was used for Crapo Hill. Using non-normal pdfs and the Monte Carlo approach over simple multiplication of mass concentration (converted from mixing ratio) and pipe flow rate increased the calculated generation rates by $5\% \pm 1\%$.

4.3 Regressions

The first step of the Methane Regression Method was to regress generated MPG vs. generated CH_4 from the sample landfill sites. The US and UK scatter plots are shown in Figures 4-2 - 4-6. Generated MPG is plotted against generated CH_4 for both open and closed landfills. The scatter plots present all the data from the Multi-landfill Study. For CFC-12 and CFC-11 there is data from both the US and UK, but for CFC-113 and CH_3CCl_3 the only data is from the US sample sites. Ideally, both the US and UK CFC-12 and CFC-11 data sets would have similar MPG to CH_4 generation ratios. This would double the number of data points for the regressions. However, as presented in Figure 4-2, the sampled US landfills emit statistically significantly less CFC-12 per unit mass of CH_4 than the UK landfills.

There could be three reasons for the different CFC-12/CFC-11 vs. CH_4 ratio

Table 4.2: Type of Data Available for Calculating Average Annual 2006 CH₄ and MPG Emissions

Data Type ^a	Flow Rate	MPG mixing ratio ^b	CH ₄ mixing ratio
UK			
No. of points	annual average	1-2 values/landfill	1-2 values/landfill
Year	2006	2004, 2006, 2007	2004, 2006, 2007
US except Crapo Hill			
No. of points	1-2 samples/landfill	1-2 samples/landfill	1-2 samples/landfill
Year	Fall 2006	Fall 2006	Fall 2006
Crapo Hill			
No. of points	daily averages	monthly samples	daily averages
Year	2006	2006	2006

^aNo. of points refers to the type and number of samples taken at each landfill. Year refers to the year when the samples were collected.

^bMPG mixing ratio refers to CFC-12, CFC-11, CFC-113, and CH₃CCl₃ mixing ratios for the US data including Crapo Hill, but refers only to CFC-12 and CFC-11 mixing ratios for the UK.

observed between the US and UK data sets: 1) UK landfills release CFC-12/CFC-11 faster than US landfills due to age, climate, engineering design, etc.; 2) the US and UK waste have different CFC-12/CFC-11 content; and/or 3) there is a bias in the measurements. We can get an idea of whether we would expect the UK to have a higher generation rate of CFC-12 by using estimates of total emissions of CFC-12 and landfill emissions of CH₄ for the US and UK. Landfill emissions of CH₄ per person in 2005 were 2.12×10^4 g in the US (EPA, 2007a; U.S. Census Bureau, 2007) and 1.54×10^4 g for the UK (Jackson et al., 2007; ONS, 2007). Total CFC-12 emissions were ~ 50 g and ~ 8 g per person in 2005 for the US and UK, respectively (Li et al., 2005; Hurst et al., 2006; Manning, 2007; U.S. Census Bureau, 2007; ONS, 2007). If anything, this indicates that more CFC-12 should be generated per unit mass of CH₄ from landfills in the US. Further analysis of the difference between the generation rates for the two countries is beyond the scope of this Ph.D. Either there is an interesting phenomenon waiting to be studied or there is a measurement bias. Measurement bias is always a possibility, especially because the US and UK measurements in this study use different sampling techniques (see Section 4.2). However, the amount of measurement bias needed to produce the large difference between the US and UK CFC-12/CH₄ and CFC-11/CH₄ generation ratios observed in this study seems highly

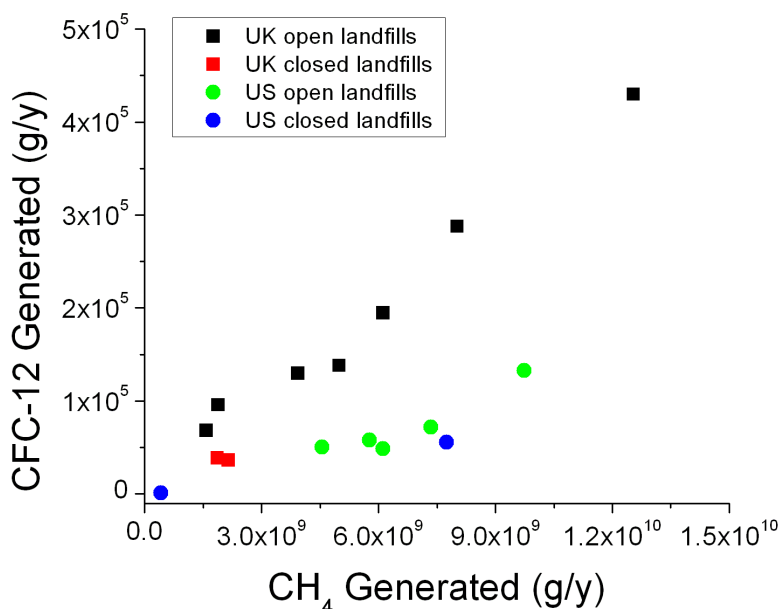
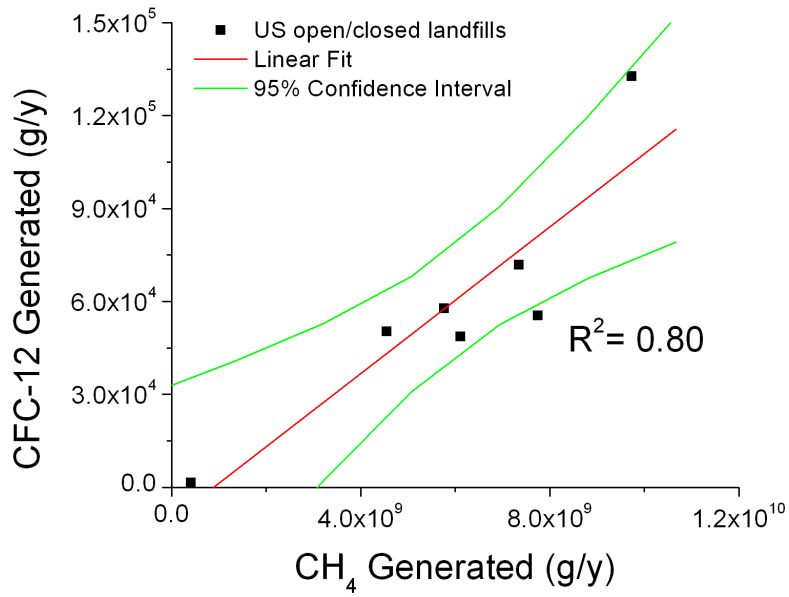


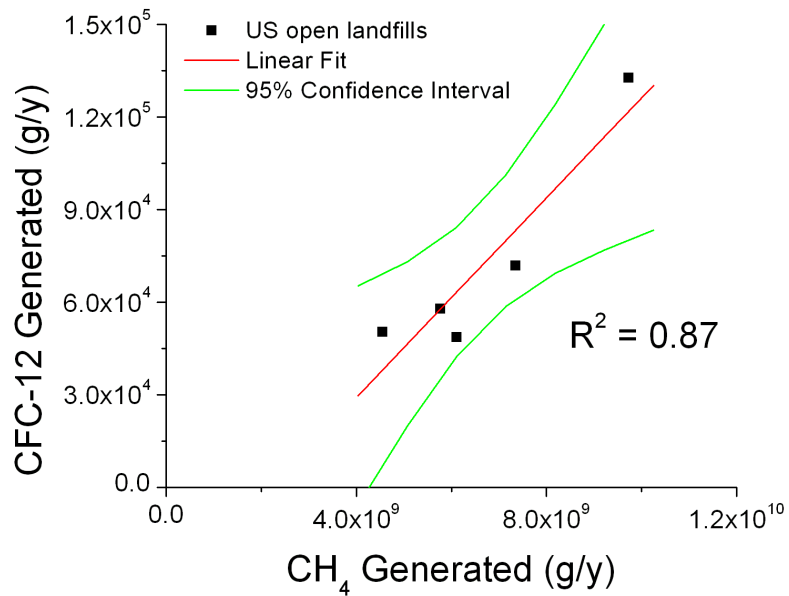
Figure 4-2: Open and closed US/UK municipal solid waste (MSW) landfills

unlikely. The possible effect of measurement bias on the estimates is discussed in Section 4.7. For the following analysis, the US and UK data sets are separated. Each are used to provide quantitative estimates for their respective countries only.

The regressions are presented in Figures 4-3 - 4-7. For CFC-11, one open landfill from the US data was removed from the analysis because it had CFC-11 mixing ratios $> 3\sigma$ (standard deviation) above the mean for the other landfills. The regressions are separated by country and MPG, with the US regressions plotted first. For the compounds where the open and closed landfills have similar generated MPG to generated CH₄ ratios, data from both landfill types is included in the regression to increase the number of data points. US CFC-12, UK CFC-12, and UK CFC-11 all have regressions which include open and closed landfills. For US CFC-12 a second regression is fit using only the open landfills, because one of the closed landfills with generation rates very close to zero may overly influence the combined regression. A second regression using only open landfills is unnecessary for the UK data sets. There is $< 5\%$ difference between emission estimates using only open or open and closed landfills for UK CFC-12. For UK CFC-11, other data not shown in this thesis from industrial landfills confirms that open and closed UK landfills have similar CFC-11 vs. CH₄ generation rates.

