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FINAL PROJECT REPORT

A NEW FIELD-VALIDATED GREENHOUSE GAS INVENTORY METHOD FOR LANDFILL METHANE EMISSIONS

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PREFACE

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A New Field-Validated Greenhouse Gas Inventory Method for Landfill Methane Emissions is the final report for PIER Contract Number 500-05-039: Improved Landfill Methane Inventory Methodology. The information from this project contributes to Energy Research and Development Division's Energy-Related Environmental Research Program.

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ABSTRACT

The California Landfill Methane Inventory Model is a new science-based, site-specific, field-validated annual greenhouse gas inventory method for typical annual methane emissions from daily, intermediate, and final cover materials at municipal solid waste landfills in California. This model, a freely available Java software tool, is a Tier III Intergovernmental Panel on Climate Change method, which includes a user-friendly template for entering information on site-specific cover materials and extent of engineered gas extraction, globally validated United States Department of Agriculture climatic and soil temperature/moisture models, and a one-dimensional model based on diffusion for estimation of typical annual emissions inclusive of seasonal methane oxidation. Unlike previous inventory models that relied on hypothetical methane generation models, the California Landfill Methane Inventory Model provides a more realistic emphasis on seasonally varying transport, oxidation, and emissions processes in specific California landfill cover materials. This method is the product of a three-year project (2007-2010) — in cooperation with the California Department of Resources Recycling and Recovery and the California Air Resources Board—to develop an improved method within the context of the California greenhouse gas inventory. Oxidation modeling was based on extensive supporting laboratory studies using California cover soils. Field validation was conducted over two annual cycles at a Northern California coastal site and a Los Angeles County site (Scholl Canyon) with additional supporting emissions data from the Lancaster, Tri-Cities, and Kirby Canyon sites.

Keywords: Methane, methane emissions, methane oxidation, methanotrophy, landfill, global warming, GHG inventory, transport modeling

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EXECUTIVE SUMMARY

Background

Methane is the second most important greenhouse gas, as it has a 100-year global warming potential 25 times greater than carbon dioxide. In addition to natural wetlands, atmospheric methane has multiple anthropogenic (caused by people) sources, including ruminant (cud-chewing) animals, natural gas and coalbed leakages, rice production, biomass burning, and landfills. Because methane has a short atmospheric lifetime of about 12 years, reductions in methane emissions can begin to reduce atmospheric concentrations within a decade. Consequently, reductions in methane emissions can be an effective shorter-term strategy to assist with emission reduction targets. Due to uncertainties associated with current methane emission estimates, better numbers are needed using improved methods to assess quantitatively multi gas emission reduction strategies at the state and regional level.

Better numbers are especially needed for landfill methane emissions. The Intergovernmental Panel on Climate Change has estimated that uncertainties associated with the current inventory methods range from a low of 10-30 percent to more than 200 percent. According to global estimates summarized in the *Intergovernmental Panel on Climate Change Fourth Assessment Report*, current landfill methane emissions of approximately 600 million-700 million tons carbon dioxide equivalents per year constitute half the total emissions from the waste sector, which are about 1-2 percent of the total global anthropogenic greenhouse gas emissions of about 49 gigatons carbon dioxide equivalents per year.

In the United States, landfills are estimated to be the second largest single anthropogenic source of methane after ruminant animals. For California, the state greenhouse gas inventory estimates that 2006 landfill methane emissions were 6.3 million tons carbon dioxide equivalents per year, which is 1.3 percent of gross anthropogenic emissions. In general, the methane generated by the anaerobic (absence of air) microbial decomposition of organic waste in landfills can be partitioned into several possible pathways: methane recovered by engineered extraction systems; methane oxidized by indigenous aerobic microorganisms in landfill cover materials; methane emitted to the atmosphere; methane that is temporarily stored in the landfill volume; and, especially at older unlined sites, methane that can laterally migrate in the subsurface.

Existing landfill methane emissions estimates rely on Intergovernmental Panel on Climate Change Tier I and II methods, which estimate annual emissions based on the application of a methane generation model using annual landfilling rates and waste composition. Two subtractions are permitted: (1) methane that is recovered and quantified by engineered gas utilization/flaring projects; (2) a further 10 percent reduction for microbial methane oxidation in landfill cover materials. Overall, the Intergovernmental Panel on Climate Change method is termed *First Order Decay* because it relies on a multi component first order kinetic equation (equation that describes an object in motion) in which methane generation is estimated from waste quantity and composition for waste landfilled in a particular year summed with methane generation from waste landfilled in previous years. The application of First Order Decay models to emissions began more than 15 years ago and largely pre dated field campaigns for

direct measurement of emissions. Indeed, the original application of the First Order Decay models during the 1970s was for modeling landfill methane generation for commercial landfill gas utilization projects using site-specific First Order Decay models. Moreover, the original "validation" of the First Order Decay models for emissions was based on recovery data, not on field data for emissions.

Recent published literature with detailed quantification of multiple methane pathways in a field study has demonstrated that modeled methane generation does not correlate to residual methane emissions at sites with engineered gas recovery. This lack of correlation is especially significant for California because data compiled by CalRecycle indicate that more than 90 percent of the waste in permitted California landfills is under active gas extraction. Moreover, other deficiencies of the First Order Decay model approach include: (a) assumption of homogeneous waste composition and decomposition rates through use of a kinetic equation suitable for a well-mixed anaerobic digester; (b) exclusion of physical retardation effects of cover materials on emissions; and (c) exclusion of variability of methane oxidation rates in daily, intermediate, and final cover materials related to seasonal soil moisture and temperature variations. The global literature has indicated that methane emissions and oxidation rates for landfill cover soils can vary by more than six orders of magnitude. Thus, an improved inventory method is clearly needed that can, on a site-specific basis, realistically estimate typical annual emissions for daily, intermediate, and final cover materials inclusive of seasonal methane oxidation (combination of a substance with oxygen).

Purpose

Based on the deficiencies, omissions, and uncertainties associated with the current Intergovernmental Panel on Climate Change method, this project was to develop an improved, science-based, field-validated greenhouse gas inventory method for measuring landfill methane emissions in California.

Objectives

The specific objectives of this project were to:

- Develop an improved, field-validated, user-friendly annual inventory model that is capable of realistically modeling annual site-specific landfill methane emissions.
- Develop and complete complementary laboratory incubation studies for improved understanding and modeling of the limits and dynamics of methane oxidation in California landfill cover soils.
- In a field study validate the new landfill methane inventory model for seasonal emissions over two annual cycles at Northern and Southern California landfills.

Conclusions and Recommendations

This project has developed an improved field-validated landfill methane inventory model for California that relies on well-researched and accepted theoretical relationships, previous field and laboratory studies, existing globally validated United States Department of Agriculture models, and extensive supporting laboratory studies on methane oxidation in California landfill

cover soils (including more than 2000 individual incubations). Field validation (more than 800 measurements using static chambers) was conducted over two years on daily, intermediate, and final covers at two California landfill sites, including the northern coastal Marina Landfill (Monterey County) and the southern Scholl Canyon Landfill (Los Angeles County). Additional limited field validation was conducted for intermediate covers at the Lancaster, Kirby Canyon, and Tri-Cities Landfills through the cooperation of Waste Management, Inc. Oxidation was quantified through the use of a stable carbon isotopic method, which relies on the preference of methane-oxidizing microorganisms for the carbon isotope of smaller mass (^{12}C) versus the heavier carbon isotope (^{13}C).

The California Landfill Methane Inventory Model is a freely-available, Java-based Web tool [www.lmem.us/CALMIM/ CALMIM42.exe] for estimating typical annual, site-specific landfill methane emissions based on the respective areas and properties of daily, intermediate, and final cover materials, as well as the extent of engineered gas extraction. A major change from the Intergovernmental Panel on Climate Change Tier I default method is that emissions are decoupled from a methane generation model. Instead, the emission processes at the top of the landfill are modeled directly. Another major change is that seasonal methane oxidation is also modeled directly rather than relying on a 10 percent oxidation "default." In terms of the Intergovernmental Panel on Climate Change structure, the California Landfill Methane Inventory Model is an Intergovernmental Panel on Climate Change Tier III "validated, higher quality" method for typical annual methane emissions from California landfills. The California Landfill Methane Inventory Model consists of four major integrated components:

- Data-Input Template
- Meteorological Model
- Soil Microclimate Model
- One dimensional Emissions/Oxidation Model

With regards to the data-input template, input data are required on the surface area, thickness, and properties of the various cover materials for a particular site. Additional data on the extent of gas extraction and surface vegetation for each cover type are also required (as percentage of surface area for each cover type). To make data input easier, the template limits the site-specific data requirements to the most pertinent inputs needed for inventory calculations. Also, major California cover types, including soil covers and permitted non soil alternative cover materials and designs, can be directly selected as defaults. The template also contains a user-customizable "advanced" screen, which can be accessed if the user has sufficient site-specific data to adjust of calculation parameters rather than use model defaults based on published literature and data. Site locations can be queried by name and are linked to the California Solid Waste Information System for latitude and longitude information. With regard to the meteorological model and the soil microclimate model, these models rely on modified versions of the following globally validated United States Department of Agriculture models: Global TempSIM, Global RainSIM, Solarcalc, and Soil Temperature and Moisture. In particular, the soil temperature functions for soil temperature and moisture were modified to accommodate

the landfill heat source below the cover. The latitude and longitude of a site are used to find out the daily climatic conditions, as well as the soil microclimate conditions for 10 minute intervals for a minimum of 2.5 centimeters depth increments for any landfill cover soil up to about 2.5 meters thick. With regard to the one-dimensional emissions/oxidation model, the emissions model is based on a one-dimensional transport of methane based on gaseous diffusion through each specified cover material. The driving force is the methane concentration gradient through the cover materials, which depends on the presence or absence of engineered gas recovery, the thickness and properties of the cover materials, and seasonal methane oxidation rates. Methane oxidation is modeled through the use of scaled results relative to maximum oxidation rates for the full range of soil temperature and moisture conditions, based on extensive laboratory studies for California landfill cover soils (more than 2000 incubations) and published literature. Oxidation is quantified by the difference in the California Landfill Methane Inventory Model runs, testing 10 minutes and intervals over an annual cycle with and without oxidation for each cover type. The California Landfill Methane Inventory Model also calculates total annual site emissions by summing the emissions for all specified cover types.

The California Landfill Methane Inventory Model is a regional site-specific landfill methane emissions model for annual greenhouse gas inventory applications in California. Because shorter-term fugitive emissions from gas system leakages and cover maintenance issues are typically remediated quarterly —as indicated by surface scans for elevated methane concentrations required for regulatory compliance — these are not included in this model. Although this model has been developed specifically for California, the embedded United States Department of Agriculture models have been globally validated. Further field validation is anticipated along with concurrent model modifications and improvements. The use of this model is not recommended without modification for purposes other than annual greenhouse gas inventory estimates (for example, changing existing regulatory requirements; monetization of greenhouse gas offset credits). As shown during Beta testing, because the California Landfill Methane Inventory Model uses average climatic and soil microclimate data to calculate typical annual emissions, results may not be representative for atypical climate conditions (for example, drought years) or where there are large differences in relief relative to regional weather stations. The site-specific application of the California Landfill Methane Inventory Model can be significantly improved through the use of "advanced" functions and site-specific data, including field measurement of the methane concentration gradient through specific cover materials to directly quantify the major driving force for emissions.

Future research recommendations include:

- Expansion of the California Landfill Methane Inventory Model structure to promote the routine use of local meteorological and soil microclimate data.
- Development of a reference soils database for landfill cover soils.
- Development of a statistically valid field protocol to determine the methane concentration gradient through daily, intermediate, and final landfill cover materials at specific landfill sites.

- In addition to diffusion, add other flux mechanisms to the field-validated landfill methane inventory model for California, as appropriate under certain conditions. Those mechanisms could include convection, wind-driven convection, boiling, and, under some circumstances, plant-mediated transport.
- Addition of the ability to model and maintain mass balance on the stable carbon isotopes (^{13}C, ^{12}C) of methane through the various cover soil profiles.
- Addition of the ability to model and maintain mass balance on other carbon and nitrogen cycle gases (especially carbon dioxide, nitrous oxide) through various soil profiles.
- Additional field validation for the current model to be conducted in parallel with ongoing field measurements of methane emissions and oxidation at other California, United States, and international sites by various landfill research groups.
- Application of the California Landfill Methane Inventory Model structure to model gaseous transport in other natural and managed ecosystems.

Note: All tables, figures, and photos in this report were produced by the authors, unless otherwise noted.

CHAPTER 1:
Background and Project Overview

1.1 Introduction

Methane (CH_4) is an important greenhouse gas: the total positive climate forcing attributed to CH_4 since 1750 is 30-40 percent that of carbon dioxide (Hansen, 1998; Forster et al., 2007; Solomon et al., 2007). In addition, CH_4 has a relatively short atmospheric lifetime of about 12 years (Forster et al., 2007); therefore, changes in CH_4 sources can affect atmospheric concentrations on decadel or shorter time scales. Deciphering the dynamics of the global CH_4 cycle requires an understanding of the temporal behavior of individual sources and sinks through seasonal cycles. Terrestrial CH_4 sources include natural wetlands, rice production, ruminant animals, termites, fossil fuel production & transport, geologic sources, termites, biomass burning, wastewater, and landfills. The anthropogenic sources collectively account for more than half of the annual atmospheric input of 500-600 Tg CH_4 (Khalil, 2000; Heinman, 2010), and there is considerable uncertainty with respect to their individual magnitude and variability, as discussed in recent literature (Heinman, 2010; Shakhova et al., 2010; Bloom et al., 2010).

The major sink for atmospheric CH_4 is reaction with tropospheric OH. Methane oxidation in soils (Dutaur and Verchot, 2007), including landfill cover soils, provides a secondary sink. Methane oxidation is accomplished by aerobic methanotrophic microorganisms and can range from negligible to 100 percent of the soil CH_4 flux. Under some circumstances, as originally quantified using static chambers in tundra ecosystems (Whalen and Reeburgh, 1990), atmospheric CH_4 may be oxidized at the landfill surface (Bogner et al., 1995; 1997a,b; 1999; Borjesson, 1996; Borjesson and Svensson, 1997: Scheutz et al., 2003). The thickness, physical properties, and moisture content of cover soils directly affect CH_4 oxidation, because rates are limited by the transport of CH_4 upward from anaerobic zones and oxygen (O_2) diffusion downward from the atmosphere.

For landfills, historic estimates of global CH_4 emissions have varied over a wide range from 9 to 70 Tg CH_4 yr^{-1} (Bingemer and Crutzen, 1987; Richards, 1989; Bogner and Matthews, 2003; Bogner et al., 2007). In the U.S., national estimates indicate that landfills are currently the second largest anthropogenic source of CH_4 after ruminant animals (US EPA, 2010). According to the most recent global estimates summarized in the Intergovernmental Panel on Climate Change (IPCC) 4th Assessment Report (AR4), the 2005 annual landfill CH_4 emissions of approximately 640 Mt CO_2 eq yr^{-1} constituted about half of the total emissions from the waste sector, or between 1 and 2 percent of total anthropogenic GHG emissions of about 49 Gt CO_2 eq (US EPA, 2006; Monni et al., 2006; Bogner et al., 2007; Rogner et al., 2007). Using the 100-year Global Warming Potential (GWP) of 21 for CH_4 which was consistently used for the IPCC AR4 for Working Group III (based on the IPCC Second Assessment Report and currently used for Kyoto Protocol compliance), this amounts to about 30 Tg CH_4 yr^{-1}. A higher 100-year GWP of 25 was recommended in the IPCC AR4 Working Group I report (Forster et al., 2007; Solomon et al., 2007). For the California state GHG inventory, using the current IPCC categories and methods

(IPCC, 2006), current estimates indicate that, similar to the global estimates, landfill CH_4 in 2008 accounted for 1.4 percent of total gross anthropogenic GHG emissions by IPCC category (California Air Resources Board, 2010). The largest single contributors to total anthropogenic GHG emissions in California are Energy Industries (category 1A1) and Transport (category 1A3) at approximately 36 percent each (California ARB, 2010).

In general, the fraction of global anthropogenic GHG emissions (when normalized to CO_2 eq) attributed to landfills has decreased due to relative increases in CO_2 emissions from higher rates of fossil fuel combustion (Rogner et al., 2007), relative improvements in data & models for other sources, decreases in landfilling due to recycling and diversion initiatives, and increases in engineered landfill gas recovery as a locally-important source of renewable energy. Global numbers for landfill CH_4 recovery and utilization are uncertain, but it is generally agreed that a minimum value would be >1100 projects recovering >105 Mt CO_2 eq yr^{-1} based on older survey data (Willumsen, 1993). Currently, there are 519 operational commercial landfill gas-to-energy projects in the U.S. alone [see www.epa/lmop], increasing recovery rates at European landfills, and more projects in developing countries under the Kyoto Protocol Clean Development Mechanism (CDM) [see http://cdm.unfccc.int/Projects]. In California, unpublished data compiled by CalRecycle indicate that more than 90 percent of the waste in place in permitted California landfills is under active gas extraction.

For estimating GHG emissions for global inventory purposes, the IPCC has developed standardized methodologies through the IPCC Task Force on National GHG Inventories [see www.ipcc-nggip.iges.or.jp]. This is an important 4th function of IPCC in addition to Working Groups I-III, which are responsible for the periodic assessment reports and special reports on climate change science (Working Group I), impacts and adaptation (Working Group II), and mitigation (Working Group III). Current methods for estimating landfill CH_4 emissions, and indeed for all sources, are referenced to the latest IPCC National GHG Inventory Guidelines (IPCC, 2006). These guidelines provide a tiered system for reporting GHG emissions for the various sources and provide default values for required parameters if country-specific data are lacking. The U.S. and other developed ("Annex I") countries annually report their GHG emissions to the UNFCCC using IPCC methodologies; however, annual reporting is not required for developing countries. These methodologies are periodically subjected to major revisions (previous version was 1996) and may be adjusted by expert groups convened by the IPCC between major revisions.

For landfill CH_4, the current Tier I (default) method (IPCC, 2006) consists of a spreadsheet-based multicomponent first order kinetic equation which estimates hypothetical CH_4 generation based on the annual quantities and composition of landfilled waste. For individual biodegradable waste fractions, the kinetic equation incorporates a value for the ultimate CH_4 generation potential (mass CH_4 mass $waste^{-1}$) and a kinetic constant (k, in y^{-1}) which has been generally related to assumed climatic conditions (wet/dry, temperate/tropical). The CH_4 generated by each of the biodegradable fractions (food, paper products, garden waste, etc.) in landfilled waste from a particular year is estimated and summed with the estimated CH_4 generation from waste landfilled in previous years. The IPCC terms this methodology a First Order Decay, or FIRST ORDER DECAY, model (IPCC, 2006). Emissions are then estimated by

subtracting the measured CH_4 recovery for a region (e.g., from engineered recovery & utilization systems) and, in developed countries, subtracting 10 percent of the remainder as a default value for CH_4 oxidation in cover materials (based on Czepiel, 1996a). Tier II methods allow a country-specific FIRST ORDER DECAY model, while Tier III methods permit a "validated higher quality method" not necessarily tied to an FIRST ORDER DECAY model.

According to IPCC (2006), uncertainties in national landfill CH_4 emissions using these methodologies range from a minimum of 10-30 percent to greater than 200 percent, depending on whether country-specific waste data or default data were used, as well as the suitability of parameters and methods for individual countries. The uncertainty analysis stresses that "the FIRST ORDER DECAY method is a simple model of a very complex and poorly understood system" (IPCC, 2006). In addition,

- "Decay of carbon compounds to CH_4 involves a series of complex chemical reactions and may not always follow a first-order decay reaction. Higher order reactions may be involved, and reaction rates will vary with conditions" at specific sites.
- Landfills "are heterogeneous. Conditions such as temperature, moisture, waste composition and compaction vary considerably even within a single site, and even more between different sites in a country. Selection of 'average' parameter values typical for a whole country is difficult."
- "Use of the FIRST ORDER DECAY method introduces additional uncertainty associated with decay rates (half-lives) and historical waste disposal amounts. Neither of these are well understood or thoroughly researched."

In spite of these major issues, the IPCC analysis concludes that "it is likely that the main source of uncertainty lies in selection of values for parameters for the model, rather than with the methodology of the [FOD] model itself."

Another major issue is that the FOD model-based estimates for CH_4 generation and emissions, as discussed above, were historically "validated" via comparisons of estimated generation to measured CH_4 recovery. Thus, these models were never validated with respect to field measurements of emissions. Also, as discussed below, field data on landfill CH_4 emissions and oxidation published during the last decade for specific sites span several orders of magnitude and do not correlate well to either modeled generation using an FOD approach or to the calculated residual emissions using an FOD approach with IPCC defaults (subtractions for recovery & 10 percent oxidation).

Moreover, the current IPCC (2006) methodology cites relatively few refereed papers published during the previous decade (1996-2006), a period of many international research projects which directly addressed field measurement of landfill CH_4 emissions and oxidation (e.g., see Scheutz et al., 2009, Bogner and Spokas, 2010, and references cited therein). Starting around 1999 (e.g., Tregoures et al., 1999), the published literature has included comparative field measurements using various techniques for landfill CH_4 emissions in which (a) several techniques were deployed side-by-side at the same sites; and (b) the ability of those techniques to measure

emissions at field scale was evaluated in blind tests via controlled CH_4 releases whose magnitude was unknown to investigators (e.g., see Babillotte et al., 2009 a,b; Spokas et al., 2006). These investigations have indicated the complexity and variability of landfill CH_4 emissions at field scale, as well as the fact that no single technique can be unambiguously recommended for field-scale measurements under all circumstances. All of the techniques that have been investigated [tracer methods using SF_6 and N_2O; eddy covariance and other micrometeorological approaches, static and dynamic chambers, vertical and horizontal radial plume mapping using tunable diode laser (TDL) instruments, and differential absorption lidar (DIAL)] have strengths and weaknesses that must be taken into consideration when planning specific site investigations (Scheutz et al., 2009). It is often recommended that two or more techniques be deployed in tandem for whole site investigations: for example, static chambers are the best choice to measure the variability of emissions across specific cover materials, while the above-ground techniques can, depending on their deployment, include both the emissions associated with various cover materials and fugitive emissions from leakages associated with site operations and maintenance activities (e.g., piping systems; cover "cracks"). All of the above-ground techniques are limited by site-specific constraints that must be addressed during individual deployments. These constraints include variable topography, variable wind speed and direction relative to cell configurations and instrument deployment, and the proximity and magnitude of adjacent non-landfill CH_4 sources (wetlands, wastewater treatment plants, refineries, feedlots).

In California, by legislative mandate, a statewide annual inventory on GHG emissions is conducted by the California Air Resources Board (ARB). The latest inventory (California Air Resources Board, 2010) addressed 2000-2008 emissions. The ARB has generally adopted the most recent IPCC (2006) methodologies for landfill CH_4 and other sources. A major driver for this project to develop a new methodology for landfill CH_4 emissions in California was a review by Farrell et al., (2005), which concluded that an improved inventory methodology for landfill CH_4 emissions in California was a research priority. In response, this project was initiated in 2007 by the California Energy Commission in cooperation with CalRecycle and the ARB. Concluded in 2010, this project has developed a new methodology specifically based on landfill CH_4 emissions rather than hypothetical CH_4 generation. The model developed and field-validated for this project, CALMIM (California Landfill Methane Inventory Model), directly models site-specific annual landfill CH_4 emissions inclusive of seasonal CH_4 oxidation in daily, intermediate, and final cover soils. Importantly, the CALMIM model is consistent with the current IPCC structure as a Tier III "validated, higher quality" method.

During the development of CALMIM, some specific considerations for California landfill CH_4 emissions included:

1. Most of the waste in place in permitted California landfills is under active gas extraction (>90 percent; CalRecycle data); therefore residual CH_4 emissions are expected to be more closely related to the seasonal properties of specific daily, intermediate, and final cover materials than to a hypothetical generation equation;

2. In general, landfill gas extraction systems at California landfills are operated to minimize emissions related to normal operations & maintenance activities. Fugitive emissions related to landfill gas piping and cover irregularities (i.e., cracks) are regularly monitored, detected and remediated on a quarterly basis via surface monitoring of CH_4 concentrations at ground level. As of the writing of this report, under California statewide landfill regulations to be implemented as a result of the passage of Assembly Bill 32 (The California Global Warming Solutions Act of 2006), new surface monitoring requirements will revise the current rigorous South Coast Air Quality Management District (SCAQMD) Rule 1150.1 monitoring techniques with statewide reduced methane concentration limits and concurrent leak checks on gas collection & control systems. Therefore, these types of fugitive emissions, which are remediated on a quarterly basis as part of normal operations, are not considered in the context of an annual inventory method. This is a difference between current regulatory methods and annual inventory methods.

3. California has a strongly seasonal wet-dry climate in most parts of the state; thus, distinctive seasonal trends in methane oxidation would be expected to drastically affect residual methane emissions at California landfills and should be included in an annual inventory model. The inclusion of seasonal trends is consistent with recent literature for a wide range of ecosystems (e.g., Treat et al., 2007; Turetsky et al., 2008; Fumoto et al., 2008) which recognizes the strong seasonality of emission trends and supports a linkage with climatic and soil microclimate trends over an annual cycle.

With respect to the CALMIM methodology, it is important to emphasize that this methodology is designed for annual inventory reporting of landfill methane emissions. This inventory methodology is not intended to replace methodologies developed for other purposes, including: (a) methods required under current local, state, and Federal regulations, and (b) methodologies for monetization of greenhouse gas offset credits at sites where landfill methane recovery, destruction, and utilization is "additional" to mandated recovery under regulatory requirements. Especially with respect to regulatory methods, annual greenhouse gas inventory methods require certain simplifications, as these are typically applied on a national or regional basis once a year for large numbers of diverse sites. It is neither feasible nor desirable to incorporate shorter-term operational issues as required by regulatory methods, especially since those methods also require mitigation for non-compliance over timescales much shorter than a year. From a scientific perspective, both regulatory and inventory methodologies can benefit from periodic revisions based on advances in scientific understanding through basic and applied research.

As a follow up to this project, we anticipate that there will be a potential implementation between the Air Resources Board, other California agencies (CalRecycle, Energy Comission), and stakeholders from the solid waste and environmental communities with respect to CALMIM and the implementation of this improved methodology within the state GHG inventory process. Implementation of the CALMIM model has the potential for greatly-improved site-specific quantification of landfill CH_4 emissions for future California inventories. In addition, the application of this model can assist with better definition of landfill CH_4

emissions relative to other sources in the context of other ongoing California research activities related to improved quantification of emissions (e.g., Zhao et al., 2009). Finally, via follow-up activities, we anticipate that future field validation projects external to California could guide the implementation of this methodology in the U.S. and abroad as an improved, science-based, user-friendly IPCC Tier III method.

1.2 Technical Background and Justification of CALMIM Approach

In this section, we will first provide a brief overview of existing modeling approaches and strategies; secondly, address some limitations of the FOD approach for landfill CH_4 emissions; and thirdly, describe the technical approach for this project. The CALMIM model is the first to decouple landfill CH_4 emissions from a first order kinetic equation for CH_4 generation by directly modeling the processes which control emissions, namely, the properties of the cover materials, the presence or absence of engineered gas extraction, and seasonal methane oxidation in landfill cover soils. Therefore, CALMIM directly models emissions inclusive of seasonal oxidation on a site-specific basis and, unlike the FOD model approach, has been field-validated for its application to emissions.

At the global level, the most comprehensive estimates of climate change have historically relied on general circulation models (GCMs) and earth system models (ESMs); however, these have limited ability to assess "aggressive" future emissions reduction policies (Huntingford et al., 2009), especially for multiple GHGs at regional levels. The atmospheric chemistry models require the specification of emissions as boundary conditions, and in preparation for the IPCC 5th Assessment Report (AR5), there has recently been a concerted effort to harmonize existing databases (such as EDGAR, RETRO) for gridded emissions estimates for 40 regions and 13 sectors from 1850-2100 (Lamarque et al., 2009). In addition, techniques such as variable resolution GCMs are being investigated, as well as limited area models (LAMs) for dynamic downscaling through several coordinated projects, including the North American Regional Climate Change Assessment Program (NARCCAP), Ensemble-Based Predictions of Climate Changes and Their Impacts (ENSEMBLES), and the Coordinated Regional Climate Downscaling Experiment (CORDEX) (Rauscher and Ringler, 2009). For emission estimates for specific GHGs such as CH_4, one can rely on either "top down" or "bottom up" strategies. The "top down" strategies focus on inverse methods for partitioning the atmospheric CH_4 mixing ratio to various sources (e.g., Bergamaschi et al., 2005; Kort et al., 2008), while "bottom up" approaches focus on measurement and modeling of individual contributing sources (e.g., Walter and Heimann, 2000, for CH_4 from wetlands; Fumoto et al., 2008, for rice systems). For CH_4, a major difficulty is the complexity of multiple CH_4 sources at local and regional scales. In preparation for the AR5, the Atmospheric Chemistry and Climate Initiative (AC&C) is aiming to improve modeling of atmospheric chemistry-climate interactions for aerosols, tropospheric ozone, CFCs, N_2O, and CH_4, including critical comparisons with observational data sets (Doherty et al., 2009). Historically, there have been few regional "top down" studies which have included landfill CH_4—for example, a 'top-down' study for sources of atmospheric CH_4 in London used stable carbon isotopes to model the relative contribution of several potential sources, including landfill CH_4 (Lowry et al, 2001). Recently, for central California, Zhao et al.,

(2009) included landfill CH_4 in a study which involved the comparison of a three-month time series of CH_4 mixing ratio measurements from a tall tower (500 m) with three inverse model estimates for regional surface emissions of CH_4 in central California. Difficulties with regional modeling of landfill CH_4 include the dispersed nature of individual landfill sources and the complexity of multiple CH_4 sources in most areas, including wide ranges in emission rates and overlapping isotopic signatures with other sources. Generally speaking, there is much research yet to be done to better harmonize top-down and bottom-up approaches for CH_4 from various sources at the local and regional scale. With respect to landfill CH_4 specifically, the site-specific processes of oxidation and net emissions are largely controlled by soil biogeochemistry relative to seasonal climate; thus landfill soil systems can be considered a more intensively-engineered endpoint to natural wetland ecosystems and managed agricultural systems (Bogner et al., 2000).

Figure. 1 provides a landfill CH_4 mass balance as a framework for more detailed discussion justifying an emissions-based model as a substantial improvement over an FOD model-based approach. In general, for a landfill cell,

CH_4 generation = Σ (CH_4 recovery + CH_4 oxidation + CH_4 emissions + CH_4 migration

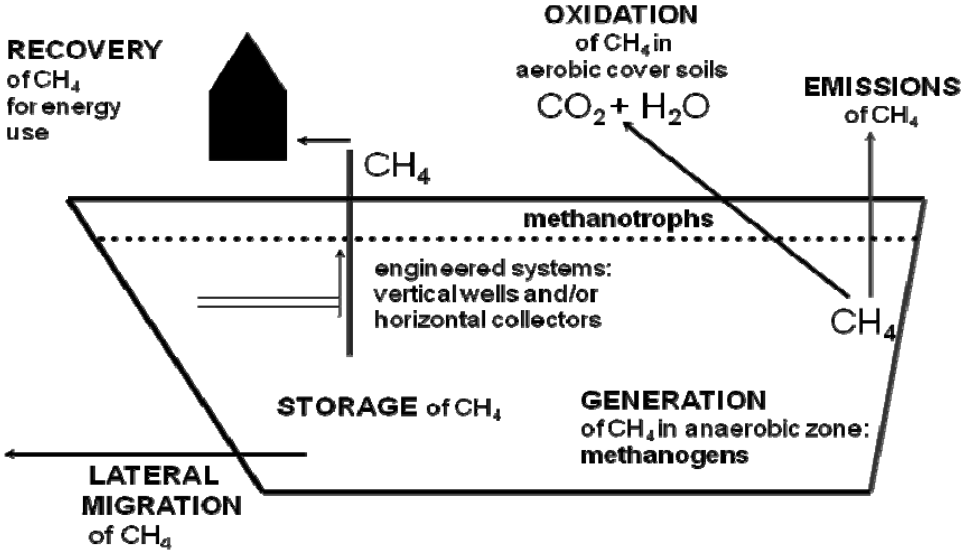
+ Δ CH_4 storage).

Units = mass t^{-1} (Bogner and Spokas, 1993).

As shown above and in Figure 1, it is important to emphasize out that there are several pathways for the CH_4 generated in a landfill cell, only one of which is emissions. Using methods described in IPCC (2006) and discussed above, the Tier 1 FOD Model estimates landfill CH_4 generation based on annual solid waste generation and composition, the fraction landfilled, and the fraction landfilled that is expected to biodegrade anaerobically yielding CH_4. In general, the IPCC (2006) FOD methodology for emissions is based on a simplified mass balance where the emissions are estimated using the modeled generation minus the measured recovery, plus a further 10 percent reduction for oxidation.

Landfills are not optimized laboratory systems nor homogeneous, highly-controlled anaerobic digestors where a theoretical kinetic equation can be realistically applied. When solid waste is

Figure 1. Landfill CH4 mass balance. Modified from Bogner and Spokas (1993).



Landfill methane mass balance:

CH_4 generated = Σ (CH_4 recovered + CH_4 emitted + CH_4 oxidized + CH_4 migrated + Δ CH_4 storage)

[units = mass/time]

buried in a landfill, the biodegradable fractions decompose via a complex series of microbial reactions under non-optimized anaerobic conditions. These fractions include readily degradable food waste, more slowly degradable paper (cellulosic) wastes, and garden or commercial wastes containing slow to rapidly degradable components. In developed countries, landfilled solid waste typically contains total biodegradable components of 60-75 percent (w/w) with degradable organic carbon (DOC) of approximately 15-25 percent (w/w) (Bingemer and Crutzen, 1987). Major intermediate products during decomposition include acetic acid (CH_3COOH), other carboxylic acids, carbon dioxide (CO_2), and hydrogen (H_2). The terminal reaction is the production of CH_4 by methanogenic microorganisms via either acetate cleavage or reduction of CO_2 with H_2. As a result of these two pathways, landfill gas consists of 50-60 percent CH_4 (v/v) with the remainder primarily CO_2 (Bogner et al., 1996). If decomposition reactions proceed at optimized rates, then the mass of CH_4 would be expected to directly depend on the mass of DOC landfilled, i.e., the waste composition. Bingemer and Crutzen (1987), in the first, and highest, global estimate of landfill CH_4 emissions, assumed that 0.77 of the landfilled DOC was "dissimilated", that is, anaerobically converted to biogas carbon (CH_4 and CO_2). This was based upon a temperature-dependent equation for optimized low-solids anaerobic decomposition for *wastewater* and, using a typical waste DOC composition for developed countries, was equivalent to a CH_4 yield of 0.10 kg CH_4 kg^{-1} (dry) solid waste. The theoretical maximum CH_4 yield, based upon an empirical equation for U.S. solid waste composition, is approximately 0.18 kg CH_4 (dry) kg^{-1} solid waste (Halvadakis et al., 1983). In

contrast, optimized laboratory studies of solid waste decomposition from the U.S., Germany, and Italy have shown that the dissimilated DOC fraction ranges from negligible to a maximum of 0.25 – 0.47 (Table 4, Bogner and Spokas, 1993), which is equivalent to maximum yields of 0.04 – 0.08 kg CH_4 kg^{-1} (dry) solid waste. Methane yields in field settings are lower; indeed, Richards (1989) assumed a yield of 0.036 kg $CH_4 \cdot kg^{-1}$ (dry) solid waste, based on commercial landfill CH_4 recovery data. Other sources in the literature have proposed CH_4 yields ranging from 0.07 – 0.13 kg $CH_4 \cdot kg^{-1}$ (dry) solid waste (Kura and Lee, 1995; Li et al., 1999). Eleazer et al. (1997), in a laboratory investigation of the anaerobic biodegradability of individual waste components concluded that, although there was a general relationship between carbohydrate (cellulose + hemicellulose) composition and total CH_4 yield in these optimized laboratory systems, there were confounding factors which precluded a quantitative relationship.

In addition to CH_4 yield, a second major issue is realistically proportioning the theoretical CH_4 generation, first, over the 20-30 year time period during which most of the anaerobic decomposition is expected to occur using a single kinetic constant (k), and secondly, estimating the partitioning to other known pathways, as shown in the equation above. It is well known that CH_4 generation can begin in landfilled waste within a few weeks of burial. When an FOD equation is used to calculate landfill gas production from the quantity of solid waste landfilled in a given year, integrated with the landfill gas production from solid waste in previous years, this approach presumes that the quantity and composition of landfilled waste as well as a rate constant can be reasonably well-defined and that field conditions are homogeneous. This is not the case in field settings.

In addition, historically, the FOD/first order kinetic equations were originally developed and have been used for predictive purposes for gas recovery since the earliest days of commercial projects in southern California in the mid-1970s. Typically, any modeling done pre-recovery was then fine-tuned post-recovery to match actual production data. The first FOD models were all developed for site-specific application to model future trends for commercial gas recovery systems (i.e., Palos Verdes Model; Scholl Canyon Model; see EMCON, 1980). It is also extremely important to emphasize that the FOD model approach has been historically validated only with respect to recovery, not to emissions, using site-specific studies where detailed waste input data were available (Reinhart et al., 2005). The most comprehensive study of this type was completed in the Netherlands during the 1990's and assisted with the validation of the IPCC FOD model. A series of first order generation equations (single component to multi-component with respect to waste composition) were compared to actual gas production at 9 landfills with well-defined waste composition, concluding that a multi-component first order model best predicted rates ± 30 percent of actual CH_4 generation (Coops et al., 1995; Oonk et al., 1993; Scheepers and van Zanten, 1994). Moreover, the U.S. EPA LandGEM model, a single component FOD model used in the U.S. for default landfill gas generation and emission calculations for air quality compliance, was also originally validated using landfill gas recovery data (US EPA, 2005; Peer et al., 1993). In general, at that time, there had been few published field measurements of landfill CH_4 emissions inclusive of oxidation; therefore, there was also little understanding of the wide dynamic range of rates for these processes in field settings.

Since landfill CH_4 production and oxidation are both microbially-mediated processes, their rates in field settings can vary by several orders of magnitude, exacerbating the problem of developing credible regional estimates. Indeed, published reviews of field and laboratory data have shown that "net" landfill CH_4 emission rates inclusive of oxidation can vary by 6 orders of magnitude (Bogner et al., 1997a; Scheutz et al., 2009). Much of the variability in emissions is, in turn, related to seasonal variability in the physical properties of cover soils (moisture, temperature) which also affect seasonal oxidation rates. In general, compared to natural and managed ecosystems (e.g., Treat et al., 2007; Turetsky et al., 2008; Fumoto et al., 2008), there have been few multi-year field campaigns for landfill CH_4 emissions, so reliable models based on latitude, climate, soils, and soil microclimate do not currently exist which are capable of predicting seasonal emissions inclusive of oxidation. Therefore, one of the major goals of this project was to incorporate seasonal CH_4 oxidation into the first such model for California.

Historically, during the development of the current project, we began with the mass balance equation shown in Figure 1 and the 2006 IPCC Tier I FOD method with the idea that we would focus on improving the CH_4 mass balance framework for the new California inventory methodology for landfill CH_4 emissions, especially with respect to seasonal oxidation. However, a review of the literature and, indeed, application of the FOD model to our two field validation sites precluded this approach. The current (2009) measured CH_4 recovery at both Scholl Canyon and Marina greatly exceeded modeled generation using the IPCC Tier I FOD model with site-specific waste input data and regional California waste composition data.

To summarize the major issues precluding reliance on an IPCC Tier I (FOD model-based) approach:

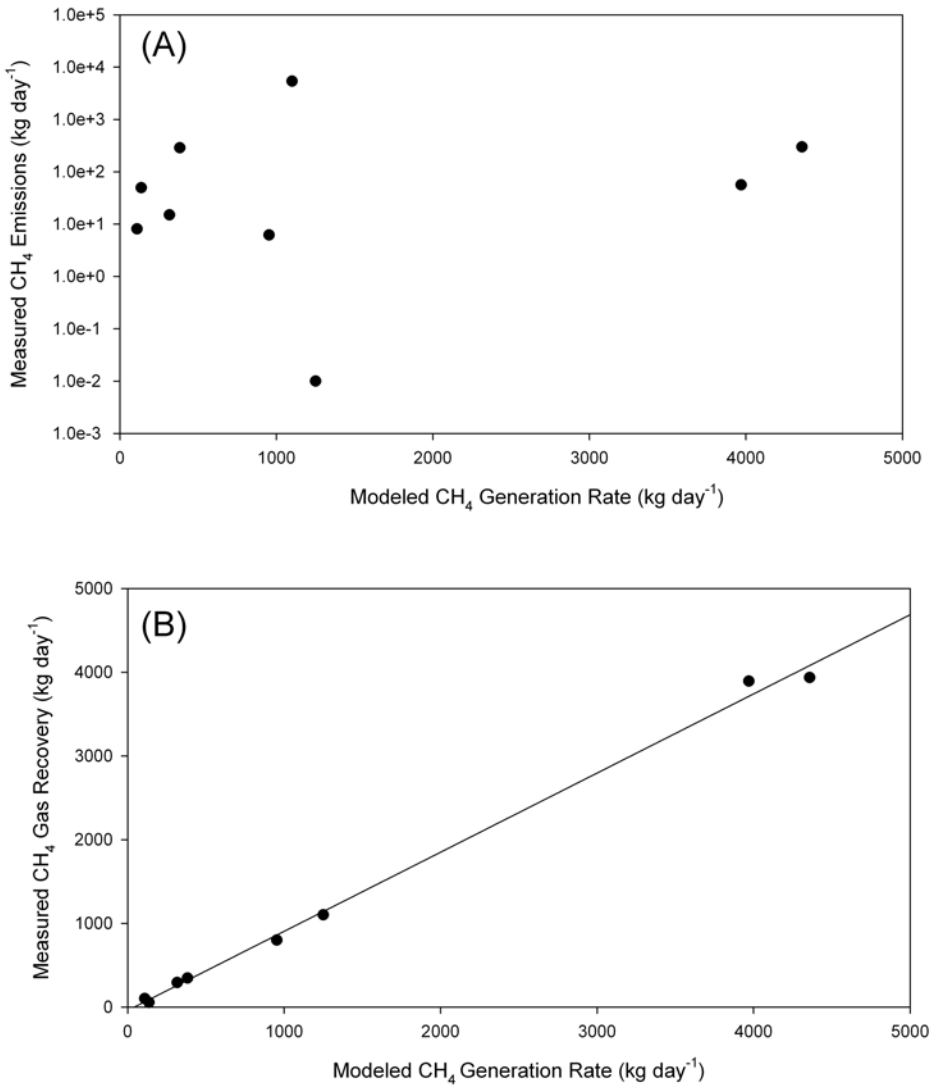
- The FOD model assumes a well-mixed optimized anaerobic digester with homogenous degradation rates inconsistent with field data, as well as with forensic field experience indicating variable decomposition during installation of gas recovery wells.
- The FOD model approach was originally developed as a predictive tool for site-specific landfill gas recovery projects during the early days of that technology (mid 1970's). This approach was never field-validated for either generation or emissions, only for recovery, with model parameters typically adjusted at specific sites so that models matched recovery history and could assist with future predictions.
- The Tier I approach does not include the effect of any cover materials to limit emissions (and promote anaerobic conditions) but nevertheless assumes a uniform 10 percent methane oxidation in cover materials (based only on Czepiel, 1996a, for annual oxidation at the 17 ha Nashua, NH landfill).

There have been few studies which have intensively studied CH_4 pathways at field scale (as shown in Fig. 1). However, as shown in Fig. 2, we can replot data from an existing study to support the decoupling of emissions from a generation model. This study (Spokas et al., 2006) was conducted over several years at 7 full-scale cells at 3 French landfills. All of the CH_4 pathways shown in Fig. 1 were measured using field data, with the exception of CH_4 generation which relied on the Dutch multicomponent model which later became the basis of the IPCC Tier

I model. Because this study was done for specific cells, there was good information regarding waste inputs and composition as the basis for the FOD modeling. As shown in the Figure (2a), and consistent with the original purpose of the FOD models, there was an excellent linear correlation ($r^2 = 0.997$) between modeled CH_4 generation and measured CH_4 recovery. However, with respect to CH_4 emissions (2b), which were measured using both an above-ground tracer method and a chamber method, there was no relationship between measured CH_4 emissions and modeled CH_4 generation. Indeed, the residual emissions varied by several orders of magnitude, with the highest value representative of the one cell without active gas extraction.

In general, the single most important factor for reduction of emissions is the installation of engineered gas recovery (Bogner et al., 1997a). Active gas extraction lowers the CH_4 concentration at the base of the cover materials so that diffusive flux is reduced. This effect is, to some extent, related to the proximity of gas wells to the point of monitoring (Bogner et al., 1997b). At sites without engineered gas recovery, typically the CH_4 concentration in soil gas at the base of the cover materials is in the range of 40-60 percent CH_4 v/v. Where there is no gas recovery, this concentration, and indeed the driving force for diffusive flux (the concentration gradient across the cover materials) is the same, regardless of whether there is 10 m of waste below the cover or 50 m of waste below the cover, indicating that the mass of waste in place is not the major driving force for emissions (via an FOD model). More importantly for California, with high rates of landfill gas recovery, emissions are related to physical and biochemical processes within landfill cover soils, including both the basic physical retardation effect of the cover to limit emissions to the atmosphere and seasonal CH_4 oxidation rates in those cover materials. Historically, the 10 percent allowance for annual oxidation can be referenced back to the first study in the literature which estimated seasonal and annual oxidation. In that study, a climatic model was used in combination with field measurements of methane emissions at the Nashua, NH landfill, a 17 ha site without active gas extraction at the time of the emissions measurements. The field measurements were extended by laboratory incubations of cover materials to determine an annual methane oxidation rate of 11 percent, taking into consideration the seasonal variability in soil moisture and temperature (Czepiel et al., 1996a, b). A variety of more recent laboratory and field studies have indicated oxidation rates over various timeframes that are significantly higher than 10 percent. In particular, a recent literature review reported that the average percent methane oxidized in cover soil was 35 ± 6 percent across a variety of latitudes (Chanton et al., 2009). Therefore, field and laboratory measurements reported in the international literature over the last decade have improved our scientific understanding of landfill CH_4 oxidation and laid the groundwork for the development of CALMIM as an improved inventory method inclusive of seasonal oxidation.

Figure 2. Comparison of predicted (modeled) CH4 generation to: (A) measured surface emissions and (B) measured landfill gas recovery rates. Data from seven full-scale field cells as described in Spokas et al. (2006). The r2 for the linear regression shown in Figure 2 (b) is 0.997.



1.3 Project Goals and Overview of Model and Methods

The purpose of this project was to develop an improved field-validated landfill CH_4 inventory model for California (CALMIM). In general, we have relied upon well-researched and accepted

theoretical relationships, previous field and laboratory studies (Spokas et al., 2003, 2006; Bogner et al., 1997b, 1999, 2010; Scheutz et al., 2003; Liptay et al., 1998; Chanton and Liptay, 2000) existing globally-validated U.S. Dept. of Agriculture models (Spokas and Forcella, 2006, 2009), and extensive supporting laboratory studies on CH_4 oxidation completed for this project using California landfill cover soils. As discussed in subsequent sections of this report, field validation was conducted over two years at two California sites, including the coastal Marina Landfill (Monterey County, CA) and the Scholl Canyon Landfill (Los Angeles County, CA). Additional limited field validation at the Lancaster, Kirby Canyon, and Tri-Cities Landfills was made possible through the cooperation of Waste Management, Inc., including field measurements of CH_4 emissions using both static chambers and an above-ground method employing a TDL (tunable diode laser) instrument for vertical and horizontal radial plume mapping (Green et al., 2009).

CALMIM is a JAVA-based web tool for site-specific methane emissions from landfills based on the respective areas of daily, intermediate, and final cover materials, plus the extent of active gas extraction. The major change from the IPCC Tier I default method is that CALMIM decouples the emissions process from a landfill gas generation model, thus moving up to the top of the landfill to directly model emissions inclusive of seasonal oxidation.

CALMIM is an IPCC Tier III model (IPCC, 2006) with four (4) major integrated components:

(1) Inventory Template;

(2) Meteorological Model;

(3) Soil Microclimate Model;

(4) 1-D Emissions/Oxidation Model.

With regard to (1), a data template inclusive of the major California cover types, ADCs (Alternative Daily Covers), and a customized "cover designer" was developed by the project team and reviewed by the Dept. of Resources Recycling and Recovery and the Air Resources Board. Because the major controls on landfill methane emissions are the thickness and properties of the cover materials and the implementation of active landfill gas extraction, the model requires site-specific input data. Required inputs include the area of each type of cover material (daily, intermediate, and final) and whether active landfill gas extraction is currently in place for each type of cover material (as percent of area). A customized "cover designer" also permits any layered sequence of cover materials, including geomembrane composite cover designs. An objective of the project was to facilitate data input by users and minimize the site-specific information requirements to the most pertinent data needed for this inventory. Site locations can be queried by name and are linked to the California SWIS (Solid Waste Information System) database. With regard to (2) and (3), the meteorological and soil microclimate models rely on modified versions of the following USDA models: Global TempSIM, Global RainSIM, Solarcalc, and STM^2 (Spokas and Forcella, 2006, 2009). In particular, the soil temperature functions for STM^2 (Soil Temperature and Moisture^2) were modified to accommodate the landfill heat source. For air temperature, the latitude and longitude of the site

are used to extrapolate the daily climatic conditions from an interpolated database based upon 30-yr (1961 – 1990) air temperature records. These records were previously compiled and interpolated by Legates and Willmott (1990a and 1990b) with further improvements by Willmott and Matsuura (1995). Diurnal temperature ranges were interpolated from monthly averages from data collected 1961-1990 and cross-validated by New et al. (1999). Average precipitation was also extrapolated from the average number of days in a month with rainfall as compiled and interpolated by Legates and Willmott (1990a and 1990b) with further improvements by Willmott and Matsuura (1995). Average monthly precipitation was taken from the interpolated data collected 1961-1990 and cross-validated by New et al. (1999). With regard to (4), the emissions model is based on 1-D bidiffusional flux of CH_4 and O_2 through cover materials where the driving force is the gas concentration gradient through the gas-filled pore space (Campbell, 1985). Finally, seasonal methane oxidation is modeled through the use of scaled results relative to temperature and moisture based on extensive laboratory batch incubations of California landfill cover soils, as well as literature cited in Chapter 2.

Field validation included extensive measurement of CH_4, CO_2, and N_2O emissions on daily, intermediate, and final cover materials at the Marina and Scholl Canyon sites in dedicated field campaigns during March and August of both 2007 and 2008. The wet (March) and dry (August) field campaigns consisting of more than 800 fluxes relied on static chamber techniques (Rolston, 1986), which is the method of choice for quantifying the variability of emissions (including both CH_4 emissions and uptake of atmospheric CH_4) across a particular cover soil. Meteorological variables and soil moisture/temperature profiles were continuously monitored during 2007-2008. The field measurements at Marina and Scholl Canyon were supplemented by static chamber and TDL data at Lancaster, Kirby Canyon, and Tri-Cities through the supporting Waste Management data. The fractional CH_4 oxidation in field studies at all 5 sites was quantified through the use of stable carbon isotopic methods developed by Chanton and colleagues (Liptay et al., 1998; Chanton and Liptay, 2000; Chanton et al., 2008) which rely on the temperature-dependent preference of methanotrophs for the isotope of smaller mass (^{12}C).

Supporting laboratory studies included batch incubations of daily, intermediate, and final cover materials from Marina and Scholl Canyon. Methane oxidation rates were determined using a time series based on the decrease in headspace CH_4 and were related to CH_4 exposure history and the full range of temperature and moisture conditions, including diurnal temperature fluctuations (>2000 incubations).

The following chapters of this report (Chapter 2-4) consist of detailed descriptions and discussion of the laboratory (Chapter 2), field (Chapter 3), and modeling (Chapter 4) aspects of this project. As discussed with CEC, those chapters (2-4) consist primarily of manuscripts submitted to refereed journals; thus there is some repetition between the background sections in these respective chapters. Chapter 5 provides a project summary and future research recommendations. Appendices to this report include: the CALMIM user manual; the published version of Chapter 2 (Spokas and Bogner, 2010); and all of the field, laboratory, and modeling data for this project. Those data are organized, first, according to field site, and, secondly, according to the type of data (field, laboratory, or model output).

CHAPTER 2:
Laboratory Studies. Limist and Dynamics of Methane Oxidation in Landfill Cover Soils

2.1 Introduction

Aerated soils represent the only identified biological sink for atmospheric methane (CH_4). The highest CH_4 oxidation rates have been observed in aerobic soils with elevated levels of CH_4 (Adamse et al., 1972; Le Mer and Roger, 2001). Of particular importance is the attenuating effect that microbial CH_4 oxidation has on reducing fugitive CH_4 emissions from landfill cover soils. Landfill surface emission measurements quantify the net result of CH_4 transport from the anaerobic waste and methanotrophic oxidation through aerobic cover soils. Field data have also documented that point measurements of both CH_4 emissions and oxidation can vary over 6 orders of magnitude (e.g. Bogner et al., 1997a). The potential range of percentage oxidation in landfill soils spans from negligible to more than 100 percent, with an average value of around 40 percent estimated with current methodologies (e.g. Bogner et al., 1997b; Börjesson et al., 1997; Chanton et al., 2009).

Landfill cover soils experience large temporal variability in soil temperatures, soil moisture, and CH_4 soil gas concentrations (from approximately 500 ml l^{-1} to sub-atmospheric levels of <1.8 μl l^{-1}). All of these environmental factors can drastically affect the oxidation capacity of the soil microbial communities and impact observed landfill CH_4 emission rates. It should be noted that soil properties, such as nutrient availability and pH, also impact oxidation rates (e.g. Albanna et al., 2007). The challenge is to develop an improved understanding of the ultimate soil oxidation capacity relative to the temporally-changing environmental conditions.

The literature indicates that fluctuating gradients of soil moisture and temperature are largely responsible for the observed dynamic range in landfill CH_4 oxidation capacities (Kallistova et al., 2005). In addition to other impacts, changes in temperature affect the rate of CH_4 oxidation (e.g. Czepiel et al., 1996a) as well as the composition and biodiversity of CH_4-oxidizing consortia (e.g. Mohanty et al. 2007). Temperature is also an important variable when selecting conditions for laboratory oxidation studies (e.g. Schnell and King, 1996; Börjesson et al., 2004). Soil moisture controls on CH_4 oxidation have been suggested as a major controlling factor in numerous studies (e.g. Gebert et al., 2003; Jugnia et al., 2008). In forest soils, soil moisture is a primary variable affecting CH_4 oxidation rates, where 78 percent of the variability in CH_4 oxidation rates has been correlated to soil moisture variability (Castro et al., 1994).

To date, the majority of studies examining the impact of soil moisture on CH_4 oxidation rates in landfill cover soils are expressed in terms of gravimetric or volumetric moisture contents, thereby further complicating the comparison between soils of differing textures (Zeiss, 2006). Soil texture and structure ultimately control moisture availability (Hillel, 1980). By utilizing soil moisture potential, which expresses soil moisture in terms of the physical force with which water is held in soil, the differences in soil texture and structure can be normalized. At a given soil moisture potential (e.g. 33 kPa; field capacity) the behavior of soil water is equivalent in

soils of different texture and structure, even though the gravimetric and volumetric moisture contents of those soils will be different. Thus, soil moisture potential is the preferred measure when examining microbial moisture limitations (Griffin, 1981). However, relationships between soil moisture potential and CH_4 oxidation rates (particularly for landfill cover soils) have not been elucidated (Mancinelli, 1995).

Furthermore, impacts of the CO_2 present in landfill gas and its corresponding effect on CH_4 oxidation rates has not been addressed for landfill settings. Current literature for non-landfill settings reports conflicting results. Phillips et al. (2001) observed a suppression of 16−30 percent in CH_4 uptake in forest soils continuously enriched with CO_2 at 200 μl l^{-1} above ambient levels. However, other studies have shown no effect of the enriched levels of CO_2 (up to 700 ul l^{-1}) on microbial CH_4 oxidation rates (e.g. Zak et al., 2000). In general, oxidation rate responses to low levels of CO_2 enrichment have been inconsistent (Sadowsky and Schortemeyer, 1997). On the other hand, elevated CO_2 concentrations (>2 ml l^{-1}) have been linked to significant suppression of microbial respiration rates (e.g. Macfadyen, 1973; Dixon and Kell, 1989; Koizumi et al., 1991). Sierra and Renault (1995) reported that microbial O_2 consumption in soil aggregates was inhibited by CO_2 levels higher than 40 ml l^{-1} (4 percent). Due to the fact that there are often soil gas CO_2 concentrations higher than 40 ml l^{-1} in landfill cover soils, CH_4 oxidation activity could be suppressed. However, no specific study exists examining the impacts of the elevated CO_2 concentrations (>50 ml l^{-1}) on CH_4 oxidation rates.