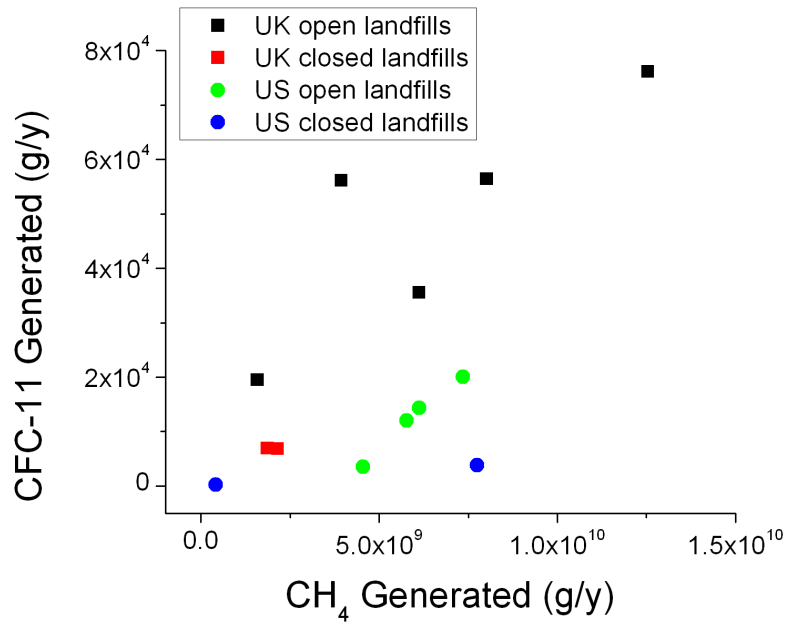


(a) Open and closed US landfills

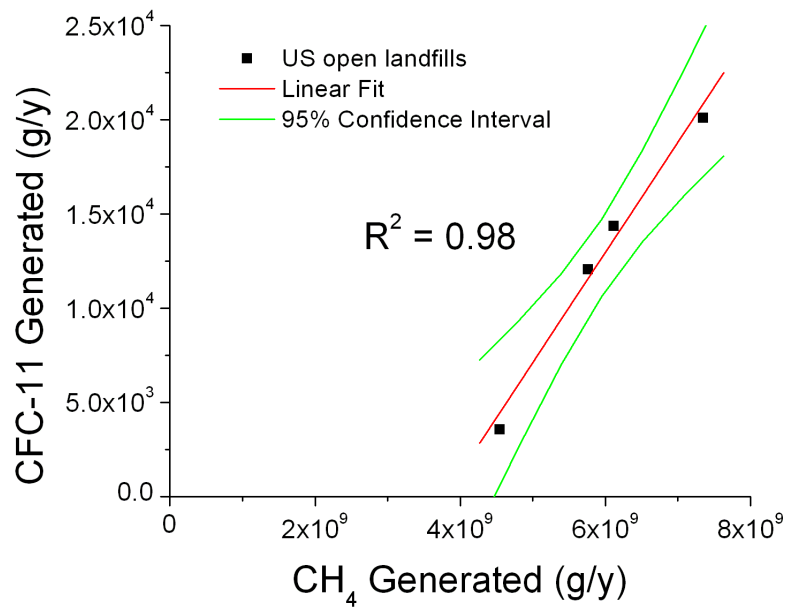


(b) Open US landfills

Figure 4-3: CFC-12 linear regressions for US MSW landfills

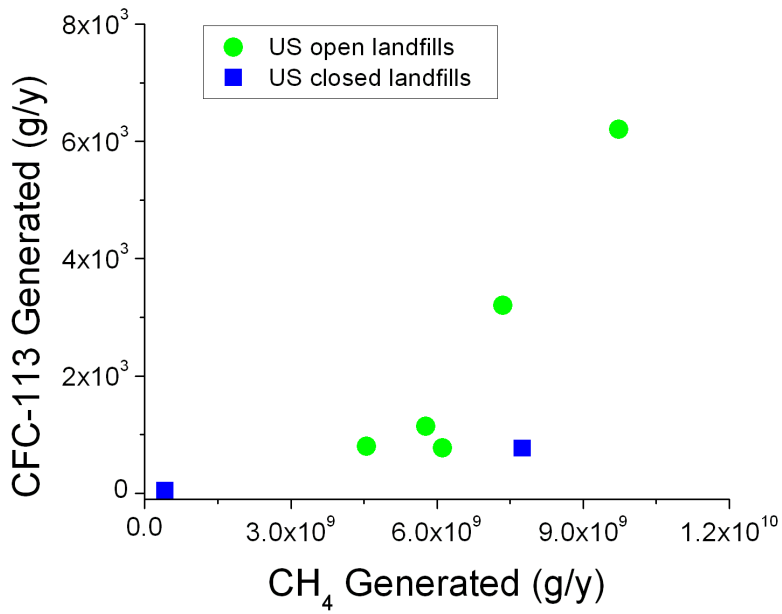


(a) Open and closed US/UK landfills

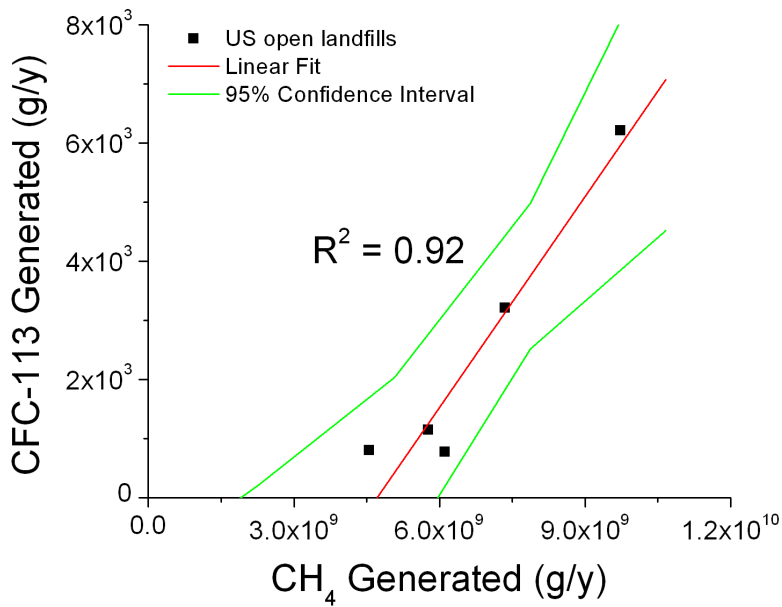


(b) Open US landfills

Figure 4-4: CFC-11 data for US/UK MSW landfills and CFC-11 linear regression for US MSW landfills