The purpose of this manuscript is to document the variability and dependencies observed in CH_4 oxidation rates as a function of soil temperature (including diurnal temperature fluctuations), soil moisture, and CO_2 concentrations. We especially focused on the moisture threshold requirements for CH_4 oxidation using soil moisture potential for six different California landfill cover soils. The study was part of a larger project which is developing improved field-validated inventory methods for landfill CH_4 emissions inclusive of oxidation for the California greenhouse gas (GHG) inventory.

2.2 Materials and Methods

Six different cover soils were collected from two California landfills for laboratory incubation studies. The two landfill sites were the coastal Marina Landfill (Monterey, CA USA; 36.71°N 121.762°W) and the inland Scholl Canyon Landfill in the Los Angeles area (Glendale, CA; 34.158°N 118.196°W). Soil was collected from each of the cover types typically used at each site: daily, intermediate and final cover areas. Marina uses onsite soils as well as composted sewage sludge and green waste for their cover materials. Both surface and subsurface (profile) samples were collected. Profile samples were collected with a hand auger (AMS Inc.; American Falls, ID) at 10 cm intervals, and surface samples (0-10 cm) were collected using shovels and hand trowels. Sampling depth at the Scholl Canyon site was limited due to the excessive compaction and high density of the cover soils. The intermediate and final covers at Scholl canyon could not be sampled with a soil corer, so these were collected using a pick axe, which limited the sample depths. All soils were stored at collected moisture state and in the dark at 4°C. Soil was sieved to 2 mm and mixed to ensure homogeneity prior to initiating incubations. Soil pH was measured in a 1:1 soil:deionized water (v:v) slurry. Other soil analyses were completed using

reference methods (Black et al., 1965) by A&L Midwest Laboratories (Omaha, NE). Supplemental soil properties are given below in Table 1.

For the profile samples, all incubations were conducted at 25°C at two different moisture contents: as collected and at field capacity. These incubations were used to document the distribution of initial CH_4 oxidation activity through the cover and examine the effect of the pre-incubation conditions on the observed CH_4 oxidation rate.

Table 1. Chemical and physical properties of the landfill cover soils in this study.

	Marina			Scholl Canyon		
Cover Type	Daily	Intermediate	Final	Daily	Intermediate	Final
Total Cover Thickness (m)	0.3	0.5	2.5	0.3	0.75	2.7
Surface Soil Properties (0-10 cm)						
Sand (%)	82	74	76	84	60	60
Clay (%)	12	10	10	4	14	14
United States Department of Agriculture Soil Type	S	SL	SL	S	SL	SL
Surface Bulk Density (g cm^{-3})	1.35	1.6	1.4	1.6	2.0(*)	2.0(*)
Field Collected Gravimetric Moisture Content (% w/w)	3.5	2.4	13.5	3	1.5	1.5
% Organic Matter	0.5	2.2	3.9	2.0	0.4	0.9
% Nitrogen	0.17	1.53	4.6	0.92	0.58	0.65
pH (1:1)	7.4	7.8	6.7	7.4	8.3	8.2

Notes: (*) Excavation method – results may be biased by the high percentage of gravel (>4mm) present in the cover soil. S represents "sand" and SL represents a "sandy loam" United States Department of Agriculture soil types.

2.2.1 Soil Moisture Retention Curves for Sieved Soils

Soil moisture retention curves were determined using standard pressure plate methods (Soil Moisture Equipment, Santa Barbara, CA; Richards and Fireman, 1943). Since the soil moisture characteristic curve is highly dependent on soil structure, the values acquired here are solely representative of the sieved soils. Briefly, sieved soil was repacked into aluminum cylinders 3.0 cm high and 5.0 cm in diameter. Repacked bulk density was 1.2 ± 0.2 g cm^{-3}. Samples in the cylinders were saturated by soaking them in a plastic tray with the water level just below the top of the cylinders. Samples were soaked for 5 days to saturate and minimize the presence of entrapped air bubbles. After wetting, soil samples were placed in contact with the porous plate inside a pressure chamber and a known air pressure was applied. For this study, the pressures examined were 0, 33, 50, 100, 500, 700, 1000 and 1500 kPa (saturated, 0.33, 0.5, 1, 5, 7, 10 and 15 bar, respectively). All samples were run in triplicate. As mentioned previously, the soil moisture potential allows a normalized expression of soil moisture behavior across soils with various textures.

2.2.2 CH_4 Oxidation Incubations

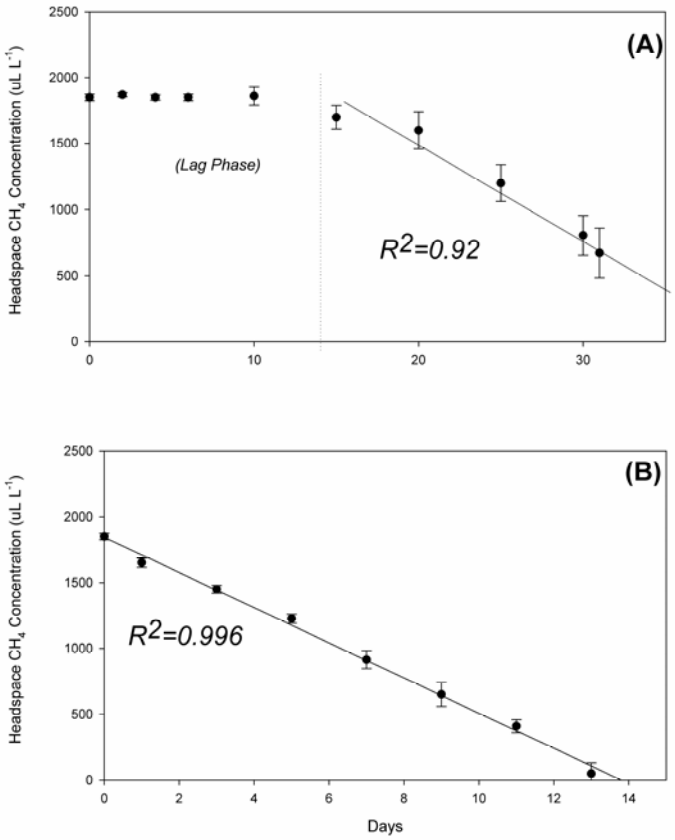
Prior to initiating the oxidation rate incubations, soil was pre incubated for 60 days in the presence of 50 ml l^{-1} CH_4 at each selected soil moisture potential. This is in agreement with other studies which have utilized 50 ml l^{-1} CH_4 in the headspace for 30 to 60 days (e.g. Kightley et al., 1995; Amaral et al., 1998). Previous work has observed that a 60 day period is sufficient to induce CH_4 oxidation activity in previously non-CH_4 consuming soils (Amaral et al., 1998). Soils were pre-incubated in 1 l plastic containers (Nalgene; Rochester, NY #2103-0032) with 200 g of soil per container with the 50 ml l^{-1} CH_4 replaced weekly in the headspace. These pre-incubations remained aerobic (>180 ml l^{-1} O_2). The soil moisture was modified to the desired soil moisture potential based on the repacked soil moisture retention curves (see Figure 4) and corrected weekly for evaporative loses. In addition, initial oxidation assessments were carried out on soil samples without a pre-incubation period (see Table 4), and assessments with a pre-incubation period of 60 days without soil moisture adjustments in the presence of 50 ml l^{-1} CH_4 were also completed.

For each incubation, five grams of pre-incubated soil (oven-dry equivalent) were then transferred to a 125 ml serum vial (Wheaton Glass, Milville, NJ) and sealed with red-butyl rubber septa (Grace Davison, Deerfield, IL) and an aluminum crimp. Next, 5 ml of enclosed headspace were removed and 5 ml of 50 ml l^{-1} CH_4 in argon was injected through the septum, bringing headspace CH_4 concentration to approximately 2 ml l^{-1}. This concentration was the average CH_4 concentration observed at 10 cm. The serum vials were then incubated at the desired temperature (with the soil already at the desired soil moisture potential). In all, thirteen temperatures (-5, 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60 and 70°C) and eight different soil moisture potentials (0, 33, 50, 100, 500, 700, 1000 and 1500 kPa) were chosen for this study. A total of 3744 individual incubations (6 soils x 6 replicates x 8 different moistures x 13 different temperatures) were established to examine the impacts of temperature and moisture on the observed CH_4 oxidation rates. Methane oxidation was determined by monitoring the change in CH_4 concentration in the headspace during periodic sampling (described below). Depending on the observed rates of oxidation, incubations were conducted for 3 to 75 days. Rates of CH_4 oxidation were quantified by the linear decrease in headspace concentration with time (Figure 3). These zero-order rate calculations are justified based on the observed linear decreases in CH_4 headspace concentrations (Figure 3B) as well as other studies which have utilized zero-order reaction rates (e.g. Börjesson et al., 2004; Spokas et al., 2007).

In order to compare the impact of temperature on CH_4 oxidation across all six cover soils at the eight different moisture potentials, normalized CH_4 oxidation rates were used. This normalized rate (ranging from 0 to 1) was calculated by dividing all the incubations for a particular soil by the maximum CH_4 oxidation rate observed for that particular soil for each of the respective soil moisture potentials evaluated. By normalizing the soils by soil moisture potentials, the effect of temperature alone could be evaluated. For each particular temperature, 144 incubations (6 soils x 8 soil moisture potentials x 3 replicates) were averaged. By using these normalized rates, the sensitivity to temperature across the various types of cover soils and different soil moisture potentials could be compared.

Similarly, to determine the impact of soil moisture across all 6 of the various cover soils, normalized CH_4 oxidation rates (rate at a given soil moisture potential divided by the maximum observed CH_4 oxidation rate for that soil at the respective temperature) were used to evaluate the sensitivity to soil moisture potential across the various cover soil types. For each particular soil moisture potential, the resulting normalized rates across various temperatures and soils were averaged. There were three temperature groupings analyzed for the soil moisture potential impacts: <5, 5 to 40, and > 40°C. These groupings were selected because oxidation rates at the lower (<5°C) and upper (>40°C) temperature ranges were very low to negligible. These normalized rates were then used to compare soil moisture effects across the different soils and to evaluate the optimum and minimum threshold soil moisture potentials within the three temperature groupings.

Figure 3. Comparisons of CH4 oxidation kinetics of (A) soil sample as collected from field (no pre incubation period) and (B) soil following 60 d pre incubation period with 5 percent CH4. Data shown is for Scholl Canyon daily cover soil. Average of six replicates shown with standard deviations indicated.



2.2.3 Examination of Cyclic Temperatures Versus Isothermal Incubations

In order to ascertain the effect of diurnal temperature cycles on CH_4 oxidation rates, two sets of triplicate incubations for each of the six cover soils were established with equivalent diurnal temperature averages. The first set was placed in a growth chamber (Percival Scientific, Perry, IA; model 35LLV1) with a temperature program from 10 to 40°C (including 12 hr at 10°C and then 12 hr at 40°C). This particular model growth chamber was limited to two temperature set-points. At 6:00 the incubator temperature was set to 40°C and then at 18:00 the temperature returned to 10°C. The temperatures inside the growth chamber were monitored with a temperature data logger at 15 minute intervals (Onset Computing, Pocasset, MA; model UA-002-08). This set was compared to a second set of equivalent diurnal temperature incubations at an isothermal temperature of 25°C. Soil incubations were established at three soil moisture potentials [field capacity (33 kPa), 300 kPa, and 1400 kPa] as described above (5 g soil; 2 ml l^{-1}). The main purpose of these incubations was to assess if there were differences in the observed rates of oxidation as a function of diurnal temperature fluctuations compared to isothermal conditions. CH_4 oxidation rates were calculated as detailed in Section 2.2.2.

2.2.4 Impact of Elevated CO_2 Concentrations

Incubations were also performed to determine the effect of 400 µl l^{-1} (lab ambient), 2 ml l^{-1}, 50 ml l^{-1} and 250 ml l^{-1} CO_2 on rates of CH_4 oxidation. For these incubations, soil moisture was adjusted to 50 kPa, and soils were pre-incubated with 50 ml l^{-1} CH_4 for 60 days (at ambient atmospheric CO_2 levels). Six replicate incubations (5 g soil at each CO_2 concentration) were conducted at 25°C for each cover soil at field capacity. Specific gas mixtures of CO_2 with 200 ml l^{-1} O_2 (balance N_2; Minneapolis Oxygen) were used to flush the incubation vials after they were sealed with a double needle arrangement for 1 minute (one needle for flush gas input [~10 l min^{-1}] and the other for venting). Following flushing of the headspace with the respective CO_2:O_2 mixture, 5 ml of enclosed headspace were removed and 5 ml of 50 ml l^{-1} CH_4 in argon was injected through the septum, bringing headspace CH_4 concentration to approximately 2 ml l^{-1} (exact initial concentrations were determined by GC below). All incubations remained above 180 ml l^{-1} O_2 (data not shown). The sole variable examined for these incubations was the range of CO_2 concentrations. Differences in N_2 concentration were assumed to have negligible impact on the rates of CH_4 oxidation. CH_4 oxidation rates were calculated as described previously (section 2.2.2).

2.2.5 GC Analysis

To sample each incubation, 5 ml of air (known composition) were injected by syringe into each serum bottle. This syringe was flushed 3 times to allow for adequate mixing with the serum bottle headspace. Five ml of gas was then withdrawn and injected into an autosampler vial that had been previously flushed with helium using a dual needle arrangement (as mentioned above for flushing the CO_2 incubations). Concentrations from the GC were corrected for dilution by the 5 ml of air.

There were 3 gas chromatographic (GC) systems used in this research. All 3 systems were connected to the same type of headspace sampler (Agilent, Foster City, CA, model 7694) that

was modified with additional sample valves to accommodate each analytical system. Details of each GC system are given in Table 2 and 3.

Table 2. Detailed analytical configuration for the gas chromatographic system at the USDA-ARS Morris, MN, location used in this research (System 1).

System 1	GC Manufacture	Varian 3700 (Walnut Creek, CA)
Column 1		
	Column Type	Haysep D (80/100 mesh; 2.4 m x 3.2 mm) (Grace Davison Discovery Sciences; Deerfield, IL)
	Sample Loop Size	1.0 ml
	Flow rate	35 ml/min Helium
	Oven Program	75°C for 2.5 minutes and ramped to 120°C (no hold)
	Detector	Flame Ionization Detector (300 °C)
	Gases Detected	CH_4 (0.8 min)
Column 2		
	Column Type	Porapak Q column (80/100 mesh; 1.8 m x 3.2 mm column) (Grace Davison Discovery Sciences; Deerfield, IL)
	Sample Loop Size	0.5 ml
	Flow rate	32 ml/min Helium
	Oven Program	60°C for 1.7 min and ramped to 127°C (no hold)
	Detector	Thermal Conductivity Detector (300 °C)
	Gases Detected	CO_2 (1.5 min)

Table 3. Detailed analytical configuration for the two gas chromatographic systems at the USDA-ARS St. Paul, MN, location used in this research (System 2 and 3).

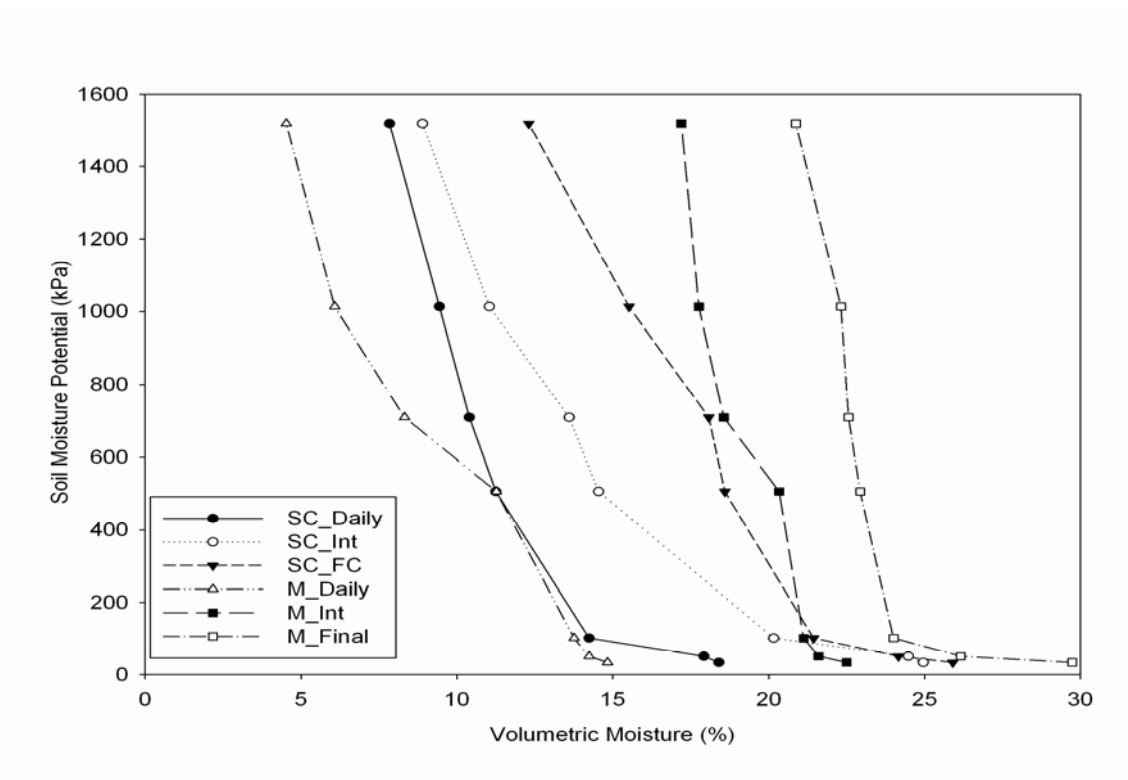
System 2	GC Manufacture	Perkin Elmer, Waltham, MA., Clarus 600
Column 1		
	Column Type	RT-Molesieve 5A (0.32 mm x 30 m) (Restek, Bellefonte, PA)
	Sample Loop Size	60 µl
	Flow rate	2.0 ml min^{-1} Helium
	Oven Program	35°C for 5 min, followed by heating to 120°C at 20°C min^{-1} with a 0 min hold time
	Detector	Mass Spectrometer (GC/MS interface = 150°C; source temperature = 150 °C) Electron ionization (EI) mass spectra; Electron energy set at 70 eV
	Gases Detected	CH_4(6.4 min; m/z=15)
Column 2		
	Column Type	RT-QSPLOT (0.32 mm x 30 m) (Restek, Bellefonte, PA)
	Sample Loop Size	120 µl
	Flow rate	2 ml min^{-1} He
	Oven Program	Same as column 1 above
	Detector	Same as above conditions
	Gases Detected	CO_2(3.5 min;m/z=44), N_2O (4.1 min; m/z=30+44)
Column 3		
	Column Type	CTR-1 column (Grace; Deerfield, IL)
	Sample Loop Size	500 µl
	Flow rate	45 ml min^{-1} Helium
	Oven Program	Same oven as column 1 above
	Detector	Thermal Conductivity (150 °C)
	Gases Detected	O_2 (2.5 min) and N_2 (4.5 min)
System 3		Agilent 5890 Series II (Foster City, CA)
Column 1		
	Column Type	Haysep D (80/100 mesh; 2.4 m x 3.2 mm) (Grace Davison Discovery Sciences; Deerfield, IL)
	Sample Loop Size	1.0 ml
	Flow rate	32 ml min^{-1} Helium
	Oven Program	Isothermal (75°C)
	Detector	Flame Ionization (300°C)
	Gases Detected	CH_4 (0.86 min)
Column 2		
	Column Type	CTR-1 column (Grace; Deerfield, IL)
	Sample Loop Size	500 µl
	Flow rate	45 ml min^{-1} Helium
	Oven Program	Same oven as column 1 above
	Detector	Thermal Conductivity (150 °C)
	Gases Detected	O_2 (2.5 min) and N_2 (4.5 min)

2.3 Results and Discussion

2.3.1 Soil Moisture Retention Curves

The average volumetric soil moisture contents at various moisture potentials for the six repacked cover soils are shown in Figure 4. Note the close clustering at higher moisture contents for the intermediate and final Scholl Canyon cover soils with lower moisture contents for the daily cover soils and higher moisture contents for the organic final cover soil from Marina with the highest moisture-holding capacity. As discussed above, an important aspect about using soil moisture potential is that the soil moisture behavior is normalized across different soil textures (Hillel, 1980). Moreover, the behavior of soil water at the same soil moisture potential is equal in disturbed and undisturbed samples, despite the fact that the resulting water contents of an undisturbed and a repacked sieved sample will be different. Therefore, at the same soil moisture potential, the availability of soil water to microbes is approximately equal regardless of the soil texture.

Figure 4. Soil moisture retention curves for the six California landfill soils. SC represents Scholl Canyon landfill, M represents Marina landfill, Daily is daily cover, Int is intermediate cover, and Final is the final cover.



2.3.2 Effects of Pre-Incubation and Soil Moisture on CH_4 Oxidation Rates

Overall, pre-incubating the soil sample with CH_4 for 60 days resulted in higher CH_4 oxidation rates than those observed without the pre-incubation period (Table 4). This increase in CH_4 oxidation rates as a consequence of pre-incubation has been observed by others (e.g. Park et al., 2002; Chanton et al., 2008). Priemé et al. (1996) and Börjesson et al. (1998) described methanotrophs as slow growing (>5 days), which could explain the relatively long pre-incubation periods needed to establish a steady state condition in the soil (Amaral et al., 1998). These incubation periods for CH_4 oxidation studies are longer than those for typical microbial assessments of 7 to 10 d (e.g. Franzluebbers et al., 1996). It is interesting to note, that for the California cover soils, steady-state conditions were not reached until 60 days. This could be due to the normally-low soil gas CH_4 values for the majority of cover types sampled (Table 4), which is at least partially attributed to effective gas extraction systems operating at the sites.

We also observed differences in the behavior of oxidation kinetics as a function of the pre-incubation period. Without the CH_4 pre-incubation, we observed a lag-phase before CH_4 oxidation was initiated (Figure 3A). However, with the CH_4 pre-incubation, soils exhibited exceptionally linear decreases in the CH_4 headspace with time (zero order kinetics, all R^2>0.95) (Figure 3B). This behavior was observed in all cover soils examined here and also been observed by Börjesson et al. (2004). This lag phase was most pronounced for the Scholl Canyon daily cover soil, which unlike the Marina daily cover, was not being stored at the landfill site and thus had no prior history of CH_4 exposure.

The use of extended 60 day CH_4 pre-incubations is examining the soil's ultimate CH_4 oxidation potential. This can be contrasted with determinations of CH_4 oxidation activity at selected conditions of soil temperature, moisture availability and exposure to CH_4. There is no consensus in the literature on the optimum pre-incubation period or on the soil moisture content during this period for landfill cover soils. Our results indicate that the 60 day incubation with 50 ml l^{-1} CH_4 (replaced weekly) was adequate to stimulate the dynamics of CH_4 oxidation activity in the cover soils (Table 2C), in order to assess the ultimate potential for CH_4 oxidation.

The data in Table 4A replicate the typical depth distribution for CH_4 oxidation rates in the literature, with the maximum rate occurring slightly below the surface. However, as seen in the subsequent sections of Table 4, this is not a static property. Table 2B indicates elevated CH_4 oxidation rates compared to Table 5A after a 60 d pre-incubation with 50 ml l^{-1} CH_4. Oxidation rates in Table 4B were directly linked to the soil moisture contents. The oxidation rates for those soils with available moisture (wetter than the wilting point) were drastically increased compared to the rates without pre-incubation (typically by an order of magnitude; Table 2A). Thus, soil moisture is a major controlling factor on the CH_4 oxidation capacities at field-collected moisture contents, as documented in other studies (e.g. Wahlen and Reeburgh, 1996).

Table 4C presents CH_4 oxidation rates with a 60 day pre-incubation period when the soil was also initially adjusted to 33kPa (field capacity). This adjustment to field capacity greatly increased the observed rates by about 2 orders of magnitude compared to Table 4A. In addition, this soil moisture adjustment reduced the variability seen across all soils to within the same order of magnitude (Table 4C; 112 to 644 ug CH_4 g^{-1} day^{-1}), as opposed to the four orders

of magnitude in the non-optimized soil moisture incubations (Table 4B; 0.9 to 277 ug CH_4 g^{-1} day^{-1}). For all samples, the combined adjustment of soil moisture and the 60 d pre-incubation with CH_4 eliminated the depth differences that were initially seen in the field data. This suggests that oxidation rates as typically measured directly on field-collected samples represent their in-situ capacity at the time of collection and not their full potential (Table 4A and 4C). Furthermore, the possibility exists that the ultimate potential rate of CH_4 oxidation could be similar for all the soils examined, but with oxidation rates in-situ controlled by soil microclimate (soil temperature and moisture) and historical soil gas CH_4 concentrations (Table 5).

Table 4. Rates of CH_4 oxidation within the depth profile of the landfill cover soils for three different pre incubation conditions: A) no pre incubation, B) pre incubation with CH_4 only and C) pre incubation with moisture amendments and CH_4. Rates are averages of six replicates with standard deviations given in parentheses.

	Marina			Scholl Canyon		
Depth (cm)	**Daily**	**Intermediate**	**Final**	**Daily**	**Intermediate**	**Final**
	(ug CH_4 g_{soil}^{-1} day^{-1})					
A. Initial Rate – No Pre-incubation at field collected moisture contents						
0-10 cm	0.05 (0.02)	0.4 (0.2)	0.3 (0.1)	0.1 (0.2)	0.2 (0.3)	0.2 (0.1)
10-20 cm	0.04 (0.08)	1.9 (0.4)	0.2 (0.1)	0.1 (0.1)	0.2 (0.1)	0.2 (0.3)
20-30 cm	#	2.5 (0.6)	2.8 (0.5)	#	-	0.1 (0.1)
30-40 cm		171.3 (22)	2.6 (0.2)		-	-
40-50 cm		211.2 (36)	0.5 (0.3)		-	-
50-60 cm		#	1.4 (0.2)		-	-
70-80 cm			0.4 (0.2)		-	-
B. Pre-incubation with 50 ml l^{-1} CH_4 and 200 ml l^{-1} O_2 at field collected moisture contents						
0-10 cm	0.4 (0.2)	0.1 (0.3)	3.6 (0.5)	1.7 (0.2)	0.2 (0.1)	0.9 (0.2)
10-20 cm	1.8 (0.1)	1.9(0.1)	2.8 (0.4)	3.6 (1.4)	0.2 (0.1)	0.5 (0.1)
20-30 cm	#	8.9 (0.4)	5.6 (10)	#	-	0.2 (0.5)
30-40 cm		384.2 (10.3)	111.3 (12)		-	-
40-50 cm		374.1 (7.1)	199.8 (14)		-	-
50-60 cm		#	219.8 (28)		-	-
70-80 cm			212.7 (23)		-	-
C. Pre-incubation with 50 ml l^{-1} CH_4 and 200 ml $l^{-1}O_2$ (60 d) at field capacity moisture content (33 kPa)						
0-10 cm	142.2 (33)	416.8 (16)	593.8 (31)	112.4 (19)	211.4 (32)	212.9 (22)
10-20 cm	132.6 (20)	412.9 (13)	573.9 (14)	112.1 (13)	212.4 (39)	212.7 (18)
20-30 cm	#	412.7 (15)	613.1 (14)	#	-	212.5 (11)
30-40 cm		412.4 (23)	594.2 (16)		-	-
40-50 cm		452.0 (12)	604.2 (15)		-	-

	Marina			Scholl Canyon		
Depth (cm)	**Daily**	**Intermediate**	**Final**	**Daily**	**Intermediate**	**Final**
			(ug CH_4 g_{soil}^{-1} day^{-1})			
50-60 cm		#	NS		-	-
70-80 cm			644.2 (28)		-	-

Notes:
"-"designates a depth interval that was not sampled and "#" designates the base of cover was reached. "NS" indicates not sampled due to lack of adequate soil sample for all incubations. Total cover thicknesses are given in Table 1.

Table 5. Corresponding CH_4 soil gas concentrations ($\mu l\ l^{-1}$) at collected depths in the cover materials.

	Marina			Scholl Canyon		
Depth (cm)	Daily	Intermediate	Final	Daily	Intermediate	Final
			Methane Concentrations ($\mu l\ l^{-1}$)			
0-10 cm	120	12000	5	3	5	3
10-20 cm	350	150000	2	5	4	2
20-30 cm	#	320000	2	#	*ns*	3
30-40 cm		390000	3		*ns*	*ns*
40-50 cm		450000	8		*ns*	*ns*
50-60 cm		#	5		*ns*	*ns*
70-80 cm			12		*ns*	*ns*

Notes: "*ns*" designates a depth interval that was not sampled and "#" designates the base of cover was reached. Total cover thicknesses are given in Table 1.

The pre-incubated rates observed in the California landfill cover soils are within the range observed in other landfill oxidation studies, ranging from 0.06 to 653 ug CH_4 $g_{soil}^{-1}d^{-1}$ (e.g. Kightley et al., 1995; Boeckx and van Cleemput, 1996; Gebert et al., 2003; Park et al., 2005). However, without the pre-incubation (Table 2A), the oxidation rates would be at the low end of observed oxidation rates reported in the literature for landfill settings.

2.3.3 Temperature Relationships

Figure 5 summarizes oxidation rates for all of the temperature incubations at the eight different soil moisture potentials. This type of temperature response for methanotrophic activity has been observed in other studies (e.g. Whalen et al., 1990; Czepiel et al., 1996a; Gebert et al., 2003; Börjesson et al., 2004; Jugnia et al., 2006). In general, CH_4 oxidation rates increase with temperature up to a maximum temperature (~30°C), and then correspondingly decreases up to a temperature maximum threshold of about 55°C. Optimal oxidation temperatures around 30°C have been typically reported (e.g. Boeckx and vanCleemput, 1996; Whalen et al., 1990). The

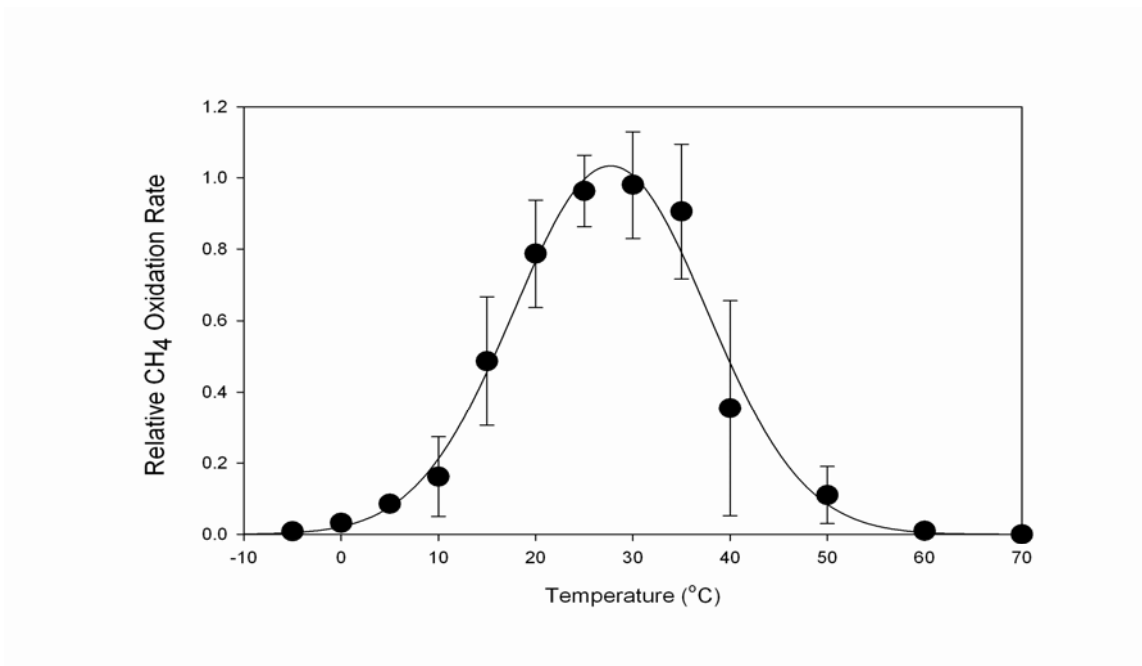
resulting relationship was fitted with a 3-parameter Gaussian peak (Figure 3; SigmaPlot 11, SysStat; San Jose, CA):

$$\text{Normalized Rate} = 1.05\, e^{-0.5\left(\frac{T-27.6}{9.59}\right)^2}, \qquad \text{(Eq. 2.1)}$$

Where T is the temperature of the incubation (or soil temperature; $R^2 = 0.981$). From the equation fitting, the optimal temperature across all soil types and soil moistures was 27.6 ± 0.5°C (Figure 5).

It is also relevant to note in Figure 5 that when soils were incubated at >50°C for 120 d no CH_4 oxidation activity was observed. CH_4 oxidation rates did not immediately recover when the temperature for these same incubations was lowered to 30°C, and an additional 7-14 d at 30°C was required before any oxidation activity was observed. This could be directly related to spore formation for survival at the elevated temperatures (e.g. Whittenbury et al., 1970). These lag periods are frequently mentioned in the literature. However, actual quantification of the lag periods as a result of combined temperature and moisture limitations requires further examination.

Figure 5. Effects of temperature on relative rates of CH4 oxidation (rate at specific temperature divided by maximum rate for the corresponding soil moisture potential for each soil) for (A) all soil combinations (n=3456) and (B) averages for each temperature with associated standard deviations and fit to a three parameter Gaussian curve.



2.3.4 Soil Moisture Potential Relationships

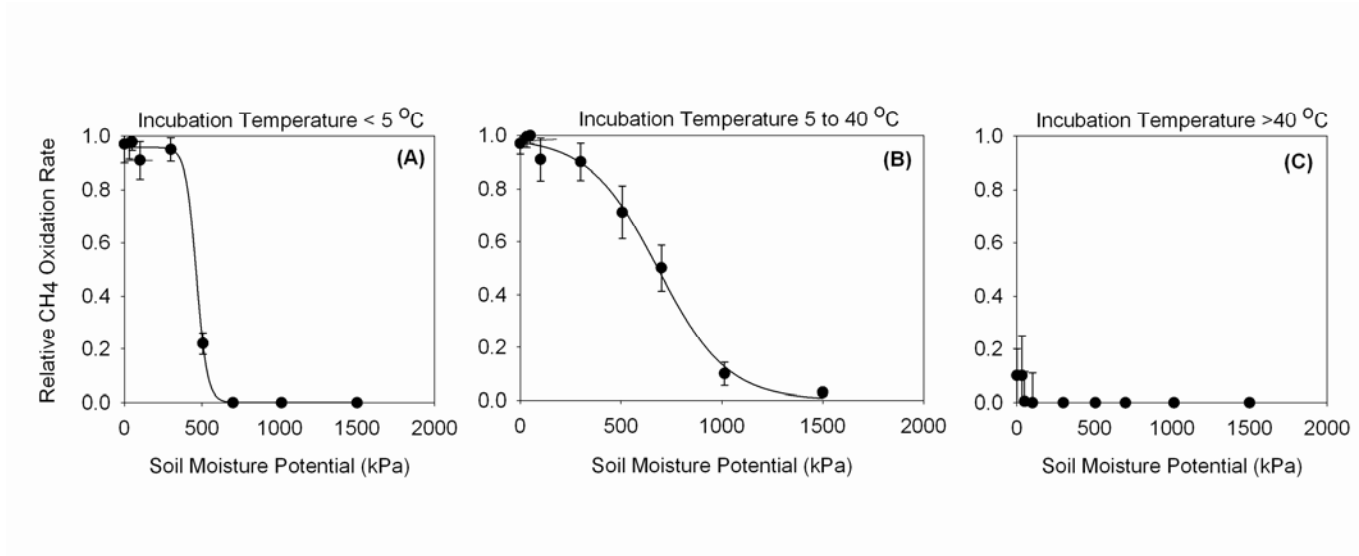
Figure 6 illustrates CH_4 oxidation rates versus soil moisture potential for the six cover soils for three different temperature groupings. For the laboratory incubations at 5-40°C, a minimum threshold of 1500 kPa was observed (Figure 6B). This threshold is also referred to as the wilting point (the soil moisture potential at which plants no longer can extract water from the soil). A threshold value of 1500 kPa was maintained if the soil was initially pre-conditioned at higher soil moisture contents and then allowed to dry. However, if the soils were initially dry and then wetted; a threshold value of 600 kPa was observed. Thus, the threshold value fluctuates depending on the soil wetting history (a hysteresis-type response). These results again illustrate the need to further elucidate the temperature, moisture and pre-incubation relationships, including time lags.

As also seen in Figure 6, the threshold soil moisture potential for CH_4 oxidation activity shifts to lower soil moisture potentials (higher moisture contents) at the extreme temperatures (<5°C; Figure 6A and >40°C; Figure 6C). At the low temperature end (<5°C; Figure 6A), the minimum soil moisture potential threshold decreases to 300 kPa. At the upper limits of CH_4 oxidation activity (>40°C; Figures 6C), the minimum soil moisture potential threshold decreases further to 50 kPa. Thus, these results strongly indicate the coupled interaction of soil moisture and temperature. The impacts of soil moisture on the rates of oxidation can be estimated through the use of a 3-parameter sigmoid function (Figure 6B; Sigma Plot 11, SysStat; San Jose, CA):

$$\text{Relative rate} = \frac{0.992}{1 + e^{\left(\frac{\text{SMP} - 683.8}{171.4}\right)}}, \qquad \text{(Eq. 2.2)}$$

where SMP is the soil moisture potential (+kPa) ($R^2 = 0.994$).

Figure 6. Effect of soil moisture on relative rates of CH4 oxidation (rate at soil moisture potential divided by maximum rate for the corresponding temperature of the incubation) for (A) temperatures less than 5oC (n=72) and (B) temperatures between 5 and 40oC (n=3192), (C) for temperatures >40oC (n=192).



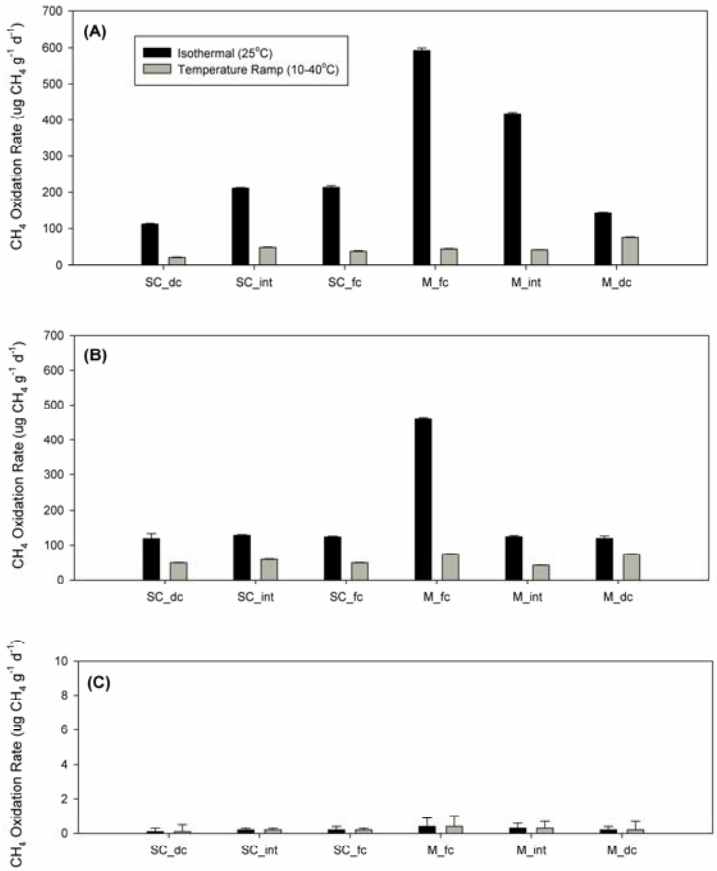
For the majority of soils examined, the optimum soil moisture potential for CH_4 oxidation was approximately 50 kPa, although this value was not statistically significant across all soil types. This 50 kPa is close to field capacity (33 kPa). The results from this study suggest that there is no single optimum moisture; rather, an upper soil moisture potential of 50 kPa or wetter does not result in statistical differences in CH_4 oxidation rates. This lack of a distinct optimum moisture content has been observed in other studies (e.g. Einola et al., 2007). However, it should be mentioned that due to the small amount of soil present in the incubation, these laboratory incubations were not exposed to the same diffusion constraints that would exist in a variably-saturated field soil. For comparison with moisture contents in the literature, 50 kPa soil moisture potential corresponds to 8.4-31.7 percent volumetric moisture for the sieved California cover soils (Figure 3), which is within the range of optimum soil moisture values that have been reported previously (e.g. Christopherson et al., 2000; Boeckx and Van Cleemput, 1996; Visvanathan et al., 1999). However, volumetric or gravimetric water contents do not provide direct information on soil water availability. From the results presented here, the use of soil moisture potential is highly recommended to normalize soil variability (e.g. soil texture and organic matter content) with respect to the effect of soil moisture on methanotroph activity.

2.3.5 Cyclic Temperature Relationships

Figure 7 indicates CH_4 oxidation rates for three different moisture levels at isothermal conditions compared to fluctuating daily temperatures. The cyclic rates for all soils were significantly lower than the isothermal oxidation rates, despite the fact that the average daily temperature for the two temperature regimes was approximately equal at 25°C (Figure 7). Overall, the observed reduction in CH_4 oxidation activity with temperature cycling at the 33 kPa

soil moisture potential was 48-93 percent (average 78 percent; Figure 7A). At 300 kPa soil moisture potential, the reductions ranged from 38-84 percent (average 60 percent; Figure 7B). This lower average reduction could result from the reduced CH_4 oxidation activity at the 300 kPa soil moisture potential compared to field capacity (33 kPa). The level of reduction was the greatest for the Marina final cover soil (93 percent at 33 kPa and 84 percent at 300 kPa). These reductions were directly correlated with the organic matter content, as the Marina final cover soil had the highest reductions and also the highest organic matter content (Table 1). These temperature effects could also be due to the impact of temperature of methantroph growth (Börjesson et al., 1998). However, the exact cause is unknown. As can be seen in Figure 7C, the highest soil moisture potential (1500 kPa) resulted in extremely low rates with a majority being non-significantly different than zero, thus confirming the soil moisture potential threshold discussed previously.

Figure 7. Illustration of the impacts of a temperature cycle compared to an equivalent isothermal incubation on the CH4 oxidation rate of various cover soils at (A) -33 kPa, (B) -300 kPa and (C) -1500 kPa. Standard deviations of the replicates are shown. SC represents Scholl Canyon, M represents Marina landfill, fc is final cover, int is intermediate cover, and dc is daily cover.



When the temperature relationship (Eq. 2.1) is applied to the actual recorded incubation temperatures, this relationship predicts an oxidation rate reduction of 81 percent which is within the range of the observed reductions (Figure 7). We are not aware of other studies of this type (ramped vs. isothermal temperatures) for landfill cover soils. Despite the fact that we do not know the exact causes behind these reductions, these results suggest that it is imperative to account for diurnal as well as seasonal temperature variability when examining landfill soil CH_4 oxidation.

2.3.6 Impact of CO_2 Concentration on CH_4 Oxidation Rate

The observed impact of CO_2 concentrations on oxidation rates is shown in Table 6 for the Marina intermediate soil. As seen in the Table, the rates of CH_4 oxidation were not significantly different (P=0.183) for the various levels of CO_2 evaluated in the laboratory incubations. Results of the incubations with the other cover soils were similar, in so far as there were no statistically significant impacts observed on the rate of CH_4 oxidation. However, despite the fact that the CH_4 oxidation rates were similar, there was a significant impact on the CO_2 respiration rates as a function of CO_2 concentration (P<0.0001). This is in agreement with other observations of decreasing CO_2 respiration rates with increasing CO_2 concentrations (e.g. Macfadyen, 1973; Dixon and Kell, 1989; Koizumi et al., 1991). These observations indicate that elevated CO2 concentrations do not alter CH4 oxidation rates in landfill cover soils, despite decreasing microbial respiration rates.

Table 6. Influence of variable CO2 concentrations on observed CO2 respiration and CH4 oxidation rates over a 25 d incubation with the Marina intermediate cover soil at 25oC. Data in the table is the average of six replicates with standard deviation given in parentheses. Rates followed by the same letter are not significantly different.

CO_2 Concentration (ml l^{-1})	CO_2 Respiration (mg CO_2 $g_{soil}^{-1}d^{-1}$)	CH_4 Oxidation (ug CH_4 $g_{soil}^{-1}d^{-1}$)
0.4	25.2 (0.95) a	419.9 (11.7) a
2	23.87 (1.0) a	411.4 (23.2) a
50	18.9 (2.4) b	415.8 (23.4) a
400	14.3 (3.1) c	390.2 (33.6) a

2.4 Conclusions

Soil moisture potential provides a more robust parameter than gravimetric or volumetric moisture for examining the dependency of landfill CH_4 oxidation rates on soil moisture. The optimal soil moisture potential was very close to field capacity (50 kPa), with the minimum threshold soil moisture potential at approximately 1500 kPa (soil wilting point). Furthermore, these limits for soil moisture potential would be directly applicable to other soils of different textures and structure.

We observed that soil temperature and moisture potential interact to influence CH_4 oxidation rates under field conditions, necessitating the need to evaluate the temporal dynamics of CH_4

oxidation relative to the soil microclimate variability within the soil profile. Simpler assumptions of an average daily temperature, or an average annual temperature and a temperature-dependent rate constant, as illustrated by the results from the cyclic temperature incubations, will lead to significant errors in the quantification of CH_4 oxidation rates. In addition, rates of CH_4 oxidation were not significantly different for the various levels of CO_2 evaluated in the laboratory incubations, despite elevated CO_2 levels suppressing microbial CO_2 respiration rates.

Our results also indicate that many landfill CH_4 oxidation rates previously reported in the literature for field samples actually represent their capacity at field conditions and not their full CH_4 oxidation potential. The pre-incubation period at field capacity moisture normalized CH_4 oxidation rates to high values within the same order of magnitude (112 to 644 ug CH_4 g^{-1} day^{-1}) for all the cover soils samples examined, as opposed to the four orders of magnitude variation in the soil CH_4 oxidation rates without pre-incubation (0.9 to 277 ug CH_4 g^{-1} day^{-1}). Therefore, we recommend a 60 day pre-incubation period (with 50 ml l^{-1} CH_4) at field capacity to determine the ultimate potential for CH_4 oxidation in landfill cover soils.

CHAPTER 3:
Field Studies. Seasonal Variability in CH4, CO2, and N2O Emissions from Daily, Intermediate, and Final Cover Materials at Two California Landfills

3.1 Background and Site Description

Landfills are the second-largest anthropogenic source of CH_4 in the U.S.; globally, landfill CH_4 accounts for 1-2 percent of total global anthropogenic greenhouse gas emissions (Bogner et al., 2007; Rogner et al., 2007; US EPA, 2010). Field studies have documented landfill CH_4 emission rates spanning 6-7 orders of magnitude with high spatial variability of 3-4 orders of magnitude within distances of <10 meters (Bogner et al., 1997a; Scheutz et al., 2009). To date, however, the literature has focused on final cover materials and not addressed seasonal variability for the full range of daily, intermediate, and final cover materials at one site, as well as emissions from fresh refuse, both prior to and after daily cover placement. Because new cells often overlie older waste, daily cover CH_4 emissions would depend on deeper methanogenic processes. Thin intermediate covers would be expected to have higher emissions than thicker final covers.

Landfill CH_4 emissions are reduced by three major mechanisms: (a) engineered collection systems for landfill gas (LFG) recovery and utilization; (b) engineered cover materials which retard CH_4 transport; and (c) CH_4 oxidation by indigeneous aerobic methanotrophs in cover soils. These mechanisms operate simultaneously to reduce emissions—for example, thicker cover materials retard transport and increase retention times to facilitate oxidation; engineered systems reduce CH_4 concentrations at the base of the cover, reducing diffusive transport to lower rates more readily oxidized. Published literature over the last two decades has concluded that landfill cover soils can develop high capacities for CH_4 oxidation with rates dependent on temporal changes in soil moisture, temperature, and other variables (Scheutz et al., 2003, 2009; Barlaz et al., 2004; Kightley et al., 1995; Czepiel et al., 1996a; Bogner et al., 1995, 1997a, 2010; Whalen et al., 1990; Chanton et al., 2009; Spokas and Bogner, 2010). Field measurements of surface emissions document the "net" flux rates inclusive of both oxidation and gaseous transport processes. In some cases, emissions are primarily controlled by oxidation, especially where landfill gas recovery reduces the "gross" flux to rates consistent with the oxidation capacity of cover soils. When landfill cover soils develop high oxidation capacities, especially where gross fluxes are low, it is also possible to initiate oxidation of atmospheric CH_4 (Bogner et al., 1995, 1997b, 2010). as has been observed in natural ecosystems (Whalen and Reeburgh, 1990; Goldman et al., 1995; Dutaur et al., 2007).

The purpose of this study was to quantify the seasonal and spatial variability of CH_4, CO_2, and N_2O emissions from fresh refuse and daily, intermediate, and final cover materials at two contrasting California landfills: a northern coastal site (Monterey County) and a southern canyon fill (Los Angeles County). Recent field measurements of landfill CH_4 emissions using a variety of above-ground techniques (micrometeorological, static and dynamic tracer, horizontal and vertical radial plume mapping) have shown wide variability in results (Babillote et al.,

2009a,b), resulting from the complex topography and micrometeorology typical at many landfills, differing interpretation algorithms, and variable emission signals from daily, intermediate, and final cover areas in close proximity to each other. In addition to CH_4 emissions, there are few studies in the literature which address landfill emissions of N_2O and CO_2 in parallel with CH_4 (Börjesson and Svensson, 1997; Bogner et al., 1999; Rinne et al., 2005; Lee et al., 2002; Zhang et al., 2008a; McBrain et al., 2005; Tsujimoto et al., 1994). We note that, for purposes of national GHG inventories (IPCC, 2006), the CO_2 emissions are considered biogenic and not separately reported for the waste sector. In order to better elucidate seasonal differences among the different types of cover materials, this study applied simple static chamber techniques across each type of cover material during wet and dry season field campaigns over two annual cycles. These field campaigns were part of a broader study to develop a new field-validated landfill CH_4 emissions inventory methodology for the state of California based on improved scientific understanding of seasonal emissions inclusive of oxidation (Spokas et al., 2009).

3.2 Materials and Methods

Fluxes were measured using 9 stainless steel (SS) static chambers, each with a cross sectional area of 0.10 m^2 and an average volume to area ratio of 0.24 m^3 m^{-2} were deployed in parallel. Previous literature (Venterea et al., 2009) supports the use of static chambers to quantify the variability of fluxes across specific soil types. Each chamber had a fixed base and a removable top with gas-tight fittings for sampling using a syringe. For each flux (30 min. maximum), 6 samples were extracted at randomized intervals, and each 5-mL sample was retained in a 10 mL He-flushed glass serum vial. Fluxes were determined by the product of the change in concentration over time (dc/dt) and the [chamber volume/chamber area] ratio (Rolston, 1986) with acceptance criterion $r^2 > 0.9$ for linear regression of dc/dt. Soil temperature (RTD probe) and volumetric soil moisture (TDR) were determined for each flux.

Four intensive seasonal field campaigns were conducted during 2007-2008 at the two field sites (Scholl Canyon Landfill, 34.158 deg. N, 118.196 deg. W, Los Angeles County; Marina Landfill, 36.71 deg. N, 121.762 deg. W, Monterey County), two during the wet season (March 2007, 2008) and two during the dry season (August 2007, 2008). During each campaign, the chambers were deployed multiple times on each cover type (minimum of 6 at any one time with partial duplication); randomized chamber locations (>850 fluxes) were recorded using GPS [Garmin]. Because of site operational constraints, fresh refuse fluxes were typically limited to single deployments [9 chambers] before daily cover placement. All gas samples were analyzed for CH_4, CO_2, and N_2O by the USDA/ARS laboratories in St. Paul and Morris, MN using GC and GC/MS systems previously described (Spokas and Bogner, 2010). The minimum detectable fluxes were ± 12 mg m^{-2} d^{-1} for CH_4, ±0.322 mg m^{-2} d^{-1} for CO_2, and ±0.7 mg m^{-2} d^{-1} for N_2O. In addition, weather stations and soil temperature/moisture sensors were installed at each site to continuously monitor wind speed, air temperature, relative humidity, and soil temperature and moisture profiles [Onset Computing]. In a related study (Spokas and Bogner, 2010), daily, intermediate, and final cover soils were also sampled at each site, characterized, and subjected to intensive laboratory incubations to determine CH_4 oxidation potential and oxidation rates

relative to soil moisture and temperature. Fugitive CH_4 emissions associated with landfill gas piping and other transient emissions (e.g., soil cracks) which, under existing regulations must be remediated during routine maintenance following quarterly monitoring of surface CH_4 concentrations, were not part of this study.

Stable carbon isotopes for CH_4 (and selected samples for CO_2) were analyzed at Florida State University for final chamber samples, composite source gas from the landfill gas recovery system, and selected shallow probes (10-12 cm). Methane oxidation was determined using published methods (Liptay et al., 1998; Chanton and Liptay, 2000) where the percent oxidation is determined from the $\delta^{13}C$ of the anoxic CH_4 vs. the emitted CH_4 (chamber or probe). Previous literature has demonstrated that when diffusion is the primary flux mechanism, use of the chamber CH_4 underestimates oxidation (Chanton et al., 2008); thus chamber oxidation results are more conservative than probe results.

3.3 Results and Discussion

3.3.1 Source Gas

The source gas characteristics were defined by sampling the composite wellfield gas and individual wells near the chamber deployment areas. Averaged across all field campaigns (± 1 SD), the Marina well gas had CH_4 39.4 percent v/v (±9.2); Scholl Canyon had CH_4 32.2 percent v/v (±9.3). Many California landfill gas collection systems are systematically operated at vacuums sufficient to minimize emissions; thus CH_4 values are typically less than the 50-60 percent CH_4 v/v of generated landfill gas due to dilution with atmospheric air, and CO_2 mixing ratios are also proportionally reduced. Note that both sites had relatively high SD's for CH_4 which can be attributed to frequent wellfield monitoring and adjustments during normal operations. Both sites had similar CO_2 mixing ratios [Marina 25.2 percent (±6.1), Scholl Canyon 25.8 percent (±4.7); v/v] but different N_2O signatures [Marina 1250 ppb (±100), Scholl Canyon <200 ppb; v/v] which bracket average atmospheric N_2O values of about 320 ppb v/v.

3.3.2 Cover Soil Properties and Emissions

Table 7 summarizes major physical and chemical properties of the cover soils. In California, it should be noted that final geomembrane composite covers are not typically used. At both sites, the cover soils consisted primarily of sand-dominated and sandy loam soils derived from local sources with moderate pH, variable organic matter [see total C Table 7], and low-to-moderate CEC. Soil thicknesses ranged from 30 cm for daily cover to >2 m for final covers. Extremely high bulk densities were achieved for the highly-compacted Scholl Canyon intermediate and final cover materials; moreover, field moisture contents were relatively low (<0.2 v/v) and below field capacity (0.20 to 0.35 v/v).

Emissions were monitored for the various cover materials and from fresh refuse at the end of the working day (no cover soil). For fresh refuse, there were no statistically-significant seasonal trends or site differences during the 4 field campaigns; hence those data were composited. Fluxes [± SD; range] from fresh refuse averaged 0.053 g m^{-2} d^{-1} for CH_4 [±0.034; 0.000569-0.107], 135 g m^{-2} d^{-1} for CO_2 [±117; 12.6-390], and 0.063 g m^{-2} d^{-1} for N_2O [±0.059; 0.005-0.181].

Table 7. Selected physical and chemical properties of cover soils.