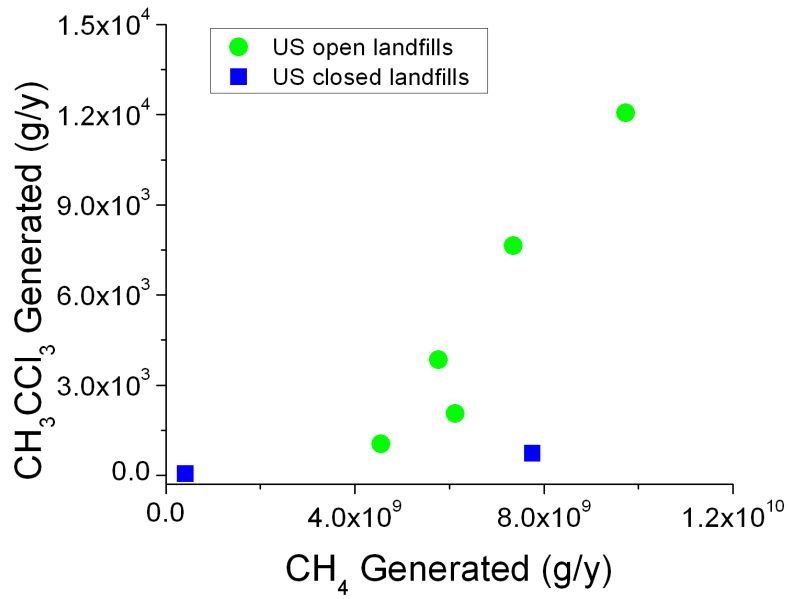


(a) Open and closed US landfills

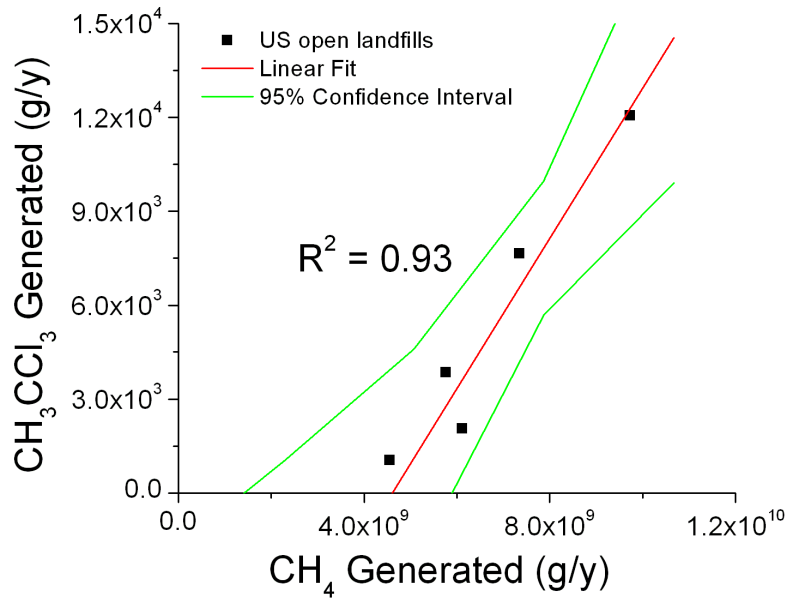


(b) Open US landfills

Figure 4-5: CFC-113 data and CFC-113 linear regression for US MSW landfills

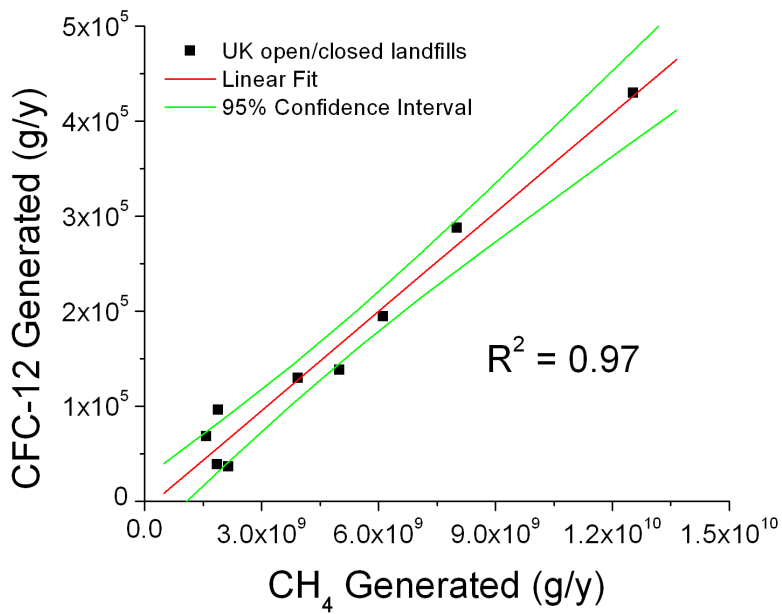


(a) Open and closed US landfills

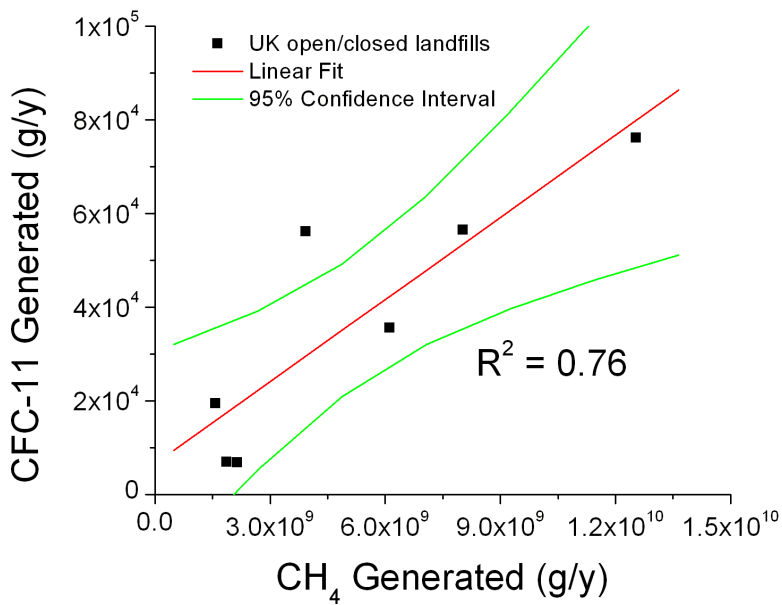


(b) Open US landfills

Figure 4-6: CH₃CCl₃ data and CH₃CCl₃ linear regression for US MSW landfills



(a) Open and closed UK landfills



(b) Open and closed UK landfills

Figure 4-7: CFC-12 and CFC-11 linear regressions for UK MSW landfills

US CFC-11, US CFC-113, and US CH_3CCl_3 do not have similar generated MPG to generated CH_4 ratios for open and closed landfills. Only the open landfills have enough data for a linear regression, so only the open landfills are used to estimate landfill MPG emissions. It would be difficult to incorporate separate regressions for open and closed landfills into one landfill MPG emission estimate. The national CH_4 emission estimates do not distinguish between emissions from open vs. closed landfills, so it would be guess work to attribute the influence to the emissions from both landfill types. We expect that using only open landfills will overestimate the landfill MPG emissions for US CFC-11, CFC-113, and CH_3CCl_3 . It is unclear how large the bias will be. The trend in the US has been towards larger but fewer landfills. Thus, we might expect the open US landfills to also be those landfills with higher CH_4 generation and therefore higher MPG emissions. This would mean open US landfills would dominate the MPG emission estimation. However, the trend has also been towards more gas recovery at US landfills. Thus, we expect open US landfills to also have a higher fraction of the total US gas capture, which would reduce the fraction of emissions from open US landfills. Assuming that all US MSW landfills have the same MPG vs. CH_4 generation ratio, we expect the regression methods used for US CFC-11, CFC-113, and CH_3CCl_3 to overestimate their emissions from US landfills. Section 4.7 provides a discussion of how the estimates would be affected if the US and UK MPG vs. CH_4 generation ratio calculated from the sampled landfills is not the same for all of the US and UK landfills.

4.4 National CH_4 Statistics

In order to estimate emissions of MPGs from US and UK landfills using the regressions in the previous section, we need national estimates of landfill CH_4 emissions. Two national estimates of annual CH_4 emissions from US landfills and one estimate from UK landfills are available. The US estimates include the official UNFCCC estimate from *EPA* (2007a), which follows the most recent IPCC guidelines (*IPCC*, 2007), while the second is from *EIA* (2006a). The biggest difference between the two US estimates is that *EIA* (2007) uses available field studies to calculate emissions from 9.2% of the total waste in place (*Thorneloe et al.*, 1994) and a first order rate model for the rest of the total waste in place (*Augenstein*, 1992). *EPA* (2007a) uses the official IPCC Tier 2 first order decay model exclusively. The UK estimate from *Jackson et al.* (2007) uses an older version of the IPCC Tier 2 first order decay model (*IPCC*, 2000).

All the models calculate landfill CH₄ emissions using a variation on the following basic equation

$$CH_{4(emitted)}(T) = CH_{4(MSW)}(T) + CH_{4(Industrial)}(T) - R(T) - Ox(T) \quad (4.2)$$

where T = year of emissions, CH_{4(MSW)} = methane generated from waste disposal at MSW landfills, CH_{4(Industrial)} = methane generated from waste disposal at industrial landfills, R = recovered methane from flaring or gas-to-energy plants, and Ox = methane oxidized in the soil cover of MSW or industrial landfills. The initial input parameter for all models is annual landfilled waste. Each model then has its own method for calculating the total amount of waste which composts over the year and the rate at which that waste produces CH₄. The IPCC models need two additional input parameters, degradable organic carbon which is the amount of carbon per unit mass of landfilled waste and a decay rate constant which depends on the precipitation rate. In the US, recovered CH₄ is calculated by utilizing existing databases of gas-to-energy projects (*EIA*, 2006b; *EPA*, 2007c) and information provided by flaring equipment vendors (*EPA*, 2007b). In the UK, reports by outside consulting firms have updated the recovery rate estimates (*Gregory et al.*, 2003; *Arnold and Yang*, 2005). For CH₄ oxidation, the IPCC models subtract oxidation after calculating generated CH₄ (oxidation ~ 10% of generation). The EIA model does the oxidation calculation internally.

Equation 4.2 estimates total CH₄ emissions from both industrial and MSW landfills. While the goal of this thesis was the estimation of MPG emissions from MSW and not from industrial landfills, industrial landfill CH₄ emissions were not subtracted from the national CH₄ estimates for several reasons. First, generated CH₄ from industrial landfills are only 7% of the generated CH₄ from MSW landfills. Second, *EPA* (2007a) is the only one of the three estimates which reports CH₄ emissions by categories. These categories list separate contributions from industrial and MSW landfill CH₄ generation and oxidation, but a combined number for gas recovery, which makes it difficult to accurately subtract the contribution to landfill CH₄ emissions from industrial landfills. Generated CH₄ from industrial landfills as a percentage of the total generated landfill CH₄ is ~ 7%. The sensitivity of the MPG estimates to calculation errors such as 7% due to the inclusion of industrial CH₄ emissions is discussed in Section 4.7.

2006 best estimates and maximum estimates for US and UK landfill CH₄ emissions are listed in Table 4.3. The best estimates account for CH₄ oxidation and gas recovery.

Table 4.3: 2006 US and UK National Estimates of CH₄ Emissions from Landfills^a

	Country	(2006)	Upper CI	Lower CI
2006 CH₄ Emissions (Best Estimates)				
<i>EPA (2007a)</i> ^b	US	6341	+ 32%	- 39%
<i>EIA (2006a)</i> ^c	US	6866	+ 33.7%	- 2.6%
<i>Jackson et al. (2007)</i> ^d	UK	933	+ 20.5%	- 20.5%
2006 CH₄ Emissions (Maximum Estimates)				
<i>EPA (2007a)</i> ^e	US	12776	+ 32%	- 39%
<i>Gregory et al. (2003)</i> ^f	UK	3332	n/a	n/a

^a2006 CH₄ emissions (best estimates and maximum estimates) are in Gg y⁻¹, while confidence intervals (CI) are in %. n/a = not available.

^b2005 estimate of CH₄ landfill emissions from *EPA (2007a)* linearly extrapolated to 2006 based on a 2006 US population of 299,398,484 (*U.S. Census Bureau, 2007*). The 2006 estimate represents a 0.975% increase over the 2005 estimate. The upper and lower confidence intervals (CI) are the 95% confidence intervals of the *EPA (2007a)* 2005 US landfill emission estimate.

^c2005 estimate of CH₄ landfill emissions from *EIA (2006a)* linearly extrapolated to 2006 based on a 2006 US population of 299,398,484 (*U.S. Census Bureau, 2007*). The 2006 estimate represents a 0.975% increase over the 2005 estimate. The upper and lower confidence intervals are the 95% confidence interval of the *EIA (2007)* 1999 US CH₄ emission estimate from all sources, not just landfills.

^d2005 estimate of CH₄ landfill emissions from *Jackson et al. (2007)* linearly extrapolated to 2006 based on a 2006 UK population of 60,587,000 (*ONS, 2007*). The 2006 estimates represent a 0.579% increase over the 2005 estimates. The upper and lower confidence intervals are those reported for the *Jackson et al. (2007)* 2005 UK CH₄ emission estimate from all sources, not just landfills, and are equal to $\pm 2 \times (\text{standard deviation}) / \text{mean} \%$ ($\sim 95\%$ confidence interval).

^e2005 *EPA (2007a)* estimate of potential US CH₄ landfill emissions, which does not account for either oxidation or gas recovery, linearly extrapolated to 2006 based on a 2006 US population of 299,398,484 (*U.S. Census Bureau, 2007*). The upper and lower confidence intervals are the 95% confidence interval of the *EPA (2007a)* 2005 US landfill emission estimate.

^fCalculated by assuming the *Jackson et al. (2007)* CH₄ best estimate is 28% of potential UK CH₄ emissions (*Gregory et al., 2003*). See text for an explanation. Confidence intervals were not available.

The US maximum estimate from *EPA* (2007a) is annual generated CH_4 , which is the amount of CH_4 which would be released if no oxidation or gas recovery occurred. *EPA* (2007a) is the only one of the three best estimates in Table 4.3 to provide a potential emissions calculation in their annual estimate. The UK maximum estimate is calculated from projections made by *Gregory et al.* (2003) that 72% of the landfill gas generated in the UK would be flared or recovered by 2005.

The two US CH_4 estimates in Table 4.3 have a 7.6% difference. This difference is due to the manner in which CH_4 generated from MSW landfills is calculated, since the two US models use similar data sources for calculating total waste landfilled and the same methodology for calculating total CH_4 generated from industrial landfills and CH_4 emissions avoided and recovered (*EIA*, 2007; *EPA*, 2007b).

To compare the US and UK CH_4 estimates, we have to exploit the fact that the the UK model uses the older version of the *EPA* (2007a) model. Assuming both the US and UK have perfect model input data, the method used for the UK best estimate (*IPCC*, 2000) calculates results which are 7% lower than the method used for the *EPA* (2007a) best estimate (*IPCC*, 2007). This is because *IPCC* (2007) corrects an error in the way CH_4 emissions are calculated in the first year after trash is landfilled (See Annex 3A.1 of *IPCC* (2007)). This comparison is true only for perfect data. In reality, each country uses their own method of calculating the model input parameters.

4.5 MPG Emission Estimates

Using the regression equations relating generated MPG to generated CH_4 in Section 4.4, the national estimates of landfill CH_4 emissions in Table 4.3 can be used to calculate US and UK estimates of CFC-12, CFC-11, CFC-113, and CH_3CCl_3 landfill emissions. Table 4.4 summarizes the US MPG landfill emission estimates for each regression method with their mean and 95% confidence intervals using the three US CH_4 landfill emission estimates described in Table 4.3. US Best Estimates 1 and 2 take into account gas recovery and CH_4 oxidation. The US Maximum Estimate represents the total possible MPG landfill emissions using the Methane Regression Method if all landfill gas generated in landfills were emitted to the atmosphere. Estimates of the landfill emissions as a percentage of total US emissions is also shown. The studies used for total MPG emissions for the US and UK are discussed in Section 4.6.

The two US CFC-12 regressions (open and open/closed) create estimates that are statistically indistinguishable. Using only open landfills gives a slightly higher mean

Table 4.4: 2006 US MSW Landfill Emission Estimates for CFC-12, CFC-11, CFC-113, and CH₃CCl₃^a

Method	US Best Estimate 1 ^b	US Best Estimate 2 ^c	US Maximum Estimate ^d
CFC-12			
Open/Closed	0.075 (0.020 - 0.16)	0.081 (0.034 - 0.17)	0.15 (0.040 - 0.31)
Open	0.10 (0.018 - 0.23)	0.11 (0.031 - 0.25)	0.21 (0.036 - 0.47)
% of Total ^e	0.58% (0.12% - 1.3%)	0.63% (0.21% - 1.4%)	1.2% (0.25% - 2.5%)
CFC-11			
Open	0.037 (0.014 - 0.069)	0.040 (0.024 - 0.075)	0.075 (0.027 - 0.14)
% of Total ^f	0.52% (0.19% - 0.96%)	0.56% (0.33% - 1.1%)	1.1% (0.38% - 1.9%)
CFC-113			
Open	0.0075 (0.0022 - 0.015)	0.0082 (0.0038 - 0.017)	0.015 (0.0044 - 0.031)
% of Total ^f	0.73% (0.21% - 1.5%)	0.79% (0.37% - 1.6%)	1.5% (0.43% - 3.0%)
CH₃CCl₃			
Open	0.015 (0.0044 - 0.031)	0.017 (0.0077 - 0.034)	0.031 (0.0090 - 0.062)
% of Total ^g	0.47% (0.14% - 0.95%)	0.51% (0.24% - 1.0%)	0.95% (0.28% - 1.9%)

^aAll estimates are in Gg y⁻¹ except for % of Total which is given in %.

^bMean (lower - upper 95% confidence interval) estimate using the regression method listed in conjunction with the *EPA* (2007a) best estimate of US CH₄ landfill emissions in Table 4.3. The confidence interval is the sum of the confidence intervals in Table 4.3 and the 95% confidence interval from the regression fit.

^cMean (lower - upper 95% confidence interval) estimate using the regression method listed in conjunction with the *EIA* (2006a) best estimate of US CH₄ landfill emissions in Table 4.3. The confidence interval is the sum of the confidence intervals in Table 4.3 and the 95% confidence interval from the regression fit.

^dMean (lower - upper 95% confidence interval) estimate using the regression method listed in conjunction with the *EPA* (2007a) maximum estimate of US CH₄ landfill emissions in Table 4.3. The confidence interval is the sum of the confidence intervals in Table 4.3 and the 95% confidence interval from the regression fit.

^e% of Total for CFC-12 = (average of open and open/closed methods) ÷ (the average between *Hurst et al.* (2006) and *Li et al.* (2005) US CFC-12 estimates). See Section 4.6.

^f% of Total for CFC-11 and CFC-113 = (open method) ÷ (the average between *Hurst et al.* (2006) and *Li et al.* (2005) US CFC-11 or CFC-113 estimates). See Section 4.6.

^g% of Total for CH₃CCl₃ = (open method) ÷ (the average between *Hurst et al.* (2006), *Li et al.* (2005), and *Millet and Goldstein* (2004) US CH₃CCl₃ estimates). See Section 4.6

estimate as we would expect, since open landfills seem to have higher MPG to CH₄ ratios than closed landfills (see Figures 4-2 and 4-4(a)). However, the 95% confidence interval for the method using open/closed landfills is smaller because the regression is forced through zero (see Figure 4-3).

CFC-12 has the highest emissions from landfills, followed by: CFC-11 > CH₃CCl₃ > CFC-113. Other studies have found CFC-12 and CFC-11 to have the highest concentrations in landfill gas of the four MPGs (*Brookes and Young, 1983; Young and Parker, 1983; Janson, 1988; Deipser et al., 1991; Rettenberger and Stegmann, 1996; Allen et al., 1997; Eklund et al., 1998*), which is due to their widespread use as blowing agents for foam insulation, refrigeration, aerosol propellants, and plastics (*Deipser et al., 1996; McCulloch, 2007*). The mean of the MPG estimates made using the *EIA (2006a)* CH₄ best estimate is 7.6% higher than the mean for the MPG estimates which use the *EPA (2007a)* CH₄ best estimate. This is the same as the difference between the two CH₄ estimates. The comparison of US Best Estimates 1 and 2 provides a good example of how much the MPG estimates differ with a 7% change in the national CH₄ estimates. 7% was the difference between subtracting the industrial landfill CH₄ generation from the total landfill CH₄ generated for the *EPA (2007a)* estimate (see Section 4.4). US Best Estimates 1 and 2 are only slightly different.

The 95% confidence intervals, given in %, averaged over US Best Estimates 1 and 2 are: -72% and +119% for CFC-12, -53% and +86% for CFC-11, -62% and +103% for CFC-113, and -62% and +102% for CH₃CCl₃. That means the Methane Regression Method gives us an estimate which is accurate to within about a factor of 2. CFC-12 has the widest error bars, which is to be expected since it also had the worst linear fit. CFC-113 and CH₃CCl₃ have identical % error bars.

Table 4.5 summarizes the UK MPG landfill emission estimates for each regression method with their mean and 95% confidence intervals using the best and maximum estimates of UK CH₄ landfill emissions as described in Table 4.3. Estimates of the UK landfill emissions as a percentage of total UK emissions is also shown. The studies used for total MPG emissions for the US and UK are discussed in Section 4.6.

The 95% confidence interval for the UK best estimate of MPG landfill emissions is -34% and +40% for CFC-12 and -72% and +99% for CFC-11. CFC-12 has the best regression fit of any of the MPGs. The mass of emitted CFC-12 and CFC-11 from landfills in the UK is smaller than that for the US, but landfill emissions as a percentage of total country emissions is higher for the UK. In particular, UK CFC-12 landfill emissions are 6.4% of total UK emissions. The maximum estimate of

Table 4.5: 2006 UK MSW Landfill Emission Estimates for CFC-12 and CFC-11^a

Method	UK Best Estimate ^b	UK Maximum Estimate ^c
CFC-12		
Open and Closed	0.032 (0.022 - 0.046)	0.12 (0.077 - 0.16)
% of Total ^d	6.4% (4.2% - 8.9%)	23% (15% - 32%)
CFC-11		
Open and Closed	0.0055 (0.0015 - 0.011)	0.020 (0.0054 - 0.039)
% of Total ^d	0.81% (0.22% - 1.60%)	2.9% (0.79% - 5.7%)

^aAll estimates are in Gg y⁻¹ except for % of Total which is given in %.

^bMean (lower - upper 95% confidence interval) estimate using the regression method listed in conjunction with the *Jackson et al. (2007)* best estimate of US CH₄ landfill emissions in Table 4.3. The confidence interval is the sum of the confidence intervals in Table 4.3 and the 95% confidence interval from the regression fit.

^cMean (lower - upper 95% confidence interval) estimate using the regression method listed in conjunction with the maximum estimate of UK CH₄ landfill emissions in Table 4.3. The confidence interval is the 95% confidence interval from the regression fit.

^d(CFC-12 or CFC-11 landfill emission estimate) × 100 ÷ (average of 2005/2006 UK estimates of total CFC-11 or CFC-12 emissions (*Manning, 2007*)). See Section 4.6.

UK CFC-12 emissions is 23% of total UK emissions. UK CFC-11 landfill emissions are almost an order of magnitude less than UK CFC-12 landfill emissions, which is consistent with other European landfill studies (*Deipser et al., 1991; Allen et al., 1997*).

4.6 Comparison to National Estimates of MPG Emissions

The major goal of this thesis is to calculate accurate emission rates of MPGs from MSW landfills. Now that we have those estimates, we can compare the MPG landfill emissions to national estimates. This provides a method for testing the hypothesis that landfills are a significant source of lingering emissions of MPGs in industrialized countries.