Depth	Total C	Total N	Sand	Clay	pH (1:1)	CEC	Surface Bulk Density	Field Moisture Content	Field Capacity Moisture Content
cm	%	%	%	%		(meq/ 100 g)	(g cm^{-3})	(v/v)	(v /v)
Marina Landfill, Monterey County									
Daily Cover (30 cm average thickness)									
0-30	0.2	0.04	90	8	7.4	6.1	1.35	0.05	0.13
Intermediate Cover (50 cm average thickness)									
0-10	2.6	0.3	74	10	7.8	18.2	1.60	0.04	0.23
10-50	1.5	0.1	68	15	7.1	NA	NA	NA	NA
Final Cover (200 cm average thickness)									
0-10	4.4	0.4	76	10	6.7	21.2	1.40	0.19	0.35
10-50	1.1	0.1	65	25	NA	NA	NA	NA	NA
-90	1.0	0.2	55	35	NA	NA	NA	NA	NA
90-120	0.7	0.1	10	75	NA	NA	NA	NA	NA
120-200	NA	NA	NA	NA	NA	NA	NA	NA	NA
Scholl Canyon Landfill, Los Angeles County									
Daily Cover (30 cm average thickness)									
0-30	1.1	0.09	84	4	7.4	18.5	1.55	0.05	0.19
Intermediate Cover (100 cm average thickness)									
0-10	0.32	0.04	60	14	8.3	18.7	2.0*	0.03	0.31
10-20	0.31	0.04	60	21	NA	NA	NA	NA	NA
20-100	NA	NA	NA	NA	NA	NA	NA	NA	NA
Final Cover (>275 cm thickness)									
0-10	1.0	0.1	60	14	8.2	19.1	2.0*	0.03	0.32
10-275	NA	NA	NA	NA	NA	NA	NA	NA	NA

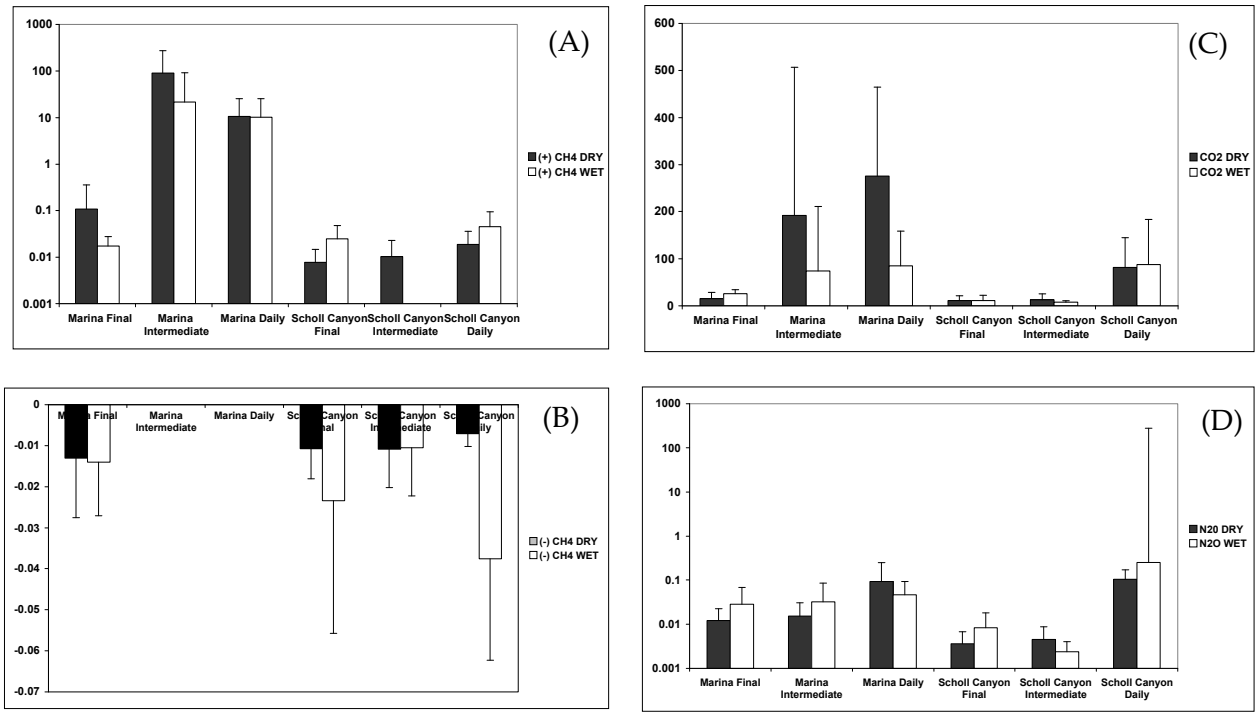
Notes: Soil was sieved (<2 mm); *gravel content (>2 mm) may have influenced values; NA – data not available.

The high CO_2 fluxes can be attributed to the rapid onset of aerobic microbial activity in the recently-deposited waste, with the higher end of the range similar to the lower end of the range for emissions from windrow composting of garden waste [Andersen et al., 2010: 250-2900 g CO_2 m^{-2} d^{-1}]. Somewhat surprisingly, the average N_2O and CH_4 fluxes were similar, but with a much wider range for CH_4. The N_2O fluxes can be attributed to the daily burial (under "semi"-anaerobic conditions) of fresh refuse with both high moisture and readily-available N, resulting in N_2O generation, under conditions that can be compared to the interior portions of windrow

waste composting operations (Andersen et al., 2010; Beck-Friis et al., 2000). CH_4 emissions are dependent on CH_4 generation, oxidation, and emissions processes in the previously-buried waste, accounting for the high variability in observed emissions. Largely because of physical difficulties with seating the chamber bases in fresh refuse, approximately 33 percent of the fresh refuse fluxes were rejected (r^2<0.9), the highest percent for any cover type.

Overall, average emissions for CH_4, CO_2, and N_2O varied across several orders of magnitude. Consistent with previous literature, high variability was also documented within cover-specific and season-specific datasets, in large part due to the complexity of gaseous transport, oxidation, and emissions processes through variable cover materials influenced by seasonal soil moisture and temperature. With a Mediterranean climate, California has distinctive wet (winter-spring) and dry (summer-fall) seasons: therefore, the field data for fluxes were composited by season for the daily, intermediate, and final covers at each of the two field sites (Figures 7a-7d). Positive and negative CH_4 fluxes were plotted separately as these represent fundamentally different processes: either methane emissions (positive fluxes) or oxidation of atmospheric methane (negative fluxes). Overall, there was more than 4 orders of magnitude variability in the positive CH_4 fluxes and less than 1 order in the negative CH_4 fluxes. Except for the Marina daily cover (MDC) and intermediate cover (MIC) which ranged between 10 and 100 g CH_4 m^{-2} d^{-1} for both seasons, all the positive CH_4 fluxes averaged between 0.01 and 0.1 g CH_4 m^{-2} d^{-1}, including both of the thick (>2 m) final cover materials. In general, maximum CH_4 fluxes from wetland ecosystems rarely exceed 0.1 g CH_4 m^{-2} d^{-1} (e.g., Jackowicz-Korczynski et al., 2010). As seen in the figures, there were no negative CH_4 emissions for the MDC and MIC for either season; also, there were no positive CH_4 emissions for the Scholl intermediate cover (SIC) during the wet season. The average positive CH_4 emissions for daily and intermediate covers were higher than the final cover for the Marina site by 2-4 orders of magnitude. For the Scholl site, the absolute values for the average negative CH_4 emissions (uptake of atmospheric CH_4) had similar ranges to the positive CH_4 emissions, suggesting that these soils could achieve oxidation rates equivalent to emissions. Other investigators have also observed negative CH_4 emissions from landfills as well as positive ranges spanning 7 orders of magnitude (Scheutz et al., 2009; Bogner et al., 1997a). In general, the average CH_4 uptake rates reported in Fig. 1b are several orders of magnitude larger than the maximum CH_4 uptake rate reported in a 3-year study of California grasslands (0.0006 g CH_4 m^{-2} d^{-1}, 37), which might be considered a natural analog for California landfills which are typically revegetated using a grass-dominated mix. The wide ranges for (+) landfill CH_4 emissions and higher values for (-) emissions (uptake) reflect high rates in landfill settings for both of the competing processes of methanogenesis in the anaerobic refuse and methanotrophy in aerobic cover soils, linked by CH_4 transport affected by seasonally-variable moisture and temperature. The higher (-) rates compared to grassland ecosystems can be largely attributed to extended exposure times to elevated CH_4 concentrations (Spokas and Bogner, 2010; Chapter 2).

Figure 8. Dry and wet season gaseous fluxes, mean value (g m-2 d-1) and standard deviation of: (A) Positive CH4 emissions, (B) Negative CH4 emissions [indicating uptake of atmospheric CH4], (C) CO2 emission, and (D) N2O emissions as indicated at the various cover types and sites. Note: Log scale for 7A and 7D.



Much of the variability in CH_4 emissions can be attributed to variable CH_4 oxidation rates at non-optimum temperatures and moistures. During the dry season, the highest average surface soil moisture (volumetric, v/v) was 0.11 ± 0.06 for the Scholl Daily Cover (SDC), while the average for all other cover types ranged from a low of 0.01± 0.03 for the MIC to a high of 0.08± 0.08 for the MDC. During the wet season, surface soil moistures for both daily covers and the MIC averaged 0.17-0.18 ± 0.12-0.34, depending on cover type, while the average surface soil moisture for the Marina Final Cover (MFC) averaged 0.11 ± 0.07 with much lower values of 0.03± 0.01 and 0.05 ± 0.05 for the SIC and SFC, respectively. Laboratory studies (14) have previously confirmed that optimum moisture contents for oxidation for these soils (at optimum temperatures) were close to field capacity, with corresponding volumetric soil moisture contents ranging from 0.14 – 0.24. Thus, all soils were below optimum soil moisture content during the dry season, while all except the two daily covers and the MIC were below optimum during the wet season. The optimum temperatures for oxidation in these soils were 25-30 ^{o}C (14), but average surface temperatures during the dry season exceeded the optimum for all of the Scholl cover soils, including SDC at 36.2 ^{o}C ±1.2, SIC at 36.0 ^{o}C ±11.3, and Scholl Final Cover (SFC) at 35.9 ^{o}C ± 9.4. Also, surface temperatures ranged up to extremely high values during the dry season (SIC and SFC maxima were 62.1 ^{o}C and 71.0 ^{o}C, respectively). Temperatures for the MIC and MFC soils averaged in the optimum range during the dry season (MIC 28.3 ^{o}C ± 4.4; MFC 25.6 ^{o}C ± 4.6). However, during the wet season, all of the Marina soils and the SIC

temperatures averaged below the optimum (15.8 -17.3 ^{o}C ± 0.1-1.1), while the SDC and SFC were in a more optimum range of 31.0 ^{o}C ± 1.7 and 28.1 ^{o}C ±7.3, respectively. Therefore, we conclude that none of the covers were routinely characterized by both optimal temperatures and moisture contents for CH_4 oxidation during either season.

For CO_2 fluxes (Fig. 7c), both of the daily cover soils and the MIC exhibited relatively high rates of 50-250 g CO_2 m^{-2} d^{-1}. This range is higher than previously-published ranges of 1-60 g CO_2 m^{-2} d^{-1} over an annual cycle for final cover soils at a seasonally-cooler midwestern U.S. landfill (Bogner et al., 1999). For the daily covers, the rates are similar to the fresh refuse and attributable to high rates of aerobic respiration in the recently-placed refuse. For the MIC, the very high CO_2 fluxes were further attributed to aerobic respiration in soils with TOC >2 percent. In a recent study (34), comparative emissions from windrow composting of garden waste were another order of magnitude higher [250-2900 g CO_2 m^{-2} d^{-1}]. The lower CO_2 fluxes from the other landfill soils are similar to (dark) respiration rates for California grassland soils (i.e., 8-20 g CO_2 m^{-2} d^{-1} for California sandy loam soils, Suarez and Simunek, 1993). Note that the higher CO_2 fluxes in the MDC and MIC occurred during the dry season, suggesting CO_2 partitioning to soil moisture during the wet season and possibly increased flux of landfill gas CO_2 during dry periods.

Average N_2O fluxes (Fig. 7d) varied by almost 2 orders of magnitude with the highest values associated with the daily cover materials, which is attributable to the combination of high moisture content, available N, and restricted aeration in the recently-placed refuse. Both the MIC and MFC exhibited higher N_2O fluxes than the SIC and SFC, which we attribute to the increased availability of N in the biosolids-amended Marina cover materials. Previous literature for N_2O fluxes from final cover soils (Bogner et al., 1999; Rinne et al., 2005; Lee et al., 2002; Zhang et al., 2008; McBrain et al., 2005; Tsujimoto et al., 1994) has shown that a zone of high N_2O production can occur at mid- to bottom-depths in thicker final cover soils (Bogner et al., 1999), as well as from final cover soils amended with high N source materials such as biosolids (Börjesson and Svensson, 1997) and from semi-aerobic landfills (Tsujimoto et al., 1994). Maximum values for N_2O fluxes from windrow composting operations (34-35, approx. 1-8 g m^{-2} d^{-1}) were an order of magnitude higher than the average N_2O emissions for the MDC and SDC (approximately 0.1 g m^{-2} d^{-1}) but within the high variability for SDC shown in Fig. 1d. Overall, N_2O fluxes from ecosystems can vary by 4-5 orders of magnitude, depending on fertilization/available N, seasonal moisture, aeration status, and other variables, with the highest values approaching 1 g N_2O m^{-2} d^{-1} (Hellebrand, 2008; Rochette et al.,2008; Du et al., 2008; Livesley et al., 2008). Similarly, the overall range shown in Fig. 1d is about 5 orders of magnitude, while the average values vary by about 2 orders of magnitude.

As discussed above, there were generally no simple relationships between observed fluxes and average soil temperatures or moisture contents. During the dry season, the Scholl Canyon surface soils exhibited an immense temperature range (22.1-71.0 ^{o}C), while the Marina soils had a somewhat smaller range of 14.1-48.0 ^{o}C. For both soils, temperatures >40 ^{o}C during the dry season resulted in severely-reduced rates of CH_4 oxidation (Spokas and Bogner, 2010; Chapter 2). When surface soils from both sites were subjected to 60-day pre-incubation with CH_4 at optimal (field capacity) moisture, CH_4 oxidation rates were uniformly >100 μg CH_4 g dry $soil^{-1}$

day^{-1} (Spokas and Bogner, 2010; Chapter 2). During the wet season, the Marina soils and the SIC exhibited little temperature variability (overall range 15.7-18.9 ^{o}C) while the SDC had higher variability (29.1 – 33.6 ^{o}C) and the SFC had a much wider range of 14.2-35.2 ^{o}C. Simple plots of gaseous fluxes vs. soil moisture did not typically indicate statistically-significant relationships; however, the average wet season N_2O fluxes (g m^{-2} day^{-1}) were exponentially related to average soil moisture (v/v) across all cover types (data not shown; $y=0.0019e^{20.93x}$, $r^2 = 0.79$). Although the vast literature on N_2O emissions from agricultural and other ecosystems generally indicates increased N_2O production and emissions at higher water-filled pore space (WFPS) below full saturation, this relationship is complex and intimately related to soil physical and chemical properties (pore volume/geometry, N sources, relative N_2O production/transport/ consumption rates, e.g., Parton et al., 2001).

3.3.3 Geospatially Averaged Emissions

Areal emissions were determined using an Inverse Distance Weighing (IDW) procedure recommended for areas characterized by heterogeneous sources (Journel and Huijbregts, 1981). Figure 8a compares the geospatially-determined CH_4 emissions to the average (+) CH_4 emissions values shown previously in Fig. 7a. In general, the geospatially-determined CH_4 fluxes for all covers are lower than the (+) CH_4 emissions values. Figure 8b indicates the percentage of each cover type with negative (-) CH_4 flux, indicating uptake of atmospheric CH_4. Most values range between about 10-40 percent, depending on cover type and season, reinforcing the variability in oxidation discussed above, and it is important to stress that four of the six cover types had significant percentages of negative (-) CH_4 fluxes. Note the wide range, from negligible (-) for MDC and MIC to 100 percent for SIC during the 2007 wet season. Using recommended criteria (Journel and Huijbregts, 1981; Spokas et al., 2003), the structure of the CO_2 and N_2O emissions datasets did not permit use of a standard geostatistical technique.

3.3.4 Methane Oxidation

While primarily relying on the conservative isotopic method discussed above using chamber samples to derive the percent oxidation (and CH_4 oxidation rate, g m^{-2} d^{-1}, using static chamber fluxes and percent oxidation), we also selectively determined percent oxidation using the $\delta^{13}C$ CH_4 in soil gas sampled from shallow gas probes (10-12 cm). The latter provide a less conservative [higher] value for oxidation (Chanton et al., 2008). In addition, we also selectively determined the $\delta^{13}C$ CH_4 and the $\delta^{13}C$ CO_2 in soil gas from deeper probes at both sites. This provided a test for other potential sources of biogenic CH_4 whose isotopic signature would differ from the source gas. Moreover, because of the relatively high percentages of negative CH_4 fluxes among the field data (Fig. 3b), where the isotopic method for percent CH_4 oxidation cannot be applied, the probe data also generally provided supplementary information on isotopic fractionation in the cover soils.

Table 8 summarizes percent CH_4 oxidation in the various cover soils at both sites using the isotopic technique applied to chamber and probe data. For both datasets, the seasonal data were composited for each site [large data ranges did not support seasonal discrimination]. The first two rows in the table indicate percent oxidation for the positive CH_4 fluxes. While the two sites has almost identical minimums, the higher maximum and larger number of high values for

Scholl Canyon elevated the average value to 52 percent, compared to 30 percent for Marina. For Marina probe samples, the average percent oxidation was almost 10 percent higher than the chamber samples, consistent with literature indicating routinely higher values (Chanton et al., 2009). However, for Scholl Canyon, because of the inclusion of deeper samples where the more limited diffusion of atmospheric O_2 reduces oxidation rates, average percent oxidation was reduced for the probe samples, reflective of the significantly-increased range of field values.

Figure 9. (a) Comparison between mean (+) CH4 fluxes ±SD and fluxes determined using a geostatistical technique (IDW). Missing values indicate all fluxes were (-). (b) Percentage of surface area with negative (-) CH4 fluxes using geostatistical technique (IDW). Wet season (March) and dry season (August) data.

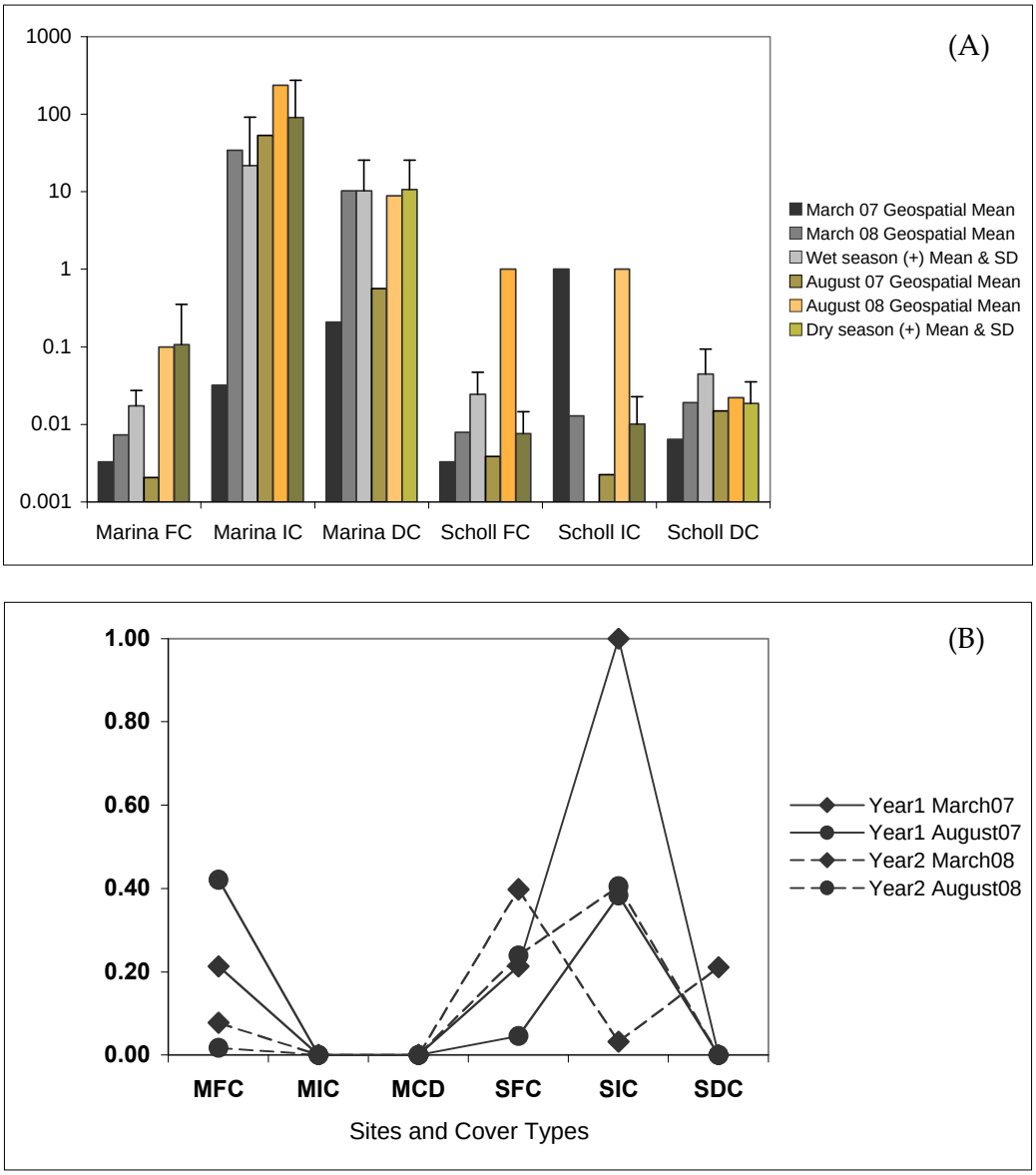
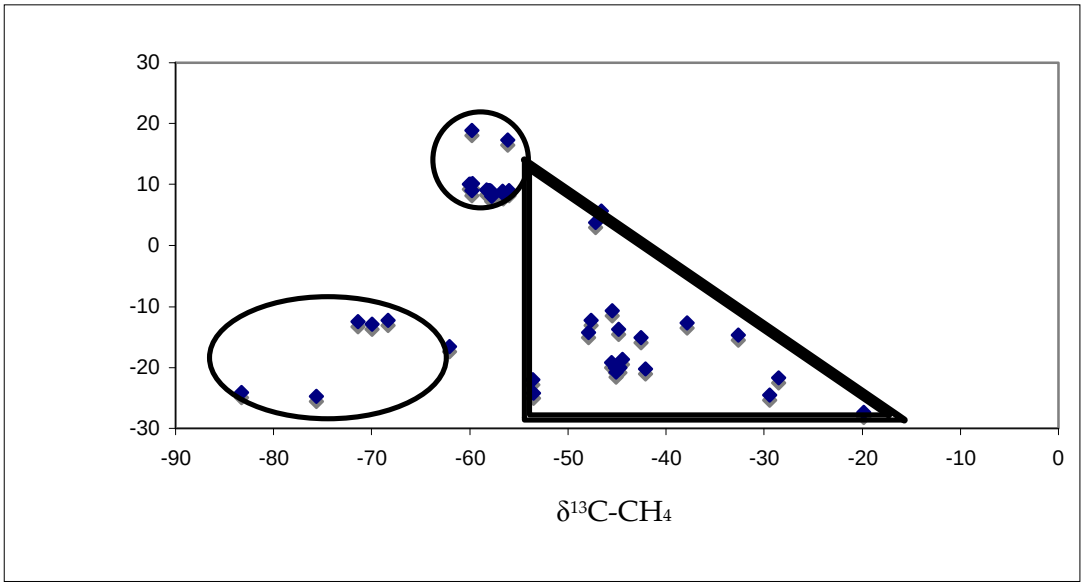


Table 8. (a) Fractional CH_4 oxidation at Marina and Scholl Canyon (based on $\delta^{13}C$ CH_4 of chamber samples compared to source gas from gas recovery wells). Data composited for all cover types at each site. Averages for all chamber data for each site where isotopic technique could be applied (non-negative CH_4 fluxes) (b) Fractional CH_4 oxidation at Marina and Scholl Canyon (based on $\delta^{13}C$ CH_4 of probe samples compared to source gas from gas recovery wells). Averages includes all probe data (depths as indicated in Table) where there was isotopic fractionation relative to source gas.

Location	Average	SD	Minimum	Maximum
	% CH_4 oxidation			
(A) Chamber Data				
Marina	30.0	12.0	10.4	42.0
Scholl Canyon	51.7	44.5	10.6	100.0
(B) Soil Gas Probe Data				
Marina: Daily & intermediate cover (10-50 cm)	39.7	21.6	0.9	81.4
Scholl: probes: Final cover (30-244 cm)	47.6	9.2	39.1	73.3

Figure 9 compares the $\delta^{13}C$ CO_2 to the $\delta^{13}C$ CH_4 for the source gas and selected probe samples from both sites, including MDC (25 cm), MIC (12-43 cm), SDC (10 cm), and SFC (30-243 cm). The Marina well gas averaged $\delta^{13}C$ CH_4 -58.37 (±1.239) while the Scholl Canyon well gas averaged $\delta^{13}C$ CH_4 -60.07 (±0.6602). All data shown in the figure are from the two wet season campaigns where we were investigating the potential for shallow secondary production of CH_4 in cover materials. Note the tightly-clustered values for the source gas from gas extraction wells0 (between -58 to -60 for the $\delta^{13}C$ CH_4 and 10-20 for the $\delta^{13}C$ CO_2). Most of the probe data indicated oxidation trends and plotted in the right triangle on this figure. However, some probe values from the MDC, MIC, and SDC plotted in the oval in the lower left portion of this figure, indicating a secondary source of biogenic CH_4. In addition, some chamber samples and other probe samples (for which the $\delta^{13}C$ CO_2 was not determined) also had $\delta^{13}C$ CH_4 in the range for the secondary source and not in the range for either the source gas or oxidized gas. Thus, we conclude that shallow secondary production of CH_4 was seasonally occurring at both sites. This issue requires further investigation in future studies, but it is likely a transient phenomenon with high spatial and temporal variability.

Figure 10. Comparison of $\delta^{13}C$ CO2 to δ^{13}13C CH4 for unoxidized source gas from landfill gas recovery wells (top circle), oxidized landfill gas (right triangle), and a secondary source of unoxidized biogenic CH4 (oval).



3.3.5 Modeling Implications of Seasonal Emissions and Oxidation Data

This is the first study which has systematically investigated seasonal GHG emissions from fresh refuse (no cover) and the full range of cover materials at the same landfill sites. The high variability with respect to CH_4 emissions among and between the various cover materials indicates that emissions models require incorporation of climatic and soil microclimate predictability to adequately model seasonal gas transport, oxidation, and "net" emissions in specific cover soils because important process controls such as soil moisture and temperature can be highly variable over an annual cycle. In addition, some cover materials are characterized by a high percentage of negative (-) CH_4 fluxes, indicating uptake of atmospheric CH_4 due to high seasonal capacities for CH_4 oxidation. Moreover, especially during wet conditions, secondary production of CH_4 in cover soils is also possible. The average CO_2 emissions generally varied within the same order of magnitude; for fresh refuse and daily cover values were consistent with (but lower than) composting systems, and for intermediate and final covers values were consistent with dark respiration rates for grassland ecosystems. The N_2O emissions are consistent with a very limited number of previous studies where the highest rates were associated with biosolids-amended cover materials. Based on the results of this study, one must call into question the routine use of existing regulatory and inventory models for landfill CH_4 emissions (27) which rely solely on a hypothetical first order kinetic model for CH_4 generation, but do not take into consideration either the properties of the cover materials or seasonal CH_4 oxidation in cover soils. Typically, inventory models allow a 10 percent reduction for CH_4 oxidation (based only on ref. Czepiel et al., 1996a); this study has indicated that percent oxidation is higher and is an important determinant of the net CH_4 emissions.

CHAPTER 4:
Model Structure and Validation: A New Field-Validated Inventory Model for Landfill CH_4 Emissions Inclusive of Seasonal Soil Microclimate and CH_4 Oxidation.

4.1 Introduction and Background

In addition to natural wetlands, atmospheric methane (CH_4) has multiple anthropogenic sources with high uncertainties (Bousquet et al., 2006), including rice production, ruminant animals, natural gas leakages, biomass burning, and landfills. Methane remains the second most important greenhouse gas (GHG) with a 100-year global warming potential (GWP) that is 25 times higher than CO_2 and a short atmospheric lifetime of about 12 years (Forster et al., 2007). Therefore, reductions in CH_4 emissions from specific sources such as landfills can positively impact atmospheric concentrations within decadal timeframes. According to global estimates summarized in the IPCC 4th Assessment Report, annual landfill CH_4 emissions of approximately 600-700 Mt CO_2 equivalent yr^{-1} constitute half the total emissions from the waste sector, or between 1 and 2 percent of total anthropogenic GHG emissions of about 49 Gt CO_2 eq. (Bogner et al., 2007; Rogner et al., 2007). In the absence of controls (such as engineered gas recovery and well-maintained cover materials) landfills can be potent local sources of atmospheric CH_4. Moreover, in both developed and developing countries with a history of landfilling, inventory estimates indicate that landfills can be one of the largest sources of atmospheric CH_4—for example, in the U.S., landfills are currently the second largest anthropogenic source of CH_4 after ruminant animals (US EPA, 2010).