A summary of the most recent observation-based estimates of total CFC-12, CFC-11, CFC-113, and CH₃CCl₃^a emissions in the US and UK is shown in Table 4.6. *Li et al. (2005)* estimate CFC-12, CFC-11, CFC-113 and CH₃CCl₃ emissions per person per year for California, Oregon, and Washington for the years 1996-2002 using AGAGE station measurements from Trinidad Head, California. *Li et al. (2005)* com-

Table 4.6: Recent Observation-based US and UK Emission Estimates for CFC-12, CFC-11, CFC-113, and CH₃CCl₃^a

	Country	CFC-12	CFC-11	CFC-113	CH ₃ CCl ₃
<i>Li et al. (2005)</i> ^b	US	16.4	7.3	0.6	2.2
<i>Hurst et al. (2006)</i> ^c	US	14.2	7.0	1.5	3.8
<i>Millet and Goldstein (2004)</i> ^d	US				3.7
<i>Manning (2007)</i> ^e	UK	0.51	0.68		

^aAll estimates are in Gg y⁻¹.

^bCFC-12, CFC-11, and CFC-113 emissions are four year mean US estimates for 1999-2002. CH₃CCl₃ emissions are two year mean US estimates for 2001-2002 (*Li et al.*, 2005). See text for an explanation.

^cCalculated by multiplying per person per year emission rates for 2003 averaged over the US and Canada (*Hurst et al.*, 2006) with a 2003 US population of 290,796,023 (*U.S. Census Bureau*, 2007).

^d2002 US estimate for CH₃CCl₃ (*Millet and Goldstein*, 2004).

^eUK estimate for the year 2005-2006. See text for an explanation of the estimation method.

pare their 1996-1998 measurements with estimates from (*Barnes et al.*, 2003) for 1996-1998 made using station measurements from Harvard Forest, Petersham, Massachusetts for the New York City - Washington, D.C. corridor to estimate total US emissions for 1996-1998. Using the same ratio for 1996-1998 of West Coast vs. East Coast emission/person/year, *Li et al. (2005)* extrapolate their 1999-2002 West Coast emission estimates for CFC-12, CFC-11, and CFC-113 and their 2001-2002 West Coast emission estimates for CH₃CCl₃ to the entire US for 1999-2002. The *Hurst et al. (2006)* estimate was made using data from the 2003 COBRA-NA airplane campaign combined with population densities. Their estimate is an average for the United States and Canada. *Millet and Goldstein (2004)* estimate US emissions of CH₃CCl₃ from three urban field campaigns. *Manning (2007)* calculates two estimates for total UK emissions of CFC-12 and CFC-11. The first estimate uses mixing ratio measurements taken at Mace Head, Ireland in combination with inversion modeling using the NAME model as described in *Ryall et al. (2001)*. The second estimate also uses the Mace Head mixing ratios. In addition, a model derived CO time series is generated for Mace Head using the NAME model. CFC-12/CO and CFC-11/CO ratios are calculated, and CFC-12 and CFC-11 emissions are extrapolated for the UK using EMEP CO emission maps. The total UK estimates calculated for CFC-12 are 0.51 Gg y⁻¹ from both estimation methods. Total UK CFC-11 emissions are 0.65 and 0.71 Gg y⁻¹ using the inversion and CO ratio method, respectively (*Manning, 2007*). The averages of the *Manning (2007)* estimates are listed in Table 4.6. It is interesting to note that total CFC-12 emissions > total CFC-11 emissions in the UK, while for the

US the reverse is true.

The landfill emission estimates (see Tables 4.4 and 4.5) are compared against the total emission estimates (see Table 4.6) in Figures 4-8 - 4-12. US Best Estimate 1 and UK Best Estimate (red line) and upper 95% confidence interval of the US and UK maximum estimates (red X) are plotted vertically, while the total estimates are the horizontal blue lines. The numbers on the plots correspond to the mean of the best estimates. For the US, the total emission estimates are for 1999-2003 and the landfill emission estimates are for 2006. Thus, we expect the actual total emissions to be slightly lower than those which are plotted and used for the % of Total calculations in Table 4.4. CFC-11, CFC-113, and CH_3CCl_3 have all shown recent decreases in global tropospheric mixing ratios, while CFC-12 mixing ratios have remained constant (*WMO*, 2007). The UK emissions are better comparisons. Total emission estimates are for 2005-2006 and the landfill emission estimates are for 2006.

The first observation is that the mean (red dash) of all of the landfill emission best estimates except for UK CFC-12 are ~ 2 orders of magnitude below the total estimates (0.47% - 0.81% of total country emissions). The maximum (red X) estimate is ~ 1 order of magnitude below the total estimates (1.9% - 5.7% of total country emissions). This provides clear evidence that MSW landfill emissions are a small fraction of total MPG emissions. Moreover, we expected the regressions for US CFC-11, CFC-113, and CH_3CCl_3 to give overestimates assuming the sampled landfills are representative of all US MSW landfills. It is only in the case of UK CFC-12 emissions that landfills seem to be a larger source of the total emissions. For UK CFC-12, the mean of the best estimate is only ~ 1 order of magnitude (6.4%) below the total estimate.

Amazingly, estimated landfill emissions as a percentage of total US emissions is about the same for each compound. This is true of the mean estimates as well as their 95% confidence intervals. This supports the idea that US landfills are emitting restricted MPGs at a rate proportional to the national average for each MPG. Using the Methane Regression Methods, CFC-12, CFC-11, CFC-113, and CH_3CCl_3 emit $\sim 0.5\%$ of the total estimated emissions for the US, with a possible maximum between 1.9% - 3.0% depending on the compound.

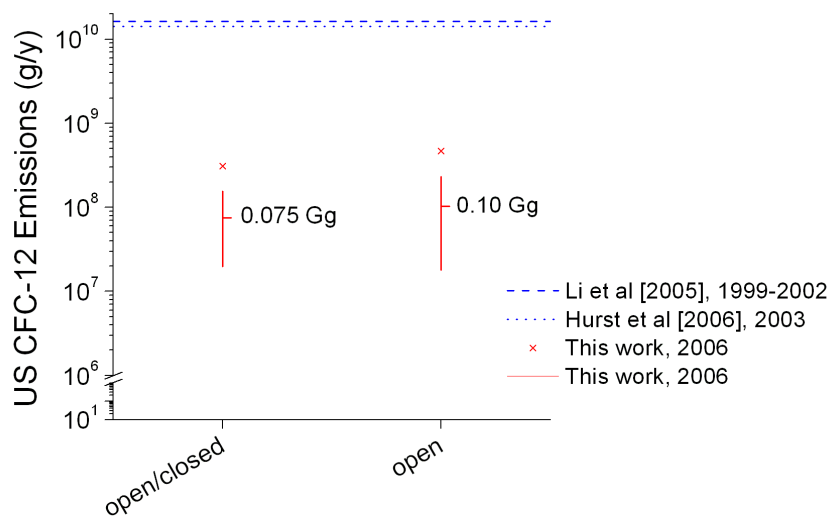


Figure 4-8: 2006 CFC-12 landfill emission estimates plotted against two recent CFC-12 total US emission estimates (see Table 4.6). The year(s) for which the estimates were made is(are) listed after the publication year. The horizontal red dash and vertical red lines represent the mean and 95% confidence interval from US Best Estimate 1. The red X marks the upper 95% confidence interval of the US Maximum Estimate. Open/closed and open correspond to the two US CFC-12 regression methods.

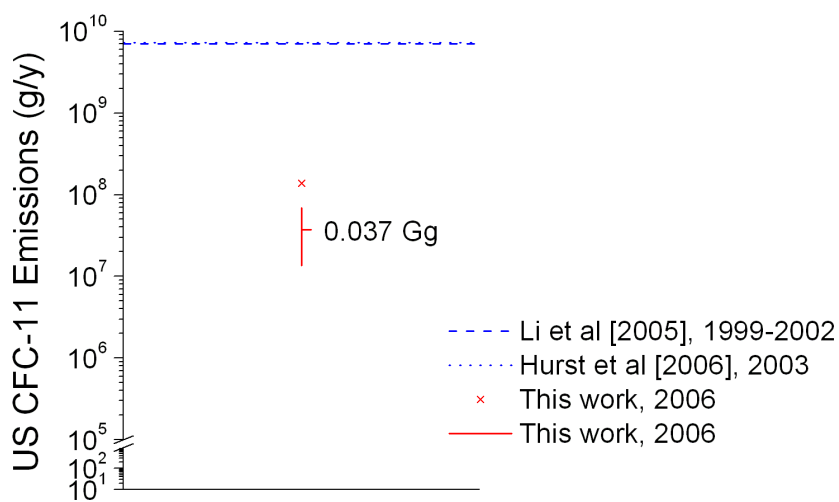


Figure 4-9: 2006 CFC-11 landfill emission estimates (represented as described in Figure 4-10) plotted against two recent CFC-11 total US emission estimates.

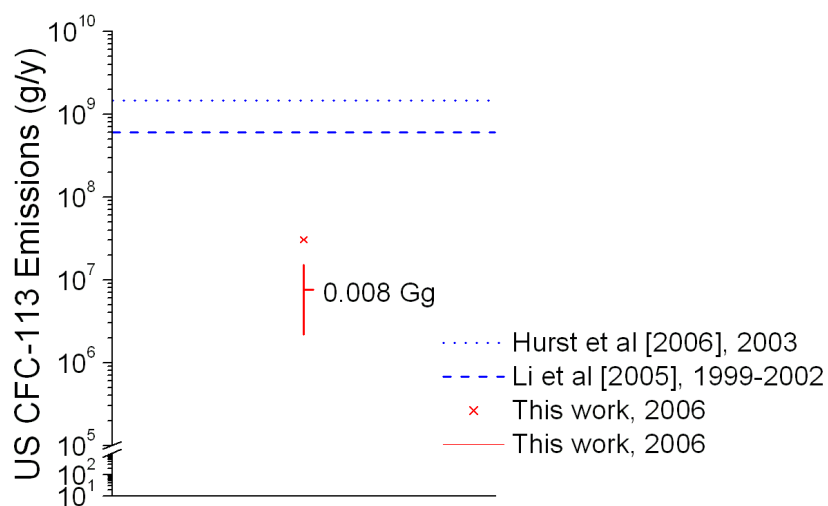


Figure 4-10: 2006 CFC-113 landfill emission estimates plotted against two recent CFC-113 total US emission estimates (see Table 4.6). The year(s) for which the estimates were made is listed after the publication year. The horizontal red dash and vertical red lines represent the mean and 95% confidence intervals from US Best Estimate 1. The red X marks the upper 95% confidence interval of the US Maximum Estimate.

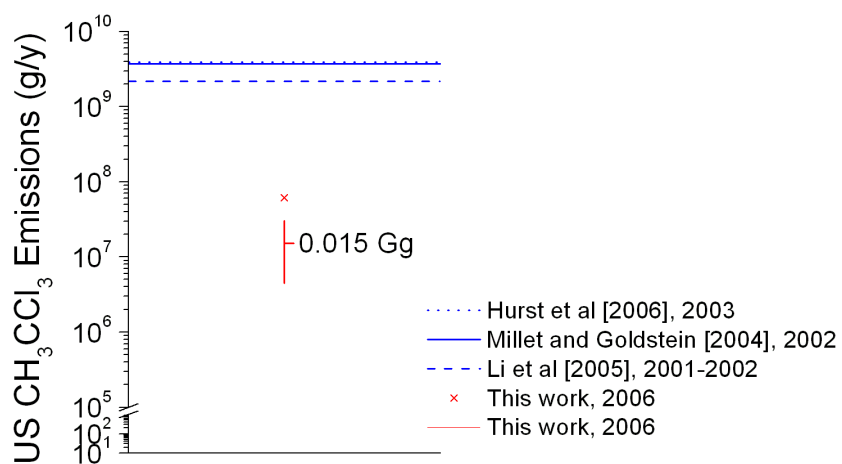
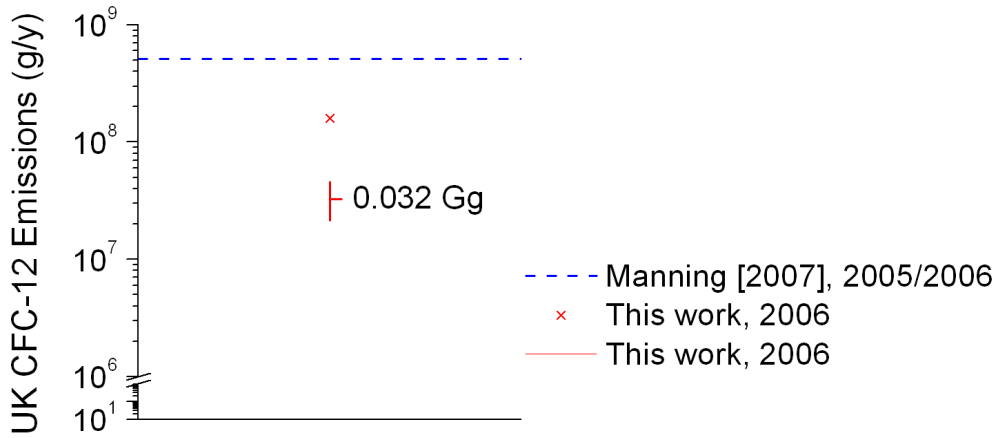
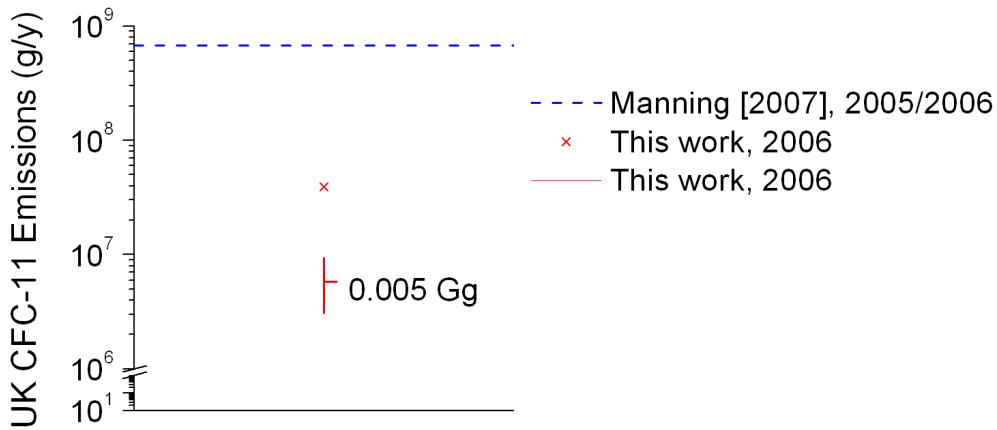


Figure 4-11: 2006 CH_3CCl_3 landfill emission estimates (represented as described in Figure 4-10) plotted against three recent CH_3CCl_3 total US emission estimates.



(a) UK CFC-12 landfill and total emissions



(b) UK CFC-11 landfill and total emissions

Figure 4-12: 2006 CFC-12 and CFC-11 UK landfill emission estimates plotted against recent UK total emission estimates (see Table 4.6). The horizontal red dash and vertical red lines represent the mean and 95% confidence interval from the UK Best Estimate in Table 4.5. The red X marks the upper 95% confidence interval of the UK Maximum Estimate.

4.7 Estimate Uncertainties

The estimates of landfill emissions from the US and UK made using the Methane Regression Method seem to universally indicate that landfill emissions of CFC-12, CFC-11, CFC-113 and CH_3CCl_3 are a small percentage of the total emissions estimated for each country. However, the sensitivity of this estimate to the assumptions and methods used has not been discussed. The following sections address the possible concerns with the accuracy of the MPG landfill emission estimates.

Regression Sensitivity to Data

One of the main concerns is that the data sets are not representative of landfills emissions in the US or UK. The regression method could be very accurate, but if it is using data which are biased, the resulting estimate will be non-representative. The possible reasons for the data used in this study to be biased are discussed in the “Limitations of Methane Regression Method” section at the end of this chapter. In the next few paragraphs, we are more interested in assessing how biased data might change the major result from this thesis, that landfills are only a small fraction of total MPG emissions.

At least for the US, it seems unlikely that MSW landfill emissions could be a much greater portion of total US emissions. The UK data sets for CFC-12 and CFC-11 provide a useful way to check how a much higher generated MPG to CH_4 ratio would affect US CFC-12 and CFC-11 landfill emission estimates (see Figures 4-2 and 4-4(a)). Using the UK CFC-12 regression and the maximum CH_4 emission estimate for the US (see Table 4.3), the maximum CFC-12 landfill emission estimate is still only 4.5% (0.68 Gg y^{-1}) of total US CFC-12 emissions. Total US emissions are calculated as in Table 4.4. The same comparison can be done for CFC-11 using the UK CFC-11 regression and the maximum CH_4 emission estimate for the US. The maximum CFC-11 landfill emission estimate would be 0.12 Gg y^{-1} or 1.73% of total US CFC-11 emissions. Even these maximum estimates, which use a CH_4 value $\sim 2x$ higher than the best estimate of US CH_4 emissions from landfills and much different regressions, are still only a few percent of total US emissions. This indicates that the US estimates are relatively robust to large changes in both the generated MPG to CH_4 ratio and to the national CH_4 value used with the regressions. Large biases within the data would not change the overall conclusion that landfills are not a significant source of lingering MPG emissions in the US. Small biases in the calculations, such as the possible 7% bias in the US CH_4 estimates from inclusion of industrial landfill

CH₄ generation, are negligible compared to the regression uncertainty (factor of 2 accuracy for the US estimates).

For the UK, it is important to make sure the data is representative for CFC-12. UK CFC-11 had similar landfill emissions relative to total emissions as for the US (best estimate (mean) = 0.81% of total, maximum estimate (mean) = 2.9% of total), so we would not expect data biases to greatly increase the importance of MSW landfills as a CFC-11 source in the UK. However, the UK CFC-12 landfill emissions were significant fractions of total UK CFC-12 emissions (best estimate (mean) = 6.4% of total, maximum estimate (mean) = 23% of total). Because the UK landfills had higher MPG to CH₄ generation ratios compared to the US landfills, we can not do the same type of check for the UK data as was just done for the US data. On the other hand, the landfills would have to be truly non-representative to make the UK CFC-12 landfill estimates underestimates. These would be biases such as discussed in the “Limitations of Methane Regression Method” section at the end of this chapter. The UK CFC-12 to CH₄ generation ratios presented in this thesis had the narrowest confidence intervals of any of the regression fits, indicating that we would not expect much variance in CFC-12 emissions among UK MSW landfills.

Accuracy of Regression Method

Since we have shown that the Methane Regression Method is relatively robust to the selection of sampled landfills at least in the US, the next concern is the accuracy of the regression method. To provide a comparison to the Methane Regression Method, generated MPG was regressed against available national waste statistics (called “Waste Regression Method”). The waste statistics used for the UK and US correlate with generated CH₄. Thus, we would expect the estimates made using the Methane and Waste Regression Methods to be proportional. Unlike the national CH₄ statistics, the waste statistics do not take into account recovered landfill gas. Therefore, we would expect the estimates made using the waste statistics to be roughly equivalent to the maximum emission estimates made with the Methane Regression Method.

The available national waste statistics were slightly different for the US and UK. For the US, MSW (municipal solid waste) landfilled per year from 1994 - 2005 was used, since 1994 is the first year the Massachusetts Department of Environmental Protection began to require annual reporting by landfills of landfilled waste. For 1994 - 2000, 2002, and 2004, MSW landfilled per year was calculated by multiplying reported MSW generation \times landfilled MSW (*Simmonds et al.*, 2006). Annual landfilled MSW in 2001 and 2003 were calculated as linear interpolations of the year before and after.