Compared to other CH_4 sources, current global estimates for annual landfill CH_4 emissions are especially problematical with high estimated uncertainties of 10-30 percent to more than 200 percent (IPCC, 2006; Bogner et al., 2007). Historically, landfill CH_4 emissions have been estimated for national GHG inventories using IPCC Tier I & II methodologies (IPCC, 2006), which are based on a first order kinetic equation for landfill CH_4 generation, termed a first order decay (FOD) model. The mass of CH_4 generated in a particular year is based on the waste landfilled in that year summed with the estimated CH_4 generated from waste landfilled in previous years. Therefore, CH_4 generation relies on the annual mass of landfilled waste, assumed or reported waste composition, a methane generation potential ($m\ m^{-1}$), and a kinetic constant (t^{-1}) for each biodegradable waste component which is linked to climate (e.g. wet/dry; tropical/temperate). As appropriate for specific countries, two subtractions can also be made from the estimated annual CH_4 generation to yield the CH_4 emitted; these subtractions are: (1) the annual CH_4 recovery as quantified by instrumentation for engineered landfill gas recovery systems; and (2) a further 10 percent reduction for methanotrophic CH_4 oxidation in cover materials, which is based on one study, Czepiel et al. (1996).

Some of the highly questionable assumptions of the current FOD methodology include:

- Landfill CH_4 generation can be reliably modeled based on national annual waste data using a kinetic equation suitable for homogeneous decomposition in a well-mixed anaerobic digester.
- There is no physical retardation effect on emissions by the site-specific daily, intermediate, and final cover materials, except for the 10 percent oxidation effect at well-managed sites.
- Modeled CH_4 generation with subtractions for measured recovery and 10 percent oxidation is a reliable measure of surface CH_4 emissions.

In addition to the assumption of homogeneous landfill decomposition, a secondary tacit assumption is that reliable annual national waste data exist. More realistically, annual waste mass and composition data are lacking for many countries, data quality is variable, national definitions are not uniform, and inter-annual variability is often not well quantified (Bogner et al., 2007). Among the current approaches to national waste data are: (a) use of data with variable quality and quantity from national waste statistics, surveys, or IPCC guidance (IPCC 1996, 2006); (b) estimates based on population alone (e.g., Nakicenovic et al., 2000); and (c) because waste generation is related to affluence as well as population, the use of surrogate variables linked to demographic or economic indicators for which national data are annually collected, including gross domestic product (GDP) per capita, energy consumption per capita, or private final consumption per capita (e.g. Richards, 1989; Bogner and Matthews, 2003; Mertins et al., 1999).

Furthermore, field and laboratory research data over the last decade have demonstrated that both landfill CH_4 emission and oxidation rates can vary by several orders of magnitude in field settings, and that measured emissions are related to the presence or absence of engineered gas extraction and the seasonal properties of site-specific cover materials to retard gaseous emissions and promote methanotrophic oxidation (e.g., Scheutz et al., 2009; Bogner et al., 1997a; Bogner and Spokas, 2010). In particular, detailed CH_4 mass balance studies at field scale (7 cells at 3 landfill sites) have shown that, while CH_4 recovery could be generally correlated to FOD modeled CH_4 generation at sites where waste inputs were well-quantified, there was no correlation between modeled generation and measured emissions, which varied over about 6 orders of magnitude (see Fig.2; Chapter 1). Finally, the 10 percent CH_4 oxidation value is derived solely from the first study in the literature to quantify annual CH_4 oxidation (Czepiel et al., 1996). This assessment relied on field measurement of emissions using chamber and tracer methods, supporting laboratory oxidation studies for cover soils, and the application of a seasonal climatic model for a single small northeastern U.S. landfill (Nashua, New Hampshire) which did not have an engineered gas recovery system. A recent review summarizing stable carbon isotopic investigations for landfill CH_4 oxidation indicated an average of 35 ± 6 percent across a variety of landfill cover materials, seasonal variability, and management practices (Chanton et al., 2009).

Importantly, neither the existing IPCC multicomponent FOD methodology for landfill CH_4 emissions (IPCC, 2006), nor the single component LANDGEM methodology used in the U.S.

(US EPA, 2005), were ever field-validated for surface CH_4 emissions. Rather, historic model validation consisted of comparing modeled generation to measured gas recovery, which is often used as a calibration for the generation model (e.g. Scheepers and Van Zanten, 1994; Van Zanten and Scheepers, 1995; Peer et al., 1993; Scharff and Jacobs, 2006; Thompson et al., 2009). In general, this historical reliance on generation models was related to the scarcity of field measurements for landfill CH_4 emissions at the time these models were developed, coupled with the original and more typical use of these models since the mid-1970's as a predictive tool for recoverable CH_4 at commercial landfill gas utilization projects. Therefore, even though the most recent guidelines (IPCC, 2006) facilitate national inventory calculations by providing a default spreadsheet, there have been no fundamental changes in the FOD model strategy for about 15 years (IPCC 1996, 2006). Indeed, the application of the IPCC model to the two field validation sites selected for this project indicated that the modeled CH_4 generation, based on site-specific disposal data and regional California waste composition data, was only a fraction of the currently-measured CH_4 recovery. Therefore, a fundamentally-different approach is needed.

The purpose of this project was to develop an improved landfill CH_4 inventory methodology for California by decoupling emissions from both a theoretical FOD model and uncertain national waste data by focusing instead on the fundamental processes which control emissions. For some time, it has been recognized that CH_4 emissions are related to cover soil thickness, texture and microbial oxidation rates which vary spatially and temporally with seasonal climatic trends (e.g. Jones and Nedwell, 1990; Kightley et al., 1995; Bogner et al., 1997b; Klusman and Dick, 2000; Scheutz et al., 2009). In addition, the published literature has concluded that landfill CH_4 emissions are not strongly correlated to CH_4 generation but rather to (a) the effect of engineered landfill gas recovery, which lowers CH_4 concentrations at the base of the cover, in turn reducing the driving force for diffusive flux of CH_4 to the atmosphere (e.g. Bogner et al., 1997b; Park and Shin, 2001; Zhang et al., 2008) and (b) major surface processes, including seasonally-variable CH_4 transport and methanotrophic oxidation in daily, intermediate, and final cover materials with distinctive physical and chemical properties (e.g. Maurice and Lagerkvist, 2003; Zhang et al., 2008; Scheutz et al., 2009). These physical and biochemical effects are strongly coupled; for example, engineered gas extraction can facilitate oxidation due to reduced rates of CH_4 flux through the cover materials. CH_4 transport and oxidation rates are strongly linked to seasonal temperature and infiltration processes, both in natural ecosystems (Morrissey and Livingston, 1992; Hargreaves and Fowler, 1998) and in landfill cover soils (Scheutz et al., 2009; Maurice and Lagerkvist, 2003). In general, both CH_4 emission and oxidation rates can vary by 6-7 orders of magnitude in landfill cover soils (Scheutz et al., 2009; Bogner et al., 1997a, 1997b), and the "net" emissions to the atmosphere inclusive of oxidation are strongly controlled by seasonal variability in the cover soil microclimate conditions, especially moisture and temperature (e.g. Scheutz et al., 2009; Spokas and Bogner, 2010).

Although the literature contains several process-based models which address gaseous carbon and nitrogen fluxes from other ecosystems [e.g. CENTURY (Parton, 1996); LPJmL (Bondeau et al., 2007); CASTANEA (Davi et al., 2006)], there have been limited models validated at field scale for landfill environments, where emissions modeling to date has generally been compared

to laboratory-scale and plot scale studies (e.g. de Visscher and van Cleemput, 2003; Mollins et al., 2008; Scheutz et al., 2009). An earlier empirical model for landfill emissions at field scale (Bogner et al., 1997b, 2000) addressed variability in landfill CH_4 emissions and oxidation using a collision-based framework for gaseous transport and an empirical fit for microbial growth dynamics (e.g. linear, quadratic, or exponential). However, this model did not include direct linkage to seasonal soil microclimate effects on CH_4 oxidation or a standard gaseous diffusion modeling framework.

In general, gas transport in the subsurface occurs by both diffusion (due to concentration gradients) and advection (due to pressure gradients), with diffusion commonly assumed to be the dominant transport mechanism in near-surface soils (e.g. van Bavel, 1951; Farmer et al., 1980; Massmann and Farrier, 1992; Rolston and Moldrup, 2002; Tang et al., 2003; Mollins et al., 2008). The model developed for this study is based solely on 1-D gas diffusion as the major gaseous transport mechanism for landfill CH_4 emissions. Recent studies have also suggested that, under certain conditions (low compaction and high air-filled porosity), advection can also be an important process (e.g. Reinecke and Sleep, 2002; Risk et al., 2002; Takle et al., 2004; Camarda et al., 2007). However, for the reasons discussed below, we concentrated on diffusion as the primary transport mechanism for this study. In general, landfill cover soils are typically highly compacted (bulk densities >1.5 g cm^{-3}; Bogner et al., 2010) resulting in low liquid permeability (10^{-3} to 10^{-5} m/s; with limits reaching 10^{-7} m/s in field measurements; Albright et al., 2004). Low hydraulic permeability is often established by regulations governing final landfill cover specifications (e.g. US EPA, 1992). A recent investigation into the gas permeability of various landfill cover materials indicated that gas permeability for most cover soils ranged between 10^{-9} and 10^{-12} m^2 (Kallel et al., 2004). From the radon literature, Clements and Wilkening (1974) predicted a convective flow of 10^{-4} cm sec^{-1} for a gas permeability of 10^{-12} m^2 for barometric pressure changes of 2 kPa. Kallel et al. (2004) observed gas flow velocities of 10^{-4} cm sec^{-1} for a 0.02 kPa m^{-1} pressure gradient in various landfill cover materials. Field observations in the landfill literature do not generally support the sustained existence of relatively-constant pressure gradients through landfill cover soils (McBean and Farquhar, 1980; Bogner et al., 1987; Borjesson and Svensson, 1997) and pressure gradients can attenuate rapidly in soils with low air-filled porosity (Kimball, 1983). An approximate magnitude of convective flux can be estimated using Darcy's law (Nazaroff, 1992) for a landfill gas cover of 1 m thickness: assuming 50 percent v/v methane in landfill gas, 0.02 kPa m^{-1} pressure gradient, total velocity of 10^{-4} cm sec^{-1} (10^{-4} cm^3 cm^{-2} sec^{-1}), and CH_4 density of 0.656 x 10^{-4} g cm^{-3} would result in a mass flux of approximately 3 g CH_4 m^{-2} day^{-1}. This value is significantly lower than measured CH_4 fluxes from intermediate (1 m thick) cover materials of 100-1000 g CH_4 m^{-2} day^{-1} reported in the literature (e.g. Borjesson and Svensson, 1997; Zhang et al., 2008; Bogner et al., 2010). Furthermore, Kim and Benson (2004) examined O_2 transport through various earthen and geomembrane soil covers associated with mining wastes, concluding that, on the basis of modeling and supporting field studies, diffusion rather than convection was the dominant mechanism for gaseous flux, accounting for approximately 99 percent of the transport. A recent study by Mollins et al. (2008) also stressed the dominance of diffusion for CH_4 transport (about 90 percent) using modeling and laboratory column studies. Situations where advection is or can be important in landfill settings include subsurface gas transport for vertical recovery

wells or horizontal collectors (small vacuum applied), cover soils with very high gas-filled porosity (e.g. some compost-amended "biocovers"), non-soil emissions including interconnected gas paths (e.g. cracks, fissures requiring maintenance), gas flow very near the base of the soil cover (Choi et al., 2002; Fredenslund et al., 2010; Mollins et al., 2008), and, depending on the magnitude of barometric pressure changes, flows generated during passing of weather fronts (Nastev et al., 2001; Czepiel et al., 2003; Poulsen et al., 2003; Gebert and Groengroeft, 2006). In these situations there is the expectation of significant pressure gradients, gas channel connectivity, and higher gas permeability. As illustrated by Mollins et al. (2008), advection-dominated flux is characterized by constant soil gas profiles with depth due to mass flow, whereas diffusion-dominated profiles have non-linear, exponentially-varying soil gas concentrations with depth, which are the typical soil gas profiles observed in landfill settings (e.g. Bogner et al., 1997b; Chomsurin, 1997; Zhang et al., 2008a,b; Bogner at al., 2010).

The model developed for this study (CALMIM, California Landfill Methane Inventory Model) is an annual landfill CH_4 emissions inventory model for California that was developed and field-validated during 2007-2010. A major driver for this study was a research review for California (Farrell et al., 2005) which indicated that an improved landfill CH_4 inventory methodology was a high priority due to high uncertainties associated with the current methods. Originally, we had intended to only address improvements with respect to the (10 percent default) CH_4 oxidation calculation within the current IPCC Tier I model. However, an important consideration for California was that, according to data compiled by CalRecycle, >90 percent of the waste in place in permitted California landfills is currently under active gas extraction. Thus, as discussed above, considering that field-scale data on surface CH_4 emissions for well-monitored cells elsewhere with engineered gas extraction were not correlated with modeled CH_4 generation (Spokas et al., 2006), and currently-measured CH_4 recovery at our field validation sites greatly exceeded modeled CH_4 generation (using the IPCC model), we developed an entirely new model that is not related to idealized CH_4 generation using a first order kinetic model. Fundamentally, our constraints included: (a) an approach which could be directly validated using field data for measured CH_4 emissions; (b) an approach in which the measured emissions could be directly related to both CH_4 transport and oxidation processes; (c) an approach in which model input parameters, as well as model outputs, could be measured at field scale; and (d) a model approach which is consistent with the structure of the current IPCC National Inventories Guidelines for CH_4 emissions from solid waste disposal sites (IPCC 2006). In terms of the IPCC structure, CALMIM is the first IPCC Tier III model using "validated higher quality" methods allowed by IPCC (IPCC, 2006), and it is the first such model designed for regional applications which rigorously decouples landfill CH_4 emissions from an FOD model.

CALMIM is a freely-available JAVA tool based on 1-D diffusion [using a 10-min. time step and 2.5 cm depth increments] for site-specific daily, intermediate, and final cover soils inclusive of CH_4 oxidation over a typical annual cycle. CALMIM includes: (1) the effect of engineered gas extraction on "net" emissions to the atmosphere; (2) the variable physical effect of daily, intermediate, and final cover materials to retard emissions; and (3) seasonal moisture and temperature effects on both gaseous transport and methanotrophic CH_4 oxidation in cover materials. Within CALMIN, the major driving force for emissions is the CH_4 concentration

gradient through user-selectable cover materials, which is, in turn, related to the presence of engineered gas extraction systems and the efficiency of CH_4 oxidation in any particular cover soil. Both transport and oxidation are rigorously linked to seasonal climatic and soil microclimate variability through modified versions of existing, globally-validated models (Spokas and Forcella 2006, 2009). As discussed below, this model has been extensively field-validated at 2 California landfills over 2 annual cycles. In addition, oxidation rates relative to CH_4 exposure, soil moisture, and temperature have been extensively investigated via supporting laboratory studies (Spokas and Bogner, 2010). This model provides an improved science-based approach for modeling annual landfill CH_4 emissions which is also consistent with recent literature emphasizing strong seasonal dependencies for CH_4 transport, oxidation, and emissions in non-landfill soil ecosystems (e.g. Cao et al., 1995; Wille et al., 2008).

4.2 Methods

4.2.1 Model Structure and Components.

Figure 10 and Tables 9 & 10 provide an overview of the model structure and components. CALMIM consists of a freely-available JAVA program (http://calmim.lmem.us) which integrates site-specific data (location and cover design) to climatic simulation and one dimensional soil microclimate and gas diffusion models. The model estimates annual CH_4 emissions while accounting for climate-induced variability in soil microbial oxidation. Although more complex models exist for predicting the flow of landfill gas as a function of diffusion and advection (e.g. Findikakis et al. 1979, 1988; Lang et al., 1989; Kindlein et al., 2006; Donovan et al., 2010; Yu et al., 2010), a number of the assumptions in these models are often violated in field settings (e.g., waste mass as a homogeneous porous medium with known characteristics, including uniform composition and static CH_4 generation rate at every point). Moreover, required model input parameters are often unknown, highly variable or cannot be directly measured in field settings (e.g. gas flux to the base of soil cover). Thus, the theoretical complexity of existing models linked to various uncertainties relative to field settings hinders our ability to arrive at a robust tool that can be field-validated for prediction of surface CH_4 emissions. Therefore, we relied on a 1-D gaseous diffusion model based on first principles, since this approach focuses directly on the factors that control surface emissions (e.g. cover soil characteristics, microbial methane oxidation, climate, and CH_4 concentration gradient through the cover materials). Each of the model components shown in Figure 10 will be described in separate sections below. Many components have both default settings as well as settings which can be customized by the user based on field measurements or site management practices. Site-specific practices including various cover materials and engineered gas recovery are extremely important for landfill settings, which compared to other CH_4-emitting settings such as wetlands or rice production systems, represent a highly-managed endpoint (Bogner et al., 2000). CALMIM is the first model to link landfill CH_4 emissions predictions to seasonal climatic variability at the 0.5 by 0.5 degree latitude-longitude scale grid.

Table 9. Overview of CALMIM input parameters and default boundary conditions.

		Description	Value/Units/Reference
Model Inputs	Site	Latitude	Decimal degrees (+N , -S)
		Longitude	Decimal degrees (-W, +E)
		Waste Footprint	Acres
	Cover Characteristics	Coverage	0-100% of waste footprint
		Organic Matter	Low-high (0-5%)
		Vegetation Presence	0-100% cover (slider bar)
			Modifies incoming solar radiation
			[Si = (1-Veg%)*Si]
		Gas Recovery System	0-100% coverage
			(slider bar)
			Reduces the lower methane concentration in default cover scenarios

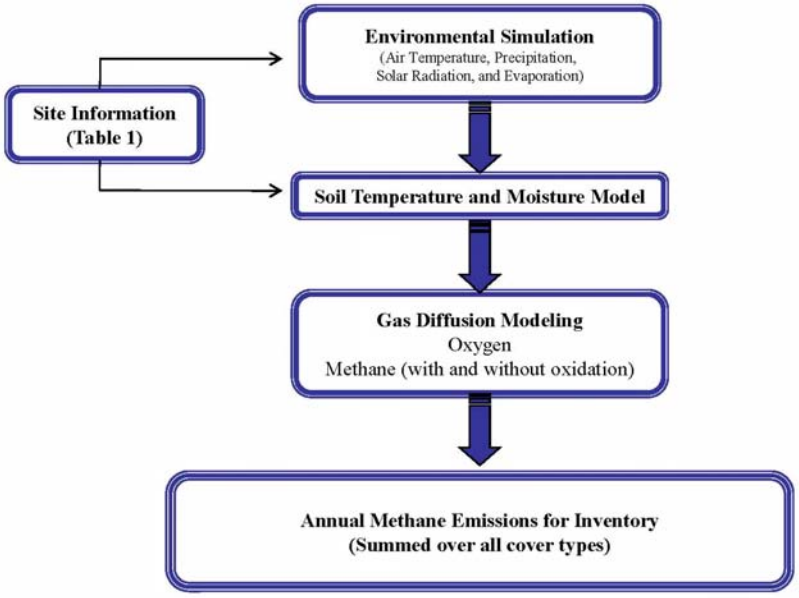
Default Boundary Conditions For Cover Type Selection.

		Daily Cover	Intermediate Cover	Final Cover
Temperature	Upper	*Air Temperature Simulated (GlobalTempSIM)*		
	Lower	25 °C	35 °C	40 °C
CH_4 Concentration	Upper	2 ppmv		
	Lower	0.3% (v/v)	45% (v/v)	55% (v/v)
O_2 Concentration	Upper	20% (v/v)		
	Lower	5% (v/v)	1% (v/v)	0% (v/v)
Oxidation Rate ($\mu g\ CH_4\ g_{soil}^{-1} d^{-1}$)		1	200	400

Table 10. Description of incorporated models and model outputs.

		Description	Value/Units/Reference
Bundled Models	GlobalTempSIM	Air temperature simulation	Spokas and Forcella, 2009
	GlobalRainSIM	Precipitation simulation	Spokas and Forcella, 2009
	SolarCalc	Solar radiation simulation	Spokas and Forcella, 2006
	STM[2]	Soil temperature and moisture model	Spokas and Forcella, 2009
	Gas Diffusion	Oxygen and methane diffusion	Campbell, 1985
Model Outputs	*Model outputs are written directly to Excel compatible files for each cover type*		
	Daily Surface CH_4 emissions	With oxidation	g CH_4 $m^{-2}d^{-1}$
		Without oxidation	g CH_4 $m^{-2}d^{-1}$
	Soil Nodes (2.5 cm layer in cover)	Soil Temperature	^oC
		Soil Moisture	Volumetric (cm^3 cm^{-3})
		Air-filled porosity	cm^3 cm^{-3}
		Oxygen Concentration	% O_2
		CH_4 With oxidation	% CH_4
		CH_4 Without oxidation	% CH_4
		CH_4 oxidation rate	g CH_4 $m^{-2}d^{-1}$
		CH_4 oxidation percentage	%
		Bulk density	g cm^{-3}
		Fraction of time oxidizing	0 to 100% (0-1)
	Simulated Weather Data	Maximum air temperature	^oC
		Minimum air temperature	^oC
		Precipitation	mm

Figure 11. Graphical overview of the CALMIM model.



4.2.1.1 Climate Simulation Models

The existing models SolarCALC, GlobalTempSIM and GlobalRainSim (Spokas and Forcella 2006, 2009) were incorporated into CALMIM to simulate a typical annual cycle of air temperature, precipitation, and incoming solar radiation referenced to site latitude and longitude (Table 10). These models were previously validated for a number of global locations (Spokas and Forcella, 2006, 2009; Kahimba et al., 2009) and rely on 30-yr (1961 – 1990) interpolated databases of Legates and Willmott (1990a and 1990b), Willmott and Matsuura (1995), and New et al. (1999). Although the CALMIM model was developed for application in California, these bundled simulation models confer global applicability. Average diurnal air temperature patterns are simulated in CALMIM using methods described by Cesaraccio et al. (2001) yielding air temperature values interpolated down to minute intervals for an annual cycle.

4.2.1.2 Soil Microclimate Model

The soil microclimate simulation is linked to both site-specific designs for daily, intermediate, and final cover soils (discussed in the next section) and a modified version of an existing soil temperature/moisture model, STM^2 (Spokas and Forcella, 2009). The original STM^2 boundary conditions, developed for agricultural settings (Spokas and Forcella, 2009), were altered for

CALMIM (Table 10) to account for the fact that landfills have a heat source (decomposing refuse) at the cover/refuse boundary. In addition, due to the presence of saturated landfill gas at the cover/refuse interface, a saturated boundary condition was also assumed. CALMIM permits the user to override these defaults through user selectable boundary conditions (Table 1 and Figure 2c). In general, CALMIM incorporates default soil physical properties based on the soil texture and alternative cover materials (Table 2), including allowed California alternative daily cover materials. It should be noted that the soil properties were derived from literature and databases for a variety of ecosystems (e.g. Clapp and Hornberger, 1978; Bouma, 1989; Wösten and van Genuchten, 1988) and not specifically for managed landfill settings. Compared to agricultural and other non-landfill soils, landfill covers are typically compacted to higher bulk densities (Bogner et al., 2010). Although this under-estimation is a source of error in the modeling, it adds conservatism to the transport modeling for annual inventory purposes since the more compacted landfill soils would result in further reductions of effective diffusion coefficients and correspondingly lower surface fluxes.

4.2.1.3 Landfill Site Properties (including cover materials and engineered gas recovery)

Required CALMIM inputs include the site location (latitude and longitude), cover description (material type and layer thickness), and the corresponding CH_4 concentration gradient. The site information is collected from the user through data input screens (Figure 11). Each daily, intermediate, and final cover material, up to a total of 10 different covers, is modeled separately with the results summed for an estimate of annual total site emissions. The user can choose between typical California cover designs [see Table 1] or a customized sequence using the "cover designer" where any layered soil sequence can be entered. For a particular cover, the minimum thickness for any layer is 2.5 cm and the maximum total thickness of about 2.5 m is related to limits for typical PC memory resources. USDA standard soil texture classes, alternative daily cover (ADC) and other non-soil materials (e.g. composts, biosolids, tire chips, geomembranes) are also available with their corresponding transport properties taken from published literature (Table 11). If the concentration gradient is not known, the model utilizes default settings based on the cover type selected (daily, intermediate, or final) (Table 9). The default settings are based on values taken from the literature and reflect mature methanogenesis (e.g., higher base CH_4 concentrations) underlying the intermediate and final cover soils.

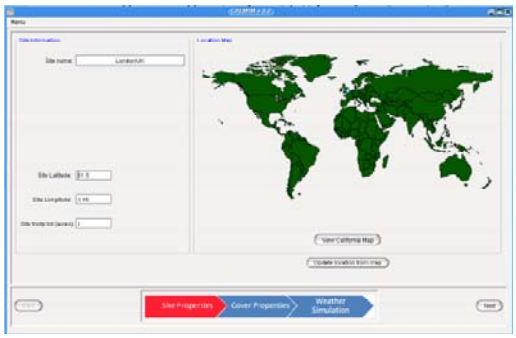
Table 10. Summary of cover materials contained in CALMIM

Soil Materials	Sand (%)	Silt (%)	Clay (%)	Bulk Density (g cm^{-3})	Saturated Conductivity (kg m^{-3})	Volumetric Moisture (33 kPa)	Volumetric Moisture (1500 kPa)	Beta (Campbell, 1985)	Total Porosity (33 kPa)
SAND	93.6	3.06	3.34	1.63	0.002703	0.091	0.039	2.01	0.386
SANDY CLAY	93.6	3.06	3.34	1.44	0.000176	0.231	0.113	10.21	0.455
LOAMY SAND	82.74	9.66	7.6	1.58	0.001760	0.116	0.051	2.86	0.402
SANDY LOAM	65.6	22.5	11.9	1.53	0.000763	0.139	0.062	4.29	0.422
SILTY LOAM	21.8	62.7	15.5	1.28	0.000137	0.276	0.125	6.86	0.518
LOAM	42.9	39.5	17.6	1.40	0.000292	0.223	0.102	6.26	0.474
SANDY CLAY LOAM	60.1	11.3	28.6	1.47	0.000356	0.2	0.095	7.42	0.445
SILTY CLAY LOAM	9	55	36	1.24	0.000052	0.321	0.151	10.36	0.532
CLAY LOAM	34.7	30.3	35	1.35	0.000125	0.264	0.125	8.94	0.489
SILTY CLAY	9.3	43.89	46.81	1.28	0.000031	0.312	0.15	13.00	0.517
CLAY	10	25	65	1.26	0.000034	0.351	0.172	14.20	0.524
SILT	7.96	63.62	5.41	1.16	0.000106	0.332	0.149	6.72	0.564
Rocks - Pebbles	93.6	3.06	3.34	1.63	0.002703	0.091	0.039	2.01	0.386
Rocks/Boulders	95.6	2.06	2.34	2.01	0.003100	0.071	0.019	2.01	0.245
ADC Foundry Sands	90	5	5	1.63	0.003703	0.1	0.04	3.00	0.39
ADC Dredged Materials	7.96	63.62	5.41	1.16	0.000106	0.332	0.149	6.72	0.564
ADC Ash	21.8	62.7	15.5	1.28	0.000137	0.276	0.125	6.86	0.518
ADC Contaminated Soils (clay)	10	25	65	1.26	0.000034	0.351	0.172	14.20	0.524
ADC Contaminated Soils (sand)	90	5	5	1.63	0.003703	0.1	0.04	3.00	0.39
ADC Contaminated Soils (loam)	42.9	39.5	17.6	1.40	0.000292	0.223	0.102	6.26	0.474
ADC Tire Shreds [small	90	5	5	1.08	0.051300	0.19	0.06	2.00	0.51
ADC Tire Shreds [large)]	90	5	5	1.63	0.003703	0.1	0.04	3.00	0.39
ADC Wood Chips (all)	90	5	5	1.08	0.081300	0.22	0.06	2.00	0.33
ADC sludge	10	80	10	1.20	0.001060	0.452	0.15	8.70	0.564
ADC ERE and Production Wastes	42.9	39.5	17.6	1.40	0.000292	0.223	0.102	6.26	0.474
ADC Composted Organic Materials	42.9	39.5	17.6	1.40	0.000292	0.223	0.102	6.26	0.474

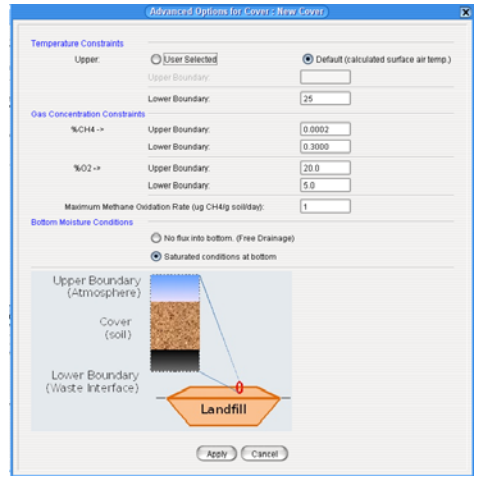
Notes: The non-soil materials (geomembranes, geotextiles, tarps, and foams) are modeled as clay soil with scaling factors to alter the corresponding diffusion, thermal and hydraulic conductivities to account for the synthetic material.

Figure 12. Illustrations of the various screens within the CALMIM model: a) site information, b) cover characteristics, c) custom boundary conditions window (defaults for daily cover type shown), and d) final model output screen.

(A)

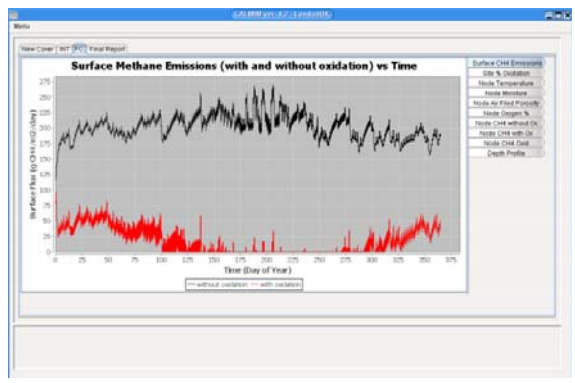


(C)



(B)

(D)



As discussed above, engineered landfill gas recovery systems consisting of either vertical wells or horizontal collectors are an important influence on emissions. Thus, CALMIM requires input parameters on whether engineered gas recovery underlies each particular cover type and the corresponding spatial extent of coverage of the recovery system. Gas recovery for each cover type is expressed as % of total area with engineered gas extraction. If the user is using the default gas concentrations, the model scales the base CH_4 concentration using the following formula:

$$CH_4 \text{ Base} = (CH_{4_Default})\ (1 - 0.3 * \text{Coverage } \%), \qquad \text{(Eq. 3.1)}$$

where $CH_{4_Default}$ is the default cover concentration (Table 9) and Coverage % is the aerial extent of the gas recovery system under the particular cover type (value 0-1 representing 0-100%). If the user enters a custom gas concentration at the base of the cover, this linear correction is not performed, since the measurement would already include the correct concentration reduction attributed to the gas recovery system (Bogner et al., 1997b; Zhang et al., 2008). The estimation of a 30% reduction due to a gas recovery system covering 100% of the cover type is a conservative estimate, based on the field observations ranging from <1% to 35% v/v CH_4 at the base of final

covers with a gas recovery system in place (e.g. Bogner et al., 1997b; Zhang et al., 2008; Bogner et al., 2010). We strongly advocate the field measurement of this boundary concentration by using a statistically-significant number of soil gas probes monitoring CH_4 concentration at the waste-soil interface under the various cover types; these values would be entered in the custom boundary dialog of the model (Fig. 11c). Field measurement of the CH_4 concentration gradient across the cover allows a direct assessment of the site-specific balance between CH_4 generation and recovery.

4.2.2 Diffusion/Oxidation Modeling and CALMIM Output

Gas diffusion was assumed to obey Fick's law, which is widely used and observed to provide satisfactorily comparisons for gas transport in soils (e.g. Grable and Siemer, 1968; Simunek and Suarez, 1993; Moldrup et al., 1998, 2000, 2003). From Fick's law,

$$J = D_s \frac{dC}{dz} \approx D_s \frac{\Delta C}{\Delta z}, \qquad \text{(Eq. 3.2)}$$

where J is the flux of gas species, $D_s = D_s(\theta,\phi)$ is the soil gas diffusion coefficient that varies with time as a function of soil porosity (ϕ) and volumetric water content (θ), C is the gas concentration, and z is depth. Moldrup et al. (1998) suggested a soil-type dependent gas diffusivity model (referred to as the Buckingham-Burdine-Campbell equation) for gas diffusivity:

$$D_S = D_{a,T}\left(\phi^2\right)\left(\frac{\theta_{air}}{\phi}\right)^{2+\frac{3}{B}}, \qquad \text{(Eq. 3.3)}$$

where $D_{a,T}$ is the free-air diffusion coefficient at temperature T (0.16 cm^2/sec @ 20C), ϕ is the total soil porosity ($cm^3\ cm^{-3}$), θ_{air} is the air filled porosity ($cm^3\ cm^{-3}$), and B is the Campbell B or the slope of the soil moisture retention curve in a log(θ)–log($-\Psi$) coordinate system (Campbell, 1985). This model of the soil diffusivity was found to provide better prediction than other models across multiple soil types (e.g. Rolston and Moldrup, 2002; Moldrup et al., 2004). Temperature also influences diffusion and can be accounted for by the relationship:

$$D_{a_T} = D_{a20C}\left(\frac{T}{293K}\right)^{1.75}, \qquad \text{(Eq. 3.4)}$$

where D_{a_T} is the free air diffusion coefficient at temperature T, D_{a20C} is the free-air diffusion coefficient at 20 ^oC and T is the temperature (^oK) (Jones, 1992). Since we know the soil texture, temperature and soil moisture content of each node at any given time step, the effective diffusivity can be calculated for each layer. For the flux calculation, Fick's law was solved at each time step using the Thomas algorithm (Campbell, 1985). The mass balance at any node N is given by:

$$J_N - J_{N-1} - U_N = 0, \qquad \text{(Eq. 3.5)}$$

Where J_N is the gas flux at node N, J_{N-1} is the flux at node N-1, and U_N is the sink at node N (of oxygen or methane). For oxygen consumption, the assumptions of Campbell (1985) were used (surface rate of 5×10^{-4} g O_2 m^{-3} sec^{-1} with an exponential decrease with depth). For CH_4 oxidation, empirical relationships developed in Spokas and Bogner (2010) for estimating the rate of CH_4 oxidation as a function of soil temperature and soil moisture potential were used for each node and each time step. The default optimum rates for CH_4 oxidation capacity as a function of cover type are given in Table 1. However, these values can be altered by the user (Figure 11c) if site-specific data are available. Due to the fact that CH_4 oxidation alters the concentration gradient and thereby the flux of CH_4 through the entire cover, the non-oxidized and oxidized scenarios are modeled independently to adequately account for the net difference in the surface emissions as a result of methanotrophic activity. This also allows the user to readily quantify the overall impact of CH_4 oxidation, as well as visualize the temporal effects (daily or seasonal) in the standard output plots.

The output seasonal graphs generated automatically by CALMIM for each simulation run include: surface CH_4 emissions with and without CH_4 oxidation, site percent oxidation estimate, graphs of the profile (surface, middle and bottom nodes) of the nodal soil temperature, soil moisture, air-filled porosity, oxygen concentration, methane concentration (with and without oxidation), and corresponding CH_4 oxidation rate, as well as the average depth profile of CH_4 oxidation. CALMIM also automatically generates EXCEL-compatible output files which archive the results of each simulation, including the calculated soil properties as a function of depth and time during model simulation [e.g. profiles for soil temperature/moisture, air-filled porosity, O_2 concentration, CH_4 oxidation rate, and CH_4 surface flux and soil gas concentrations with and without CH_4 oxidation (Figure 11d)].

4.2.3 Sensitivity Analyses

Various model runs were evaluated over a wide range of soil texture, cover thicknesses, organic matter content, and gas recovery to evaluate the impact of these parameters on CH_4 emission and oxidation predictions. In order to isolate the behavior of individual inputs, model sensitivity was determined by varying input parameters singularly and examining the impact on emission and oxidation predictions. This sensitivity analysis does not validate the model, but confirms the operation of the model and overall sensitivity to variable input parameters.

4.2.4 Field Validation

Field validation was conducted over two years at two California sites, including the coastal Marina Landfill (36.71° N, 121.762° W, Monterey County) and the Scholl Canyon Landfill (34.158° N, 118.196° W, Los Angeles County). Four field campaigns at each site focused on wet (March 2007 and 2008) and dry season (August 2007 and 2008) monitoring of CH_4 emissions using multiple deployments of 9 randomized static chambers for CH_4 emissions across the three major cover types (daily, intermediate, and final). Because static chambers can quantify the spatial variability of both positive fluxes and negative fluxes (uptake of atmospheric CH_4) across a given cover type, this is the method of choice for small-scale process-related studies. Moreover, because we were developing an annual inventory model, non-soil fluxes associated with cracks, fissures, and piping leakages were not considered, since California and U.S.

regulations require quarterly monitoring of surface CH_4 concentrations followed by remediation and re-monitoring as part of normal operations and maintenance (i.e., South Coast Air Quality Management District Rule 1150.1; see http://www.aqmd.gov/rules/reg/reg11 /r1150-1.pdf). The properties of the cover materials and soil methods are described in detail in Spokas and Bogner (2010). In addition, weather stations [Onset Computing[1]] and depth arrays of soil temperature/moisture sensors were installed at each site to continuously monitor wind speed, air temperature, relative humidity, and soil temperature and moisture profiles [Onset Computing]. Sampling and analysis techniques for chamber samples, soil gas probes, and source gas (composite landfill gas) were discussed or referenced in previous chapters of this report. Gas samples were analyzed at the USDA-ARS laboratories in St. Paul and Morris, MN. Soil moisture (TDR) and temperature (RTD) were also measured at each of the >800 chamber locations. The minimum detectable CH_4 flux was ± 12 mg CH_4 m^{-2} d^{-1}.

Field measurements of emissions on intermediate cover materials at three additional California Landfills (Kirby Canyon; 37.185 °N 121.671 °W, Lancaster; 34.747 °N 118.116 °W; and Tri-Cities/Fremont; 37.51 °N 121.99 °W; Green et al., 2009) were also compared to modeled results. All of these sites are large, active municipal solid waste landfills [>1200 metric tons d^{-1}] with operational landfill gas collection systems for the entire waste footprint. The Lancaster landfill is located in an arid, high desert region (Mojave Desert), while the Tri-Cities and Kirby Canyon sites are characterized by a Mediterranean climate. Field measurements included both static chambers and an above-ground technique using a TDL (tunable diode laser) instrument for vertical and horizontal radial plume mapping (Green et al., 2009).

For all five field validation sites, stable carbon isotopes for CH_4 for selected chamber and probe samples were analyzed at Florida State University. Fractional CH_4 oxidation (as % oxidation) was calculated using published methods (Liptay et al., 1998; Chanton and Liptay, 2000; Chanton et al., 2008) based on a comparison of the $\delta^{13}C$ for anoxic zone CH_4 compared to the emitted CH_4 (chambers or probes).

4.2.5 Statistical Model Validation

Pearson correlation coefficients (R^2) were calculated as the routine measure of correspondence. However, significant correlation coefficients do not automatically correlate to model accuracy (Willmott, 1982). Therefore, for air and soil temperature comparisons an "index of agreement" or modeling index (d) was calculated with the following expression:

$$d = 1 - \left[\frac{\sum_{i=1}^{n} (x_i - y_i)^2}{\sum_{i=1}^{n} \left(\left| x_i - \bar{x}_i \right| + \left| y_i - \bar{x}_i \right| \right)^2} \right], \qquad \text{(Eq. 3.6)}$$

[1] - Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

where x_i are the field measured values with a mean of $\bar{x}_i$ and y_i are the modeled values and corresponding $\bar{y}_i$ (Willmott 1981; Mayer and Butler 1993). The value of d will range between 0 and 1, with a value of 1 indicating perfect model agreement (Willmott, 1981). Two other statistical measures [root mean square error (RMSE) and mean absolute error (MAE)] were also calculated, since the units are the same for the parameter as the observed quantity and therefore allow a more meaningful comparison. These statistical measures have been used in other modeling comparisons (e.g. Wegehenkel 2000; Winslow et al. 2001; Spokas and Forcella, 2006) and are recommended measures in assessing model performance (Willmott, 1982).

4.3 Results and Discussion

4.3.1 Sensitivity Analysis

Various sensitivity analyses were conducted to examine the impact of varying soil textures, cover thickness, concentration gradients and recovery system presence on the output of the model for a single location. These sensitivity analyses will be described in separate sections below.

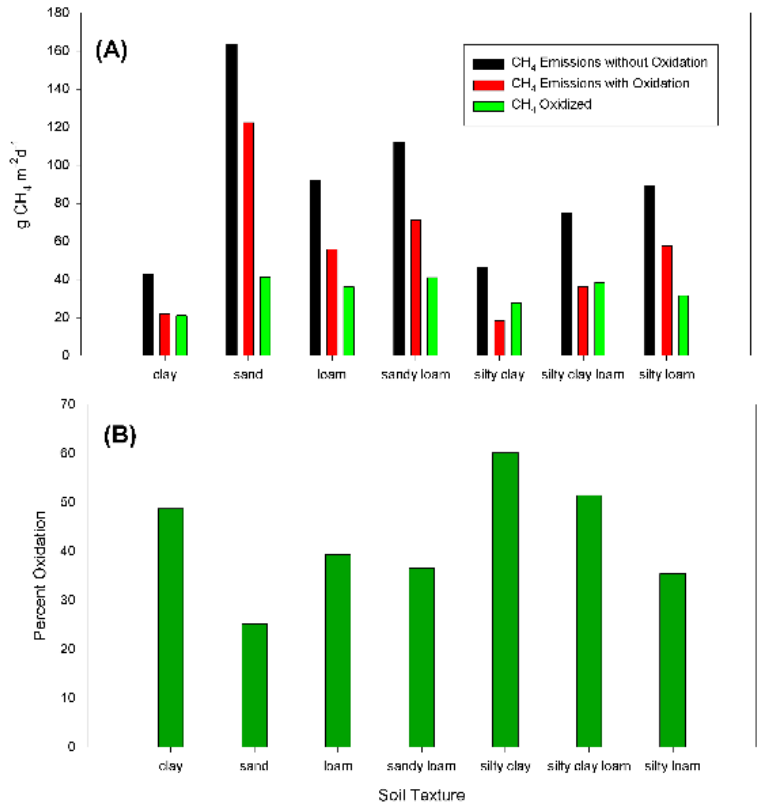
4.3.1.1 Impact of soil texture on CH_4 emissions and oxidation

A 30 cm soil cover with a base methane concentration of 10 percent (v/v) was assumed to have different soil textures and was analyzed under the same climatic conditions (Marina Landfill, Monterey County). Figure 12a indicates the variability in the CH_4 emission rate with and without oxidization along with the total estimated annual CH_4 oxidized. Diffusive flux is reduced by finer soil texture (Fig. 12a). For this scenario, the variability in the prediction ranged from 46 to 163 g CH_4 m^{-2} d^{-1} without oxidation and 18 to 122 g CH_4 m^{-2} d^{-1} with oxidation, as a function of soil texture. Typically, coarser soil textures resulted in higher predicted surface emissions rates both with and without oxidation. On the other hand, the estimated annual amount of CH_4 oxidized as a function of soil texture ranged from 21 to 41 g CH_4 m^{-2} d^{-1}. Coarser textured soils resulted in higher predicted oxidation capacities, while finer-textured soils have a lower total CH_4 oxidation capacity, which is in agreement with the literature (e.g. Scheutz et al., 2009).

The percent CH_4 oxidation (Fig. 12b) is a function of the non-oxidized diffusive flux and is the parameter commonly quantified by current isotopic methods for positive CH_4 fluxes (Liptay et al., 1998; Chanton and Liptay, 2000; Chanton et al., 2008). Unfortunately, these methods cannot be applied to negative fluxes (uptake of atmospheric CH_4) and, because of the observed variability in field results, may be difficult to apply where positive CH_4 fluxes are low. Importantly, percent oxidation is only a relative measure of the CH_4 that is oxidized in a particular landfill cover soil and is not a direct quantitative assessment of the CH_4 oxidation rate. In general, percent CH_4 oxidation is a function of the non-oxidized diffusive flux, and is therefore highly variable across soil textures and climates. This percentage varied from 25-60 percent across soil textures in the soil texture analysis (Fig. 12b) within the same climatic region, with coarser-textured soils having higher predicted oxidation capacities. However, finer-textured soils typically have higher percent oxidation due to the reduced magnitude of CH_4 flux

as a function of the soil texture (Fig. 12a). Because of these relationships, the depth- and climate-dependent oxidation rate (g CH_4 m^{-2} day^{-1}) would be the preferred measure of oxidation capacity in a particular cover soil cover for a particular climate rather than the percent oxidation. Moreover, published field data (e.g. Bogner et al, 2007; Borjesson and Svensson, 1997; Scheutz et al., 2009; Zhang et al., 2008b) and CALMIM model output indicate that the percent CH_4 oxidation at a particular site can often range from 0 to 100 percent with high temporal variability. In CALMIM, this is directly attributable to the coupling of soil cover properties and climate driving forces to the microbial thresholds. However, even though the *in situ* oxidation rate (g CH_4 m^{-2} day^{-1}) would be the preferred measure for the oxidation capacity of a particular soil cover in a particular climate (and not the change in percent oxidation), it is only possible to currently quantify the oxidation rate through numeric modeling and laboratory studies, rather than by direct field measurement.

Figure 13. Impacts of soil texture on a) net CH_4 surface emissions with oxidation, net surface emissions without oxidation, and amount of CH_4 oxidized as well as b) the comparison of the percentage oxidation of various soil textures under identical boundary conditions.



4.3.1.2 Impact of cover thickness and concentration profile

Both the thickness of various cover materials (Fig. 13a) and the concentration gradient (Fig. 13b) across a 100 cm clay cover were independently examined. There is a non-linear response to the changing thickness of the cover soil (Fig. 13a). On the other hand, alterations in the concentration gradient result in a linear relationship with surface flux (Fig. 13b), which is consistent with the assumption of diffusive flux (Eq. 3.2). As discussed above, the CH_4 oxidation percentage is determined relative to the net flux of CH_4 into the base of the cover material. This can be seen in Figure 13b, where the 100 cm clay cover was capable of oxidizing virtually all of the gross CH_4 flux to the base of the cover material.

4.3.1.3 Impact of gas recovery system

The sensitivity of the model to the presence of an engineered gas recovery system was examined for a 30-cm clay cover. This dependency was scaled by altering the base concentration according to the relationship given in Eq. 3.1 (Fig. 14a). As seen above, the assumption for diffusive transport results in a direct linear relationship between surface flux and the concentration gradient (Fig. 14b). However, the estimated CH_4 oxidation potential in

the cover is equivalent for each scenario, because this is dependent on the soil texture (e.g. O_2 diffusion profile), soil moisture, and temperature (which were held equal for all scenarios) (Fig. 14b). Therefore, the percent oxidation is not related to the amount of CH_4 oxidized (same in all scenarios), but is a function of the non-oxidized flux (Fig. 14c). The presence of a recovery system (with 100 percent coverage) for this particular scenario reduced emissions by over 50 percent (128 to 62 g CH_4 m^{-2} day^{-1}), even though the base concentration was only reduced by 30 percent, due to the increased impact of oxidation on the reduced (net) CH_4 flux to the atmosphere at the top of the cover soil.

Figure 14. Impacts of a) various soil texture on the resulting emissions (with oxidation) of various soil cover materials as a function of layer thickness and b) the relationship between base CH4 concentration and the corresponding surface emissions with and without oxidation for a 100 cm clay soil cover.

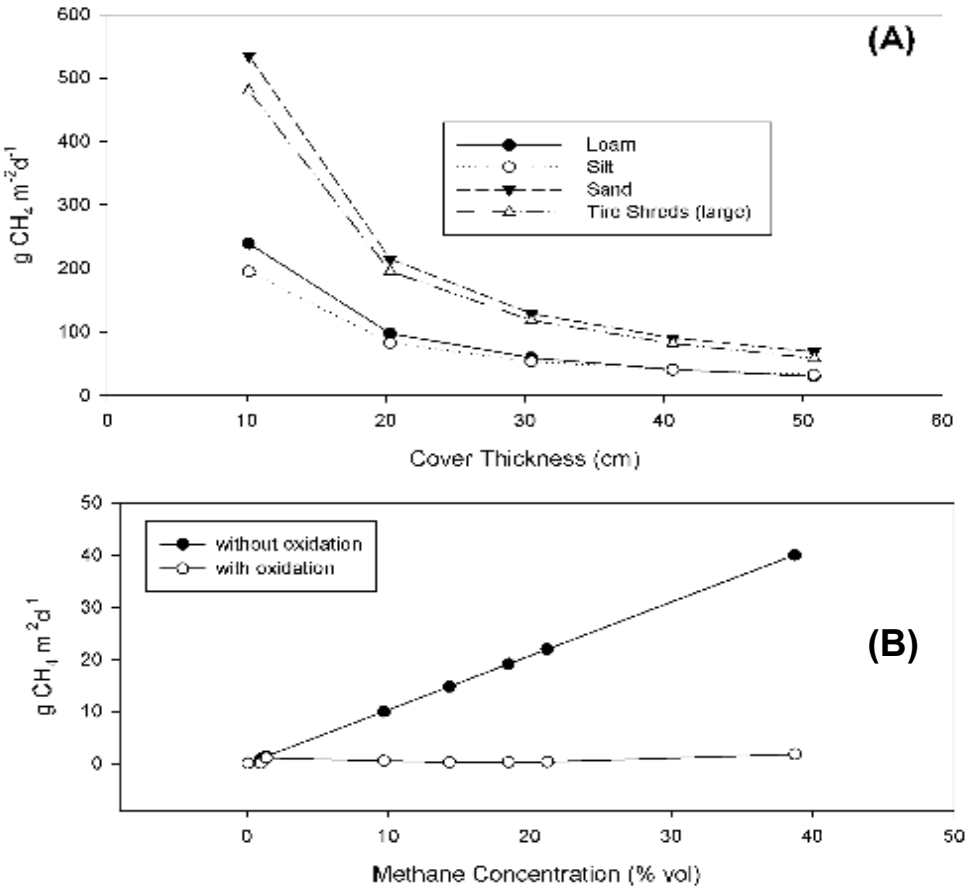
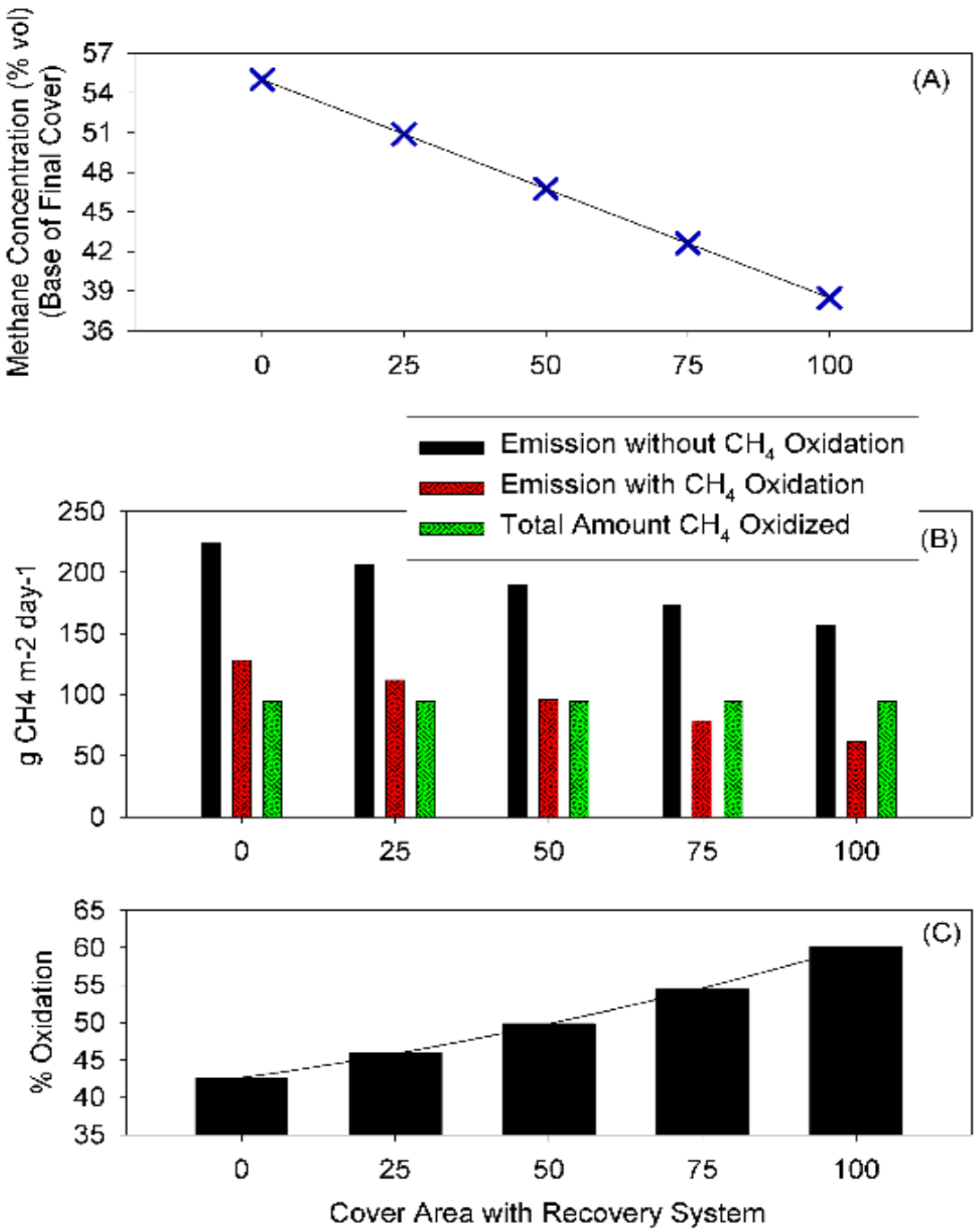


Figure 15. Comparison of the impact of the presence of a gas recovery system using the default concentration profile for a final cover (55 percent CH4 with no recovery) on a) base CH4 concentration as a function of aerial coverage of the recovery system, (b) comparisons of predicted emissions with and without oxidation and the total CH4 oxidation predicted in the cover material, and (c) comparison of the estimated percent CH4 oxidation as a function of the recovery system configuration.