Table 4.7: 2006 US MSW Landfill Emission Estimates Using National Waste Statistics for the Extrapolation

Country	Gas	2006 Estimate (Waste) ^a	% of Total Emissions	% Uncertainty of Estimate ^d
US	CFC-12	0.13 (0.060 - 0.21)	0.87% (0.39% - 1.35%) ^b	±55%
US	CFC-113	0.0085 (7.4E-04 - 0.016)	0.83% (0.072% - 1.58%) ^b	±91%
UK	CFC-12	0.057 (0.014 - 0.10)	11% (2.8% - 20%) ^c	±75%
UK	CFC-11	0.0094 (0.0029 - 0.016)	1.38% (0.43% - 2.33%) ^c	±69%

^aMean (lower - upper 95% confidence interval) of estimate in units of Gg y⁻¹

^b(CFC-12 or CFC-113 landfill emission estimate) × 100 ÷ (average of US estimates of total CFC-12 or CFC-113 emissions as shown in Table 4.6)

^c(CFC-12 or CFC-11 landfill emission estimate) × 100 ÷ (2005/2006 UK estimates of total CFC-11 or CFC-12 emissions (*Manning, 2007*))

^d% Uncertainty of estimate is lower or upper 95% confidence interval relative to the mean emission estimate. Only the regression error is included, because the waste statistics do not have error estimates.

For 2005, US population data was used to scale the *Simmonds et al. (2006)* 2004 estimate (*U.S. Census Bureau, 2007*). The best available UK waste statistics were domestic MSW from 1997 - 2003 as published in *DEFRA (2006)*. US MSW landfilled from 1994 - 2005 was estimated as 2,834,285,310 metric tons. UK domestic MSW landfilled from 1997 - 2003 was estimated as 2.09E+08 metric tons.

The landfill emission estimates are shown in Table 4.7. Only two of the US data sets, generated CFC-12 and CFC-113 had linear relationships with landfilled waste from 1994 - 2005. If we compare Table 4.7 with the estimates in Tables 4.4 and 4.5, we see that the Waste Regression Method estimates are between the estimated and maximum 2006 landfill emission estimates made using the Methane Regression Method. This suggests that if there is any underestimation with the Methane Regression Method, it is due to sample bias and not due to the regression methodology. This is also further evidence that the maximum estimates made with the Methane Regression Method are real upper limits to the estimates and that the true emissions of CFC-12, CFC-11, CFC-113, and CH₃CCl₃ from US and UK landfills are below these values.

Limitations of Methane Regression Method

The major limitation of the methodology presented in this chapter is that we have sampled only one type of landfill, actively managed MSW landfills (see Box 1.1). We assume for the estimates in the thesis that the generated gas ratios we have

measured at actively managed landfills are the same for all MSW landfills. With regard to gas management, there are two types of landfills, actively managed and passive. Passive landfills do not recover any of the generated landfill gas. According to the CH₄ estimates from *EPA* (2007b), ~ 50% of total generated CH₄ from landfills is recovered. This means we expect passive landfills to account for about half of the total landfill gas generation, but a higher fraction of the total emissions because much of the gas at actively managed landfills is recovered. In order for the maximum emission estimates of CFC-12, CFC-11, CFC-113, and CH₃CCl₃ from US landfills to be too low because we underestimated the contribution of MPG emissions from passive landfills, they would have to almost double their MPG to CH₄ generation ratio as estimated from actively managed landfills. For the UK maximum estimate to be lower than the true emissions, UK passive landfills would have to emit more than 3x the generated MPG to CH₄ ratio estimated in this study. This seems unlikely, since MPGs are biologically degraded in landfill soil covers (*Denovan and Strand, 1992; Deipser and Stegmann, 1997; Balsiger et al., 2005; Scheutz et al., 2003; Scheutz and Kjeldsen, 2005; Scheutz et al., 2007*), which would decrease total MPG emissions from passive landfills.

Chapter 5

Conclusions

5.1 Summary of Findings

The goal of this thesis was to estimate emissions of four Montreal Protocol-restricted gases (MPGs) in two industrialized countries from one possible MPG bank, namely municipal solid waste landfills. Towards this goal, two new major data sets were collected in the United States and one was made publicly available in the United Kingdom. These data sets provide the first available analysis of MPG variability, generation rates, and estimated emissions from MSW landfills in industrialized countries.

The One Landfill Study produced accurate MPG concentration measurements over a 17 month period. We studied the phenomenon which would make it possible to do the landfill emission estimates. With the installation of a gas-to-energy plant, we were able to observe how gas management can significantly lower seasonal variations in gas flow rates, MPG concentrations, and CH₄ concentrations. This lack of temporal variability allowed for a linear correlation between MPG and CH₄ generation rates among actively managed MSW landfills which we exploited for the emission estimates. Variability in MPG generation rates was mostly controlled by variability in the concentrations with a standard deviation of the mean between 16% - 34% depending on the compound over a 12 month period. During the same time period, the variability in the CH₄ generation rates was heavily dependent on flow rate which meant that the standard deviations were significantly higher for CH₄ generation rates (9.8%) than for CH₄ concentrations (3%).

For the Multi-landfill Study, CFC-12, CFC-11, CFC-113, CH₃CCl₃, and CH₄ generation rates were measured and information surveys were conducted at seven sites in Massachusetts. Data enabling the calculation of CFC-12, CFC-11, and CH₄ gen-

eration rates for nine sites throughout the UK was gathered from one UK private landfill company. The data was used to create linear regressions between MPG and CH₄ generation rates of the sampled landfills. These regressions, combined with national estimates of landfill CH₄ emissions, yielded national estimates of MSW landfill emissions of MPGs for the US and UK. The results support the idea that US and UK MSW landfills are not significant sources of Montreal Protocol-restricted gases, contrary to some prior assumptions.

US MSW landfills were estimated to emit all four MPGs at a rate approximately proportional to national emissions for each MPG ($\sim 0.5\%$), with an upper limit between 1.9% - 3.0% depending on the compound. This upper limit was estimated by assuming that all of the generated gas is emitted to the atmosphere in the same MPG to CH₄ ratio as measured at the sampled landfills. While the best estimates produced by the regression methods used in this thesis are subject to further refinement through sampling at passive MSW landfills, the upper limit estimates are very likely to be true maximum estimates. CFC-11 emission estimates for the UK were approximately the same fraction of UK national emissions as for the US measurements (0.8%) with an upper limit of 6%. UK CFC-12 was the only compound where landfill emissions were estimated to be a higher fraction of total country emissions (6%) with an upper limit of 32%. The UK upper limits are considered to be much higher than the true emissions, because the UK captures a very high fraction of its landfill gas ($\sim 70\%$). All estimates had an accuracy of $\sim 2x$ except for CFC-12 for the UK, which had 95% confidence intervals equal to +40% and -34%. The results from the regression methods were very robust to both the selection of sampled actively-managed landfills and to the national statistics used for the extrapolation.

5.2 Future Work

The results from this thesis open an entirely new field of questions to be researched in the future. First on the list is if MSW landfills are not currently the major source responsible for the lingering emissions of MPGs observed in industrialized countries, what is the major source? Or are there many small sources; which, when combined, result in the observed national MPG emissions? Based on the research done and literature read for this thesis, it seems highly possible that what is measured in national studies of MPG emissions in industrialized countries is the accumulation of many small leaks. *Barnes et al.* (2003), *Hurst et al.* (2006), and *Manning* (2007) have all found correlations between MPG emissions and population densities. Many of the

products most often cited as containing MPGs such as domestic refrigeration, aerosol cans for medicinal uses, air conditioners, and insulation are all tied to population. Andrew Glazer, an undergraduate researcher at MIT, did a study of the major sources of leaks on MIT's campus, including transportation to and from campus. The major source of CFC-12 emissions was the central utility plant on MIT's campus, which he estimated from records of MIT purchases of CFC refrigerant. Mr. Glazer estimated 630 kg/year of CFC-12 was leaked from the MIT central utility plant over the years 1998-2004. Dividing this by 15,000 people at MIT who use campus electricity full time and then multiplying by ~ 300 million residents in the US yields ~ 13 Gg of CFC-12 emissions in the US per year. This is certainly the same order of magnitude as national estimates of CFC-12 emissions. Mr. Glazer's estimates for CFC-11 had less obvious implications. The CFC-11 which leaked from the MIT central utility plant between 1998-2004 was the same amount which he estimated as was landfilled.

Another area for further research is in-situ sampling at passive MSW landfills. While it seems unlikely that passive MSW landfills could account for the gap between the landfill emissions estimated in this study and national UK and US MPG estimates, as discussed in Chapter 4, sampling at passive MSW landfills would better refine the best estimates of MPGs emissions calculated in this thesis. MPG fluxes from passive landfills is definitely an area of research where there is almost no available in-situ data. The reasons for this are the same reasons why it was not pursued in this thesis, i.e. the measurements are time consuming and would require more complicated detection and analysis, most likely through the use of a mobile lab or many surface flux chambers. Also, unlike CH_4 , MSW landfills have not been considered a large source of MPGs. Thus, surface emissions of MPGs from landfills have never been of interest to anyone before now.

It is very important to point out that just because the research in this thesis indicates that MSW landfills are not currently an important source of MPG emissions to the atmosphere, there are still several questions which this thesis did not answer and which will be important to answer in the future. The first is: what if MSW landfills are such a small source of MPG emissions because it takes a long time to emit what goes into a landfill? A good example of the need for further research on this topic is illustrated by the following comparison. There has been one rigorous modeling study based on data from laboratory experiments, which has estimated expected release rates of disposed products containing MPGs. *Kjeldsen and Scheutz* (2003) estimated annual emissions of CFC-11 for decommissioned refrigerators and freezers in the US from 1985-2010 to be between 3-8 Gg in 2006. This is 80x - 200x

of the best estimate of CFC-11 landfill emissions from this thesis. What is the reason for the large discrepancy between the *Kjeldsen and Scheutz* (2003) model and the landfill emission estimates in this study? Is the CFC-11 in refrigerators and freezers not being disposed in landfills? Or do landfill processes, not accounted for in the *Kjeldsen and Scheutz* (2003) model, such as diffusion through the landfill pore space, significantly extend the amount of time it takes for the CFC-11 in the foam to be emitted from landfills?

One area of research which may account for the long lifetimes of MPGs within landfills or even cause landfills to be a sink of MPGs is microbial degradation. *Scheutz et al.* (2007) have shown that microbial degradation and landfill diffusion rates can have an important, but highly uncertain, effect on the lifetime of MPGs within a landfill and the total fraction of CFC-12 which is ultimately released to the atmosphere. A 10-fold difference in the CFC-12 microbial degradation rate can result in 94% vs. 60% of the CFC-12 input into the landfill which is ultimately released to the atmosphere. A 10-fold difference in the landfill diffusion rate can mean that 98% vs. 52% of the initial CFC-12 content input into the landfill is emitted to the atmosphere after a 20 year period. This represents a huge uncertainty regarding the fate of CFC-12 once it enters the landfill. Much of the uncertainty in the estimates from *Scheutz et al.* (2007) stems from a lack of in-situ data on degradation and diffusion rates in landfills. One way to measure in-situ degradation rates might be to measure CFC-12/CFC-11 ratios in closed and open landfills and compare the ratios from the two landfill types. Since CFC-11 has a higher laboratory degradation rate than CFC-12, the difference in the CFC-12/CFC-11 ratios between the two landfill types would be a quantitative measure of the relative rate of microbial degradation.

If what was measured in this thesis is small because the lifetimes of MPGs within landfills are quite long, there could be a long tail of emissions from landfills which would last over many decades. It is unclear if landfill emissions have peaked or if the peak is yet to come, since this is the first estimate of landfill emissions. If landfill emissions do increase or even maintain their current emission levels in the coming decades, this could be important for stratospheric ozone recovery in polar regions, which is expected to recover to 1980s levels in the year 2065, ~ 16 years later than in the mid-latitudes (*WMO*, 2007). One way to find out whether landfill emissions have peaked or if they are continuing to increase would be to do a second estimate of MPG emissions in 5-10 years. A second analysis would also be able to measure the effect of upcoming deadlines in the Montreal Protocol. Developed countries are scheduled to phase out CFCs and CH_3CCl_3 in 2010 and 2015, respectively. Waste practices

in India and China and their impact on MPG emissions would be a very interesting study. Moreover, a second study of landfill MPG emissions would be better able to refine the split in emissions from closed and open landfills. All of the US best estimates except for CFC-12 are expected to be overestimates of the true emissions because the MPG/CH₄ ratios for closed and open MSW landfills were clearly different for US CFC-11, US CFC-113, and US CH₃CCl₃. Only two closed MSW landfills were sampled, which was not enough to create a second regression for closed landfills.

Lastly, the estimates in this thesis should be valid for as long as the MPG/CH₄ ratios remain the same. CH₄ is always $\sim 55\%$ of the bulk gas volume in MSW landfills which are still accepting waste. Thus, the future validity of the MPG/CH₄ ratios measured in this thesis will depend on the future amount of MPGs in the waste stream, as well as some of the unanswered questions presented in this section, such as the lifetime of MPGs in landfills. For the next decade, it will likely be possible to use the US and UK MPG/CH₄ ratios in this thesis along with the annual estimates of MSW landfill CH₄ emissions, which the US and UK governments publish, to calculate accurate annual US and UK updates of maximum estimates of MPG emissions from MSW landfills. The most useful estimates from this thesis are the maximum estimates of CFC-12, CFC-11, CFC-113, and CH₃CCl₃ emissions from MSW landfills, because they provide an upper limit of MSW landfill MPG emissions. The best estimates are subject to better refinement from sampling at closed and passive MSW landfills.

Appendix A

Gas-to-energy plant Exhaust Gas Measurements

Appendix A describes gas samples which were taken both before and after combustion at two landfills in Massachusetts with gas-to-energy plants. The samples were collected to provide in-situ tests of the percentage of CFCs and CH_3CCl_3 in landfill gas which remained after combustion.

A.1 Methods

Exhaust gas from the gas-to-energy plants and landfill pipe gas was collected at two landfills. The first was Crapo Hill landfill, which was the study site for the One Landfill Study in Chapter 3. Crapo Hill's gas-to-energy plant has four reciprocating engines (Caterpillar), each with a maximum output of 825 kW. Sets of duplicate 0.8 L flasks (Biospherics Research Corporation, Hillsboro, Oregon) were filled at the Crapo Hill plant port shown in Figure 3-2 and at one of the reciprocating engine exhaust ports. The flasks had been pre-cleaned according to Section 2.1.2. The samples were taken on February 28, 2006. The flasks were filled using an AC metal bellows pump (Senior Aerospace Metal Bellows, Sharon, MA, Model MB-158, P/N 28950). The sample line was flushed three times with landfill gas before filling the flasks. Line pressure was monitored using a stainless steel line gauge (McDaniel Controls Inc., Luling, LA). All fittings and tubing were 1/4" stainless steel.

The flasks were analyzed on the MIT GC- μ ECD and -FID as described in Section 2.1 on February 28 and March 1, 2006. They were also analyzed on a GC-MS (gas chromatography system with mass spectrometer, JEOL GCmate, JEOL USA) in Prof. Philip Gschwend's lab at MIT together with John MacFarlane on May 16-18, 2006.

The same column, 25 m x 0.32 mm i.d. CP Sil 5 CB capillary column (Model No. CP7680, Varian Inc.), Valco 6-port injection system, and 50 uL sample loop as used on the GC- μ ECD system were connected to the MS. The temperature program, flow rates, carrier gas, and CFC standard were also the same as for the GC- μ ECD. The MS was tuned and optimized before each session using an internal perfluorokerosene (PFK) standard. The well characterized and extensive fragmentation pattern of this compound made it possible for a user to perform mass axis calibrations over a wide range of mass to charge (m/z) values. This study used calibration mass to charge ranges from 51-219 m/z and 18-100 m/z for measuring spectra from 45-224 m/z and 17-45 m/z , respectively. Blanks were run before and after each standard analysis to ensure that there was no signal carry over. Each sample was only run once. Duplicate samples ensured that MS spectra were repeatable.

The second landfill where engine exhaust gas and landfill pipe gas was sampled was Plainville landfill in Plainville, Massachusetts. The landfill is owned and operated by Allied Waste Industries, while the gas-to-energy plant is owned and operated by Plainville Generating Company, LLC, a subsidiary of the Lorusso Corporation. The gas-to-energy plant has a total of seven reciprocating engines (Caterpillar, model G3516-LE), each rated for a maximum output of 800 kW. The pre- and post-exhaust gas samples were taken in the same manner as for the Crapo Hill samples. Plainville was sampled on October 31, 2006. The flasks were analyzed on the MIT GC- μ ECD and -FID on November 1 and 2, 2006 as described in Section 2.1.

A.2 Results

For the Crapo Hill exhaust samples, two mass scans were done from 45-224 m/z and 17-45 m/z . Figure A-1 shows the 45-224 m/z scan. Five independent peaks are discernable, labeled A-E, although the fourth peak contains more than one compound which co-eluted. Peak A (scan 25-30, 0.88-1.1 minutes) had a 80% match rate with C_2H_5OH . Peak B (scan 31-33, 1.1-1.26 minutes) had a 90% match rate with SO_2 . The 45-224 m/z scan indicated that C_2H_5F was most likely match for peak C (scan 51, 1.8-1.95 minutes), but the 17-45 m/z scan discounted C_2H_5F as a possible match. Peak D (2.8-3.6 minutes) had at least three peaks which co-eluted. The most likely matches were NO_2 , CO_2 , and methylhydrazine (CH_6N_2). Peak E (scan 116-120, 4.25-4.45 minutes) had a likely match with COS. Besides discounting C_2H_5F as a possible match for peak C, the 17-45 m/z scan was too contaminated with fragments from ambient air to provide much identification help. However, the 27 m/z fragment was

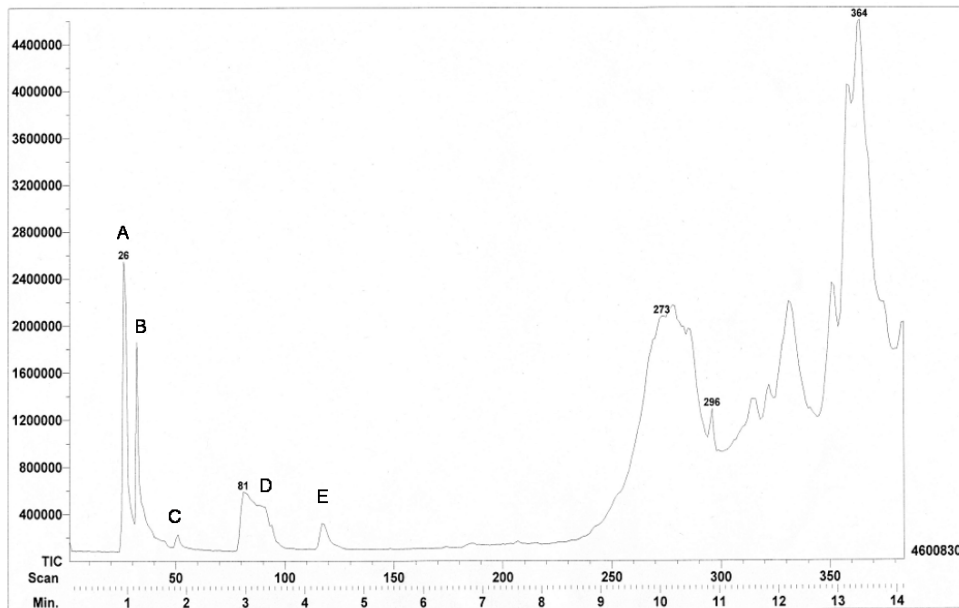


Figure A-1: GC-MS chromatogram of exhaust gas from reciprocating engines at Crapo Hill landfill's gas-to-energy plant. The numbers over the peaks represent the scan number, while the letters (A-E) label the peaks which eluted in the same time range as the four MPG's in this study.

larger than the 33 m/z fragment, which implied that CH_3F was not present in peak D, since the relative size of the two fragments should be reversed. If any CFCs or CH_3CCl_3 were present, it was below detectable levels on the GC-MS. A standard analysis of the Crapo Hill exhaust samples on the MIT GC- μ ECD also yielded no detectable CFC or CH_3CCl_3 peaks.

For Plainville landfill, 0.7% (2.9 ppb) of CFC-12, 27.4% (6.8 ppb) of CFC-11, 37.5% (1.4 ppb) of CFC-113, no detectable CH_3CCl_3 , and 0.5% (2.4 parts per thousand) of CH_4 remained in the post-exhaust samples when compared with the pre-exhaust samples.

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