4.3.2 Field Validation

4.3.2.1 Marina Landfill

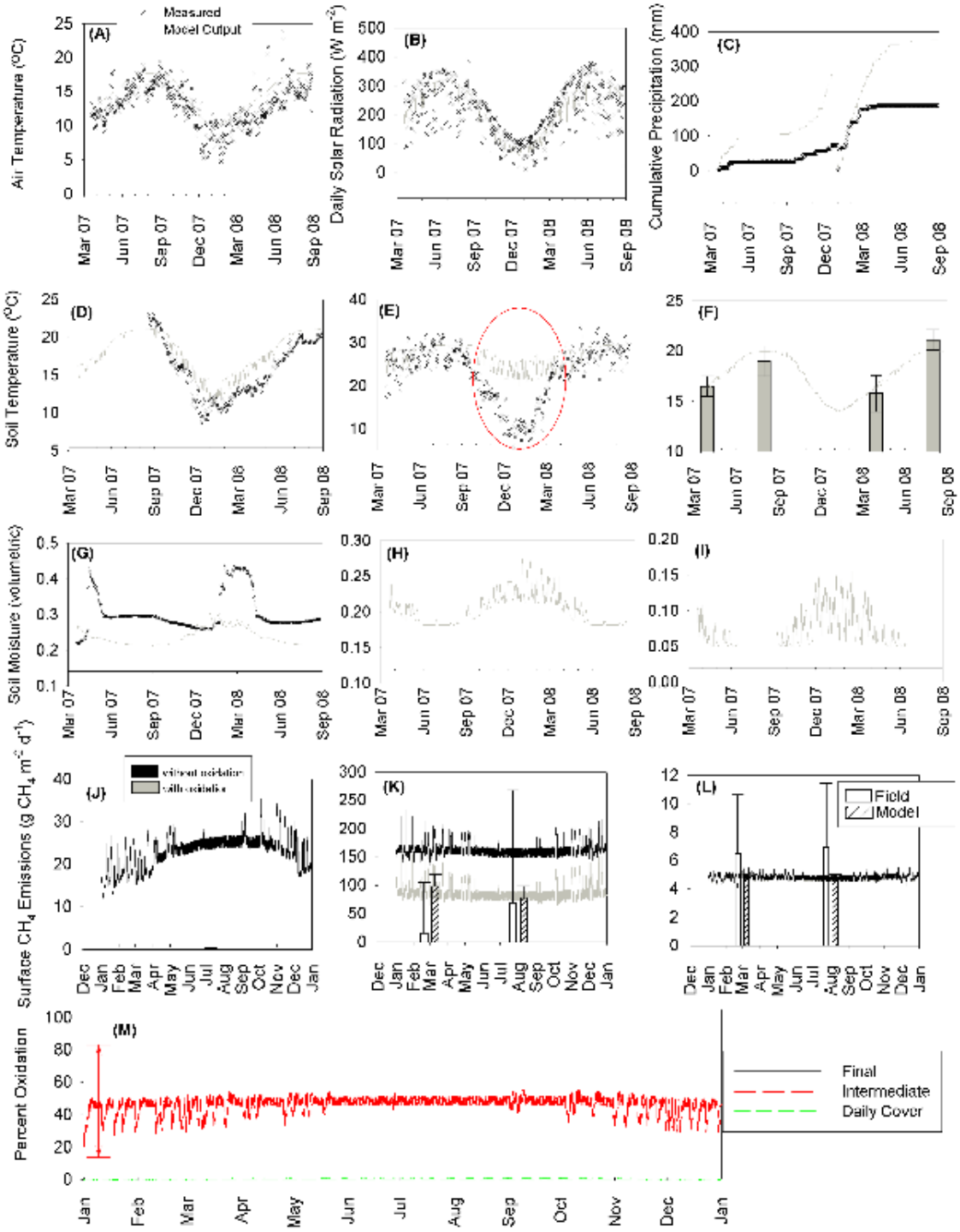
Figure 15 compares model results and field data for the northern California coastal site (Marina) using model parameters in Table 12. Average air temperature predictions (Fig. 15a) matched the overall trend (R^2 = 0.694; d-index = 0.831), with a slight positive bias (RMSE= 2.45 ^oC; MAE = +2.10 ^oC). The solar radiation predictions (Fig. 15b) were correlated (R^2= 0.572; d-index= 0.869) and had small relative errors (<10 percent) in the magnitude of the daily incoming radiation estimate (RMSE = 60.4 W m^{-2}; MAE= +46.1 W m^{-2}). Precipitation predictions were somewhat overestimated due to the ongoing drought in California during 2007-2008 (Fig. 15c). However, the Mediterranean pattern, where a majority of the annual precipitation falls in the cooler part of the year (November-March), was accurately simulated, despite relative differences in predicted quantities. Not surprisingly, results for the climate simulations were within the same order of magnitude as other published validations for these models (e.g. Spokas and Forcella, 2006, 2009; Kahimba et al., 2009).

The predicted and measured soil temperature at 10 cm in the final cover and 15 cm depth in the intermediate area are shown in Figures 15d and 15e, respectively. These shallow depths were chosen based on the observations that maximum rates of soil CH_4 oxidation are typically found in the upper portion of the soil profile (e.g. 5-25 cm) where optimum microclimate conditions exist for methanotrophic activity as a function of O_2 availability, soil temperature, moisture, and CH_4 supply (e.g. Scheutz et al., 2009). For the final cover, the model demonstrated good prediction of the overall cover soil temperature trend (R^2 = 0.919; d-index = 0.814) and a RMSE of 2.4 ^oC and a MAE of 2.1 ^oC. These errors are virtually identical to the air temperature prediction errors and similar in magnitude to errors observed in other modeling studies (e.g. Granberg et al., 1999; Cannavo et al., 2006; Bittelli et al., 2008). This is vital, due to the importance of soil temperature on microbial reactions (e.g. Riveros-Iregui et al., 2007; Or et al., 2007). It should be noted that these matches to field data were achieved using modeled site climatic data and not site-specific weather data, which could improve model comparisons. The intermediate cover did not match as well during the winter (Figure 15e) due to a localized decrease in the lower boundary temperature (at the soil-refuse interface) which was not reproduced in the modeling (steady state condition). Overall, the intermediate cover comparisons at Marina were relatively poor (R^2 = 0.462; d-index = 0.595; RMSE = 6.7 ^oC and a MAE of 4.9 ^oC). Figure 15f illustrates the modeled temperature profile for the daily cover at 5 cm. Due to operational constraints, it was not possible to monitor the daily cover on a continuous basis. Point measurements from the field measurements (average and standard deviation; Fig. 15f) were compared to model results. Overall, the model did follow the same trend as the individual measurements, and often the predicted daily temperature were within the standard deviation of the field measurements.

Table 11. Model parameters for California validation sites.

Site Name	Cover Type	Cover Layers	Vegetation (%)	Organic Matter	Lower CH_4 Concentration (base of cover)/Modifications to Defaults
Marina	Daily Cover	25 cm sand (lab)	0	Low	3000 ppm (0.3 %) (field measurement)
	Intermediate	5 cm wood chips 45 cm sandy loam (lab)	10	Low	Intermediate Cover defaults with 100% gas recovery
	Final	5 cm wood chips 55 cm sandy loam (lab) 30 cm loam (lab) 30 cm clay (lab) 60 cm sandy clay loam (lab)	100	High	Final Cover defaults with 100% gas recovery
Scholl Canyon	Daily Cover	25 cm sand (lab)	0	Low	10 ppm (0.001%) (field measurement)
	Intermediate	50 cm sandy loam (lab)	0	Low	2.4 ppm (0.0024%) (field measurement)
	Final	25 cm sandy loam (lab) 240 cm clay loam (lab)	75	Low	35% (field measurement)
Lancaster	Intermediate	45 cm sandy loam (lab)	0	Low	Intermediate Cover with 100% gas recovery defaults
Kirby Canyon	Intermediate	45 cm sandy clay (estimated)	0	Low	Intermediate Cover with 100% gas recovery defaults
Fremont (Tricities)	Intermediate	90 cm sandy loam (estimated)	0	Low	Intermediate Cover with 100% gas recovery defaults

Figure 16. Model validation at the Marina landfill site, including comparisons of A) air temperature, B) solar radiation, C) precipitation, D) 10 cm final cover soil temperature, E) 15 cm intermediate cover soil temperature, F) 5 cm daily cover soil temperature, G) 10 cm volumetric moisture in the final cover, H) 15 cm volumetric moisture in the intermediate cover, I) 5 cm daily cover volumetric moisture, J) surface emissions of the final cover, K) surface emissions in the intermediate cover, L) daily cover surface emissions, and M) estimated percentage oxidation of the three cover types with field measurements.



Volumetric soil moisture predictions for the final (10 cm), intermediate (15 cm) and daily cover (5 cm) are shown in Figures 15g, 15h, and 15i, respectively. Only the final cover at Marina was instrumented with soil moisture sensors. However, soil moisture was not compared directly, since the model used simulated annual weather data rather than actual data. Nevertheless, predicted soil moisture profiles for the final cover matched seasonal trends observed in the field data (Fig. 15g). Also, the dry season volumetric moisture content measured in the field was very close to the modeled output (~0.15), indicating a good match of measured to modeled soil physical parameters (Table 2)at this site.

Model outputs for predicted surface methane emissions at Marina during an annual cycle with and without oxidation are shown for the final (Fig. 15j), intermediate (Fig. 15k) and the daily cover areas (Fig. 15l), with the corresponding field measurement averages and standard deviations. As seen in Fig. 15k, the model results were typically within the same order of magnitude as the field measurements but slightly higher, indicating that the model results were conservative for annual inventory purposes. The final cover had very low measured fluxes (<0.1 g CH_4 m^{-2} d^{-1}, bars not visible at scale). The corresponding modeled percent oxidation is shown for the final, intermediate, and daily cover types in Figure 15m. The estimated range of percent CH_4 oxidation from the isotopic measurements was 1 to 84 percent with an average of 30 to 40 percent for all cover types depending on whether the estimation was made from chamber flux measurements or soil gas probes [see Chapter 3], which is similar to range reported in Chanton et al. (2009). In general, the model predicted nearly 100 percent CH_4 oxidation over the full annual cycle for the final cover, 50 percent for the intermediate cover, and less than 1 percent oxidation for the daily cover. In large part, these differences are related to the fact that the daily cover had a significantly lower oxidation potential compared to the final cover, because the daily cover had not previously exposed to elevated CH_4 soil gas concentrations (Table 9).

4.3.2.2 Scholl Canyon Landfill

Figure 16 (using model input parameters in Table 12) compares model results and field data for the Scholl Canyon site (Los Angeles County). The air temperature predictions (Fig. 16a) matched the overall trend (R^2 = 0.722; d-index = 0.521), with a slightly higher positive bias (RMSE = 3.9; MAE = +3.0 ^oC) than at Marina. Solar radiation predictions (Fig. 16b) were well-correlated to field data (R^2=0.779; d-index=0.608) with small relative errors (<10 percent) in the magnitude of the daily average prediction (RMSE = 57.9 W m^{-2}; MAE= +42.3 W m^{-2}). Mediterranean precipitation patterns (Fig. 16c) were simulated but with an overestimation due to the extreme drought conditions for 2007-2008 in southern California.

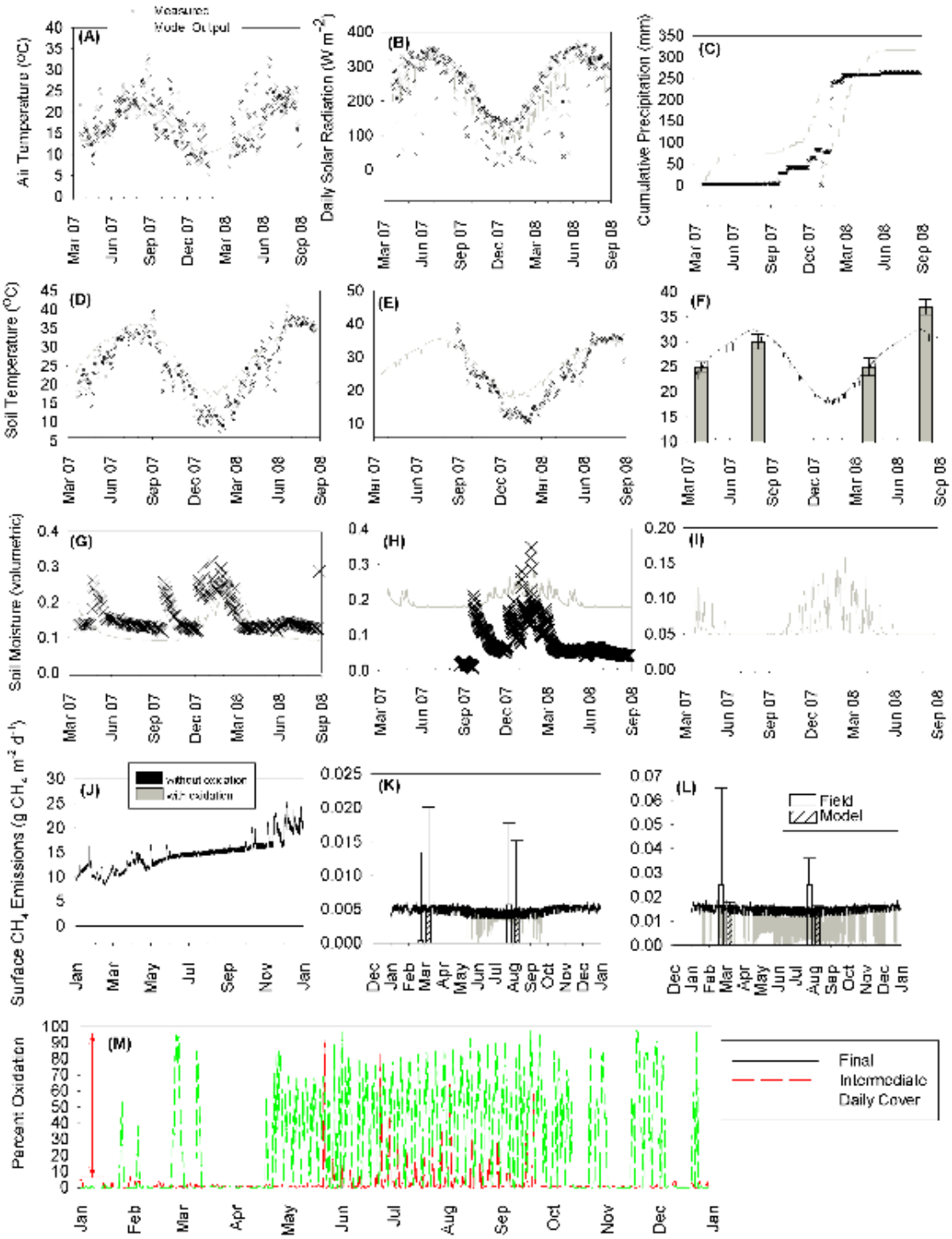
The predicted and measured soil temperature at 20 cm in the final cover and the 15 cm intermediate area are shown in Figures 16d and 16e, respectively. As discussed above, methane oxidation activity would be optimized at these shallow depths. CALMIM predicted the final soil cover temperature trend (R^2 = 0.920; d-index = 0.846) with a RMSE of 5.4 ^oC and a MAE of 4.4 ^oC. The intermediate cover was modeled adequately with a R^2 = 0.944; d-index = 0.892; RMSE = 4.7 ^oC and a MAE of 3.8 ^oC over the field monitoring period. Figure 16f illustrates the modeled temperature profile for the daily cover at 5 cm. Point measurements for the daily

cover are shown in the superimposed bars (average and standard deviation). Intermediate and final cover soils at Scholl Canyon were highly compacted (estimated 2 g cm^{-3} for intermediate and final covers; Bogner and Spokas, 2010). Therefore, we suggest that the differences between modeled and measured emissions at the Scholl Canyon site are an artifact of the assumption of the lower bulk density values in the CALMIM modeling (Table 11). This results in the lack of agreement with the dry season soil moisture content (Fig. 16d and 16e). However, for the daily cover, which is not as highly compacted as intermediate and final cover materials, there was a much improved comparison between the observed and modeled soil temperatures. (Fig. 16f).

Volumetric soil moisture predictions for the final (10 cm), intermediate (15 cm) and daily cover (5 cm) are shown in Figures 16g, 16h and 16i, respectively. As seen in the data, soil moisture responds directly to precipitation events. Moreover, the predicted soil moisture profiles from the final and intermediate covers closely match seasonal trends seen in the field data (Figures 16g, 16h). As mentioned above for the soil temperature comparisons, field deviations from the assumed soil physical properties for the highly-compacted Scholl soils could lead to observed errors in the soil moisture predictions for the dry soil conditions. This difference is more dramatic for the Scholl Canyon site compared to Marina because the Marina cover soils had lower densities closer to the assumed model parameters (Table 11).

Modeled surface CH_4 emissions with and without oxidation were compared to field measurements for the final (Fig. 16j), intermediate (Fig. 16k) and the daily cover (Fig. 16l) with modeled percent oxidation (Fig. 16m) for all three covers. From the isotopic measurements, the estimated range of CH_4 oxidation was 10-100 percent with an average of 48-52 percent depending on whether the estimation was made from chamber flux measurements or soil gas probes (Bogner et al., 2010). The model predicted 100 percent oxidation for the final cover but <1 percent oxidation for the daily cover, with rapid responses to infiltration events (Fig. 16m), both capturing the response of oxidation to moisture and indicating that very low soil moisture resulted in reduced oxidation rates. The overall response of emissions and oxidation to soil moisture events is very significant for Scholl Canyon due to the lower CH_4 fluxes with CH_4 oxidation being an important contributing mechanism to mitigating emissions.

Figure 17. Model validation at the Scholl Canyon landfill site, including comparisons of predicted A) air temperature, B) solar radiation, C) precipitation, D) 10 cm final cover soil temperature, E) 15 cm intermediate cover soil temperature, F) 5 cm daily cover soil temperature, G) 10 cm volumetric moisture in the final cover, H) 15 cm volumetric moisture in the intermediate cover, I) 5 cm daily cover volumetric moisture, J) surface emissions of the final cover, K) surface emissions in the intermediate cover, L) daily cover surface emissions, and M) estimated percentage oxidation of the three cover types with field measurements.



4.3.2.3 Other California Landfill sites

Comparisons at other California sites were limited to the intermediate cover areas at three sites (Lancaster, Kirby Canyon, Tri-Cities) and are summarized in Table 13 using model input parameters given in Table 12. In general, intermediate cover areas are the most important cover type at active landfill sites with respect to emissions because these generally comprise the largest percentage of the total surface area during the active filling phase. Intermediate covers are thinner than final soil covers, are placed when a cell is completed, and buried when new cells overlie older phases.

Table 12. Validation results: Intermediate cover materials: other California landfill sites.

Site Name	Location	Field Measurements (Green et al., 2009) Flux Chamber	VRPM	Model Annual Prediction (with oxidation)
		($g\ CH_4\ m^{-2}\ d^{-1}$)		($g\ CH_4\ m^{-2}\ d^{-1}$)
Lancaster	34.747 °N 118.116 °W	-0.21 to 0.47	1 to 5	0.47
Kirby Canyon	37.185 °N 121.671 °W	-0.04 to 0.05	8 to 11	0.14
Freemont (Tricities)	37.510 °N 121.99 °W	-0.02 to 9.2	23 to 42	3.9

Intermediate cover areas can remain exposed for extended periods of time (>3 years) but are characterized by well-established methanogenesis in the underlying waste which can result in higher surface emissions. Overall, there was good agreement between the flux measurements and the modeling results, with CALMIM outputs for the three sites exhibiting relatively low surface emission estimates. In general, the vertical radial plume mapping (VRPM; Thoma et al., 2008, 2010; Green et al., 2009) results were consistently higher than the chamber and corresponding CALMIM results. These differences are attributable to uncertainties regarding the area contributing to flux using VRPM methods along with other complicating issues [e.g. model assumptions, climate stability] (Babilotte et al., 2010). Furthermore, the VRPM method (as do all above-ground methods) captures secondary emissions from cracks, fissures, and piping system leakages. As discussed above, by regulatory mandate, these are detected and remediated on a quarterly basis as part of normal operations and maintenance and thus are not modeled for annual inventory purposes by CALMIM.

4.4 Conclusions

CALMIM is consistent with an IPCC Tier III methodology relying on "advanced field-validated" methods. Importantly, this project has developed a field-validated science-based methodology based directly on the physical and biochemical processes that control emissions and oxidation relative to landfill cover soil type and typical annual climatic variability. As

published literature has demonstrated, the "net" landfill CH_4 emissions to the atmosphere are dependent on the site-specific cover materials, their seasonal moisture and temperature profiles, the presence of engineered gas recovery, and the variability of seasonal methanotrophic CH_4 oxidation in various cover materials. A major focus of CALMIM as an annual inventory model is on the effect of larger-scale climatic processes and their influence on soil microclimate (e.g. Entin et al., 2000; Muttiah and Wurbs, 2002) which, in turn, is an important control on landfill CH_4 emissions in California. The accuracy of the global climate models embedded in CALMIM is adequate to establish typical or average conditions (Spokas and Forcella, 2009). In general, as discussed above, CALMIM can predict field CH_4 emissions within the same order of magnitude and provides an improved methodology for estimation of typical annual emissions from California. Comparisons of CALMIM modeling output to field measurements of emissions and oxidation at additional landfill sites outside of California has been initiated for both U.S. and international sites.

The current model represents an initial step with respect to the decoupling of landfill surface emission predictions from gas generation modeling. As the first diffusion-based model inclusive of global climatic factors for the assessment of surface emissions, CALMIM represents a theoretically-sound methodology for the site-specific assessment of landfill CH_4 emissions. Some anticipated future improvements include facilitating the routine use of site-specific climate and soil microclimate data, as well as developing a default soils database specifically for gaseous transport in landfill cover soils with high compaction. However, for inventory purposes, the use of the current soils database within CALMIM, based on agricultural soils, adds conservatism to the modeling output as estimated transport rates would typically be higher for agricultural soils with lower compaction. Importantly, CALMIM also illustrates the limitations of a historical dependence on the percent CH_4 oxidation as a measure of the total potential oxidation capacity of various landfill soil cover systems; rather, a more robust quantitative relationship for the actual CH_4 oxidation rate is preferred, which is dependent on the magnitude of the non-oxidized flux and is a function of soil texture, climate, CH_4 and O_2 concentration gradients, and diffusive flux rates.

CHAPTER 5:
Conclusions, Implementation, and Future Research Recommendations

5.1 Conclusions and Discussion of Model Implementation

CALMIM (CAlifornia Landfill Methane Inventory Model) is a new field-validated, freely-available, JAVA-based landfill CH_4 inventory model for California which models 1-D CH_4 transport inclusive of seasonal CH_4 oxidation in site-specific cover materials. CALMIM incorporates globally-validated USDA models for site-specific temperature, precipitation, solar radiation, and soil temperature/moisture, enabling realistic modeling of CH_4 transport and oxidation for 10-min. time steps and 1-in. depth increments for any layered cover soil over an annual cycle. Typical California cover materials, including ADCs, have been incorporated into CALMIM as defaults; however, any layered cover soil can be modeled using the customized cover designer within the model. Extensive supporting laboratory studies have permitted quantification of the limits and dynamics of CH_4 oxidation in California landfill cover soils (Spokas and Bogner, 2010); see Chapter 2. CALMIM was extensively field-validated at two California landfills during 2007-2008 [Marina Landfill; Scholl Canyon Landfill]; see Chapter 3. Additional field validation was completed at three other California landfills (Lancaster, Kirby Canyon, Tri-Cities) where CH_4 emissions have been recently monitored as part of ongoing research by Waste Management, Inc. The model structure and validation have been described in Chapter 4.

As a science-based IPCC Tier III model which has been field-validated, CALMIM represents a significant improvement over existing inventory models for landfill CH_4 emissions. Previous IPCC Tier I and II models (IPCC, 2006) have historically relied on a theoretical multicomponent first order kinetic equation for CH_4 generation from the annual mass of waste landfilled, termed an FOD (first order decay) model by IPCC (IPCC, 2006). Then, using a simplified CH_4 mass balance, the measured CH_4 recovery is subtracted from the theoretical CH_4 generation with a further subtraction of 10 percent of the remainder as a default value for methanotrophic CH_4 oxidation in cover soils. However, field research over the last decade has demonstrated that, even at sites with detailed annual data on landfilled waste (mass and composition), the modeled CH_4 generation cannot be correlated to CH_4 emissions (e.g., see Fig. 2, Chapter 1). As discussed in Chapter 1, the current IPCC Tier I (default) FOD model methodology has never been field-validated for emissions (only for recovery at a limited number of sites), excludes any physical effect of the cover materials to retard emissions, and limits CH_4 oxidation to a uniform 10 percent default value (based on one study in New Hampshire: Czepiel et al., 1996a). As discussed in the previous chapters, extensive field campaigns during the last decade have quantified landfill CH_4 emissions, addressed the highly variable dynamics of landfill CH_4 oxidation and emissions in field settings, and demonstrated the shortcomings of the current FOD model approach for emissions.

Therefore, building on the foundation of published research and model studies conducted by the project participants and other international research groups, CALMIM has been developed as an IPCC Tier III model using a "validated higher quality" method than the previous FOD model approach by focusing on the site-specific physical and biochemical processes in daily, intermediate, and final cover materials. For each cover type, CALMIM calculates annual emissions using a 1-D diffusional model where the major driver for emissions is the CH_4 concentration gradient through the various site-specific cover materials. This concentration gradient is highly dependent on the presence or absence of engineered gas recovery and could, in fact, be determined on a site-specific basis for a more rigorous quantitative application of CALMIM. Emissions are also dependent on seasonal CH_4 oxidation which is dependent both upon the CH_4 flux to the base of the cover, as well as the properties of the cover materials to achieve an oxidation rate that approaches or exceeds that rate. Rates of oxidation are highly dependent on seasonal soil moisture, soil temperature, and CH_4 exposure history, as discussed in Chapter 2. As discussed in Chapter 3, measured oxidation rates at the field sites using a stable carbon isotopic method for areas with positive CH_4 emissions generally averaged around 30-40 percent. However, as discussed in Chapters 2-4, oxidation during most of the year at the field sites did not attain optimum rates due to temperature and/or moisture limitations. Especially, oxidation rates were significantly reduced during hot, dry summer conditions.

The results of this study strongly support the implementation and use of CALMIM as a site-specific model capable of incorporating seasonal climate and soil microclimate trends. The CALMIM model can also be used as a design guide at specific sites to screen a variety of prospective cover materials with respect to their ability to retard emissions over a typical annual cycle.

The California Air Resources Board has primary responsibility for the California GHG inventory. As discussed with ARB, in cooperation with CalRecycle and the CEC, it is anticipated that the completion of this research project will result in a potential implementation by ARB with respect to the implementation of CALMIM for the California inventory. Some key issues for this potential implementation include discussion of user-selectable options (vs. default values), potential addition of other site-specific features, and amendments/revisions to the current user manual consistent with model revisions. Possible additional site-specific testing may also be recommended as part of this potential implementation. The current user manual developed for CALMIM v 4.2 is included as an Appendix to this report. The final version of CALMIM (v.4.2) developed for this project, as well the JAVA source code, are freely-available to all interested users.

The project participants advise caution with respect to the use of this model for purposes other than an annual GHG inventory. As discussed in Chapter 1, this model is not intended to replace existing regulations or regulatory models, which are used to guide engineering decisions, daily operations, and both routine and emergency maintenance activities at landfill sites in California and elsewhere. Moreover, this model is not intended in its current form to be applied, without modification, to long-term post-closure activities with reduced levels of maintenance or to projects which seek to monetize carbon credits from various waste management activities.

5.2 Future Research Recommendations

As the first field-validated IPCC Tier III model for landfill CH_4 emissions, it should be recognized that, although CALMIM provides significant advantages over previous models, it also has certain constraints relating to (a) linkages with existing climatic and soil microclimate databases, and (b) gaseous transport which currently only includes 1-D diffusional transport for selected gases (CH_4 and O_2). However, CALMIM is structured so that future research can readily expand upon the current model to provide additional refinements, extensions, and applications for landfill CH_4 emissions. In addition, as discussed below, the CALMIM structure could be adapted to other natural and managed ecosystems for improved GHG inventory accounting.

Our recommendations for future research include:

1. Expansion of the CALMIM model structure is recommended to facilitate the routine use of local meteorological and soil microclimate data. In addition, supporting recommendations should be developed for where and under what circumstances the climate and soil microclimate databases in CALMIM should be replaced by local data. For example, during BETA testing, we observed that, in mountainous regions with high relief, specific sites may be located where there is a rain shadow effect not reflected by the closest 30-year meteorological data. For California specifically, an effort to link the CALMIM model with other detailed California weather databases and local data sources would also greatly improve localized results.

2. A majority of the existing soil property databases used for CALMIM were collected from agricultural and forest ecosystems. There is a need to develop a companion collection of soil properties for landfill cover soils, so that cover placement, typical compaction, and other management conditions for landfill covers are more rigorously accounted for in the model. However, it should be stressed that the current reliance on properties for non-landfill ecosystems adds conservatism to the modeling, i.e., an overestimation of CH_4 emissions due to lower assumed densities (lower compaction) than typical landfill cover materials (higher compaction).

3. Development of a statistically-valid field protocol to determine the CH_4 concentration gradient through daily, intermediate, and final landfill cover materials at specific landfill sites. This protocol could be a prerequisite for permitting deviation from default values for site-specific applications and would permit a closer match to site conditions for this critical transport parameter. In addition, these measurements could assess the seasonal variability of the concentration profiles in the various cover materials.

4. Addition of other flux mechanisms to CALMIM, in addition to diffusion, as appropriate under certain conditions. Those mechanisms could include convection, wind-driven convection, ebullition, and (under some circumstances) plant-mediated transport.

5. Addition of the ability to model and maintain mass balance on the stable carbon isotopes (^{13}C, ^{12}C) of CH_4 through the various cover soil profiles. In cooperation with a critical

number of soil gas profiles at field sites, this tool could greatly improve our understanding of *in situ* CH_4 oxidation during gaseous transport through a soil profile.

6. Addition of the ability to model and maintain mass balance on other carbon and nitrogen cycle gases (especially CO_2, N_2O) through various soil profiles.

7. Additional field validation for the current model to be conducted in parallel with ongoing field measurements of CH_4 emissions and oxidation at other California, U.S., and international sites by various landfill research groups.

8. Application of CALMIM structure to modeling gaseous transport in other managed and natural ecosystems. This would consist of retaining the basic structural design of CALMIM, including linkages to climate and soil-microclimate models, but with appropriate soil profile, source term, and transport mechanism modifications to develop similarly-structured user-friendly, freely-available JAVA models appropriate for modeling gaseous transport over an annual cycle in other ecosystems (natural wetlands, forests, grasslands; managed agricultural systems).

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