

Atmospheric Ethane-Methane Relationship and Implications for the Arctic

By Angie Hollister
University of Colorado at Boulder

A thesis submitted to the
University of Colorado at Boulder
in partial fulfillment
of the requirements to receive
Honors designation in
Environmental Studies
May 2013

Thesis Advisors:

Detlev Helmig, ATOC Department, Committee Chair
Dale Miller, ENVS Department & Honors Council Representative
Darin Toohey, ATOC Department

© 2012 by Angie Hollister
All Rights Reserved

TABLE OF CONTENTS

ABSTRACT	1
PREFACE	1
INTRODUCTION	2
BACKGROUND INFORMATION	4
LITERATURE REVIEW	6
OZONE.....	7
BACKGROUND VOCS	8
RELATIONSHIP BETWEEN METHANE AND ETHANE	9
ETHANE.....	9
<i>Ethane Sources</i>	10
<i>Venting and Flaring of Fossil Fuels</i>	10
<i>Biomass Burning</i>	11
<i>Biofuels</i>	12
<i>Ethane's Sink</i>	12
<i>Ethane's Distribution and Statistics</i>	14
METHANE.....	15
<i>Methane Sources</i>	16
<i>Fossil Fuel Use</i>	17
<i>Biomass Burning</i>	18
<i>Biological Production</i>	18
<i>Agriculture</i>	19
<i>Landfills</i>	19
<i>Termites</i>	20
<i>Wetlands</i>	20
<i>Methane Gas Hydrates</i>	20
<i>Oceans</i>	21
<i>Permafrost</i>	21
<i>Methane's Sink</i>	22
<i>Methane's Distribution and Statistics</i>	23
METHODS.....	23
DESCRIPTION OF THE NOAA GLASS FLASK METHOD	23
RESULT CURVE GRAPH METHODS	30
<i>Filtered Data Points</i>	31
<i>Smoothed Curve Data</i>	31
<i>Seasonal Cycles</i>	32
<i>Growth Rates</i>	32
STATISTICAL UNCERTAINTY.....	33
DISCUSSION.....	34
CURRENT RESEARCH.....	34
DATA AND RESULTS	36
CONCLUSIONS	42
<i>Recommendations</i>	42
BIBLIOGRAPHY.....	43

Atmospheric Methane-Ethane Relationship and Implications for the Arctic

An Honors Thesis by Angie Hollister

Abstract

The purpose of this project is to evaluate hydrocarbon concentrations, their chemistry in the atmosphere, and the corresponding implications for arctic ecosystems. Recently, methane's increasing threat as a greenhouse gas has warranted much research in the scientific field as global warming trends continue. A subject of significantly less research but perhaps of equal importance are ethane emissions, which are crucial to the understanding of methane's growth. Though methane and ethane share anthropogenic sources, methane concentrations in the atmosphere vary due to biogenic sources specific to the chemical compound. Due to this constraint, co-measurement of methane and ethane is important because of the strong correlation between the two chemicals due to their shared anthropogenic sources. A significant upturn in methane growth without a corresponding increase in ethane may indicate releases of methane from biogenic sources such as melting permafrost. Recent studies have shown that ethane concentrations are decreasing worldwide, likely due to sequestration of anthropogenic fossil fuel emissions. However, methane concentrations are becoming a focus of concern for environmentalists.

Preface

This thesis is submitted in partial fulfillment of the requirements for Honors Designation for a Bachelor's Degree in Environmental Studies. It contains work from the spring of 2012

through spring of 2013. This thesis has been made solely by the author; most of the text however, is based on the research of others and references have been provided for these sources.

My work at the Institute for Arctic and Alpine Research (INSTAAR) both provided inspiration as well as access to the data used in this research. The data used in this research was the joint contribution of INSTAAR and the National Oceanic and Atmospheric Administration's Global Monitoring Division. My work on the Global Atmospheric Watch Program for Volatile Organic Compounds sparked my interest in the measurement of hydrocarbons in the Arctic. This project is the culmination of my educational experience at the University of Colorado at Boulder and encompasses a unique constellation of subject matter I have encountered in my studies.

I would like to thank my advisors, Detlev Helmig, Dale Miller, and Darin Toohey, for great inspiration, support, invaluable discussion, and an endless stream of knowledge. The expertise and wisdom you have imparted upon me has been a great help and support throughout the course of this project, and in my education. I truly appreciate and value everything I have learned from you all.

Introduction

In recent decades there has been a notable and observed change in the Earth's atmosphere, generally believed to be caused by anthropogenic sources. These chemical changes within the atmosphere increasingly affect the Earth's climate and ecosystems, as well as human health. As atmospheric chemistry becomes an increasingly important and complex field, research institutions and global alliances facilitate our understanding of Earth systems, on which we have

great influence. However, before seeking solutions we must first understand the complex processes of the Earth's environment.

Though methane and ethane share anthropogenic sources, methane concentrations in the atmosphere vary due to biogenic sources specific to methane. Co-measurement of methane and ethane emissions reveals a decrease in ethane emissions unmatched by those of methane. These data imply that the disparity in emission sources can then be attributed solely to methane's biological emission sources. Investigation into the relationship between methane and ethane can be used to determine the source of methane's increased emissions. As methane and ethane share anthropogenic sources, if an increase in methane emissions is seen without a corresponding increase in ethane concentrations, then the source of increased methane emissions can reasonably be assumed to have been contributed by a source unique to methane. To follow, each of methane's additional sources is examined in an effort to pinpoint the cause of the compound's divergence from ethane emission volumes.

This research questions the growth of methane and the sources from which it originates, speculating that increased methane emissions are caused by the destabilization of gas hydrates in the Arctic. My hypothesis is that the increasing concentration of methane in the atmosphere is from biogenic sources, specifically those released from the destabilization of methane hydrates. Predictions for this thesis research include higher concentrations of both ethane and methane in the Northern Hemisphere as is consistent with population distribution over the globe, and smaller concentrations of methane occurring in the Southern Hemisphere. Examination of the methane-ethane relationship in the context of the two hemispheres has not yet been documented and may prove to be valuable in further research.

The data contributed are invaluable in atmospheric research, for uses such as assessing changes in emission sources, oxidation chemistry, and the global distribution of the hydroxyl radical. This research also addresses implications for Arctic ecosystems as methane further contributes to global warming through positive feedback loops due to temperature increase.

Background Information

In 2004, National Oceanic and Atmospheric Administration's Global Monitoring Division (NOAA GMD) in collaboration with INSTAAR's Atmospheric Research Laboratory (ARL) began a program for measurements of Volatile Organic Compounds (VOC) in air samples collected at remote locations around the globe. This research is one of the core components of the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) program for Volatile Organic Compounds (WMO-GAW 1996).

Motivated by the growing interest in global VOC data and progress made in measurement techniques, the WMO Global Atmosphere Watch has been guiding the implementation of a global VOC monitoring program. Incorporating non-methane hydrocarbon (NMHC) measurements into greenhouse gas sampling networks offers the opportunity to provide spatially resolved measurements for investigations on the hemispheric and global distribution of NMHC. Essential components of this program include surface stations with regular, in situ measurements of VOCs, analyses in samples collected in flasks within existing sampling networks for wide geographical coverage, and a concerted calibration and data quality control effort (WMO-GAW 1996).

Approximately 45 sites have been included since the onset of the program (Figure 1). A few sites have been added and several others have been discontinued over recent years. Whole air samples are collected in a pair of 2.5L glass flasks weekly to bi-weekly at each site and shipped to INSTAAR in Boulder, Colorado for analysis.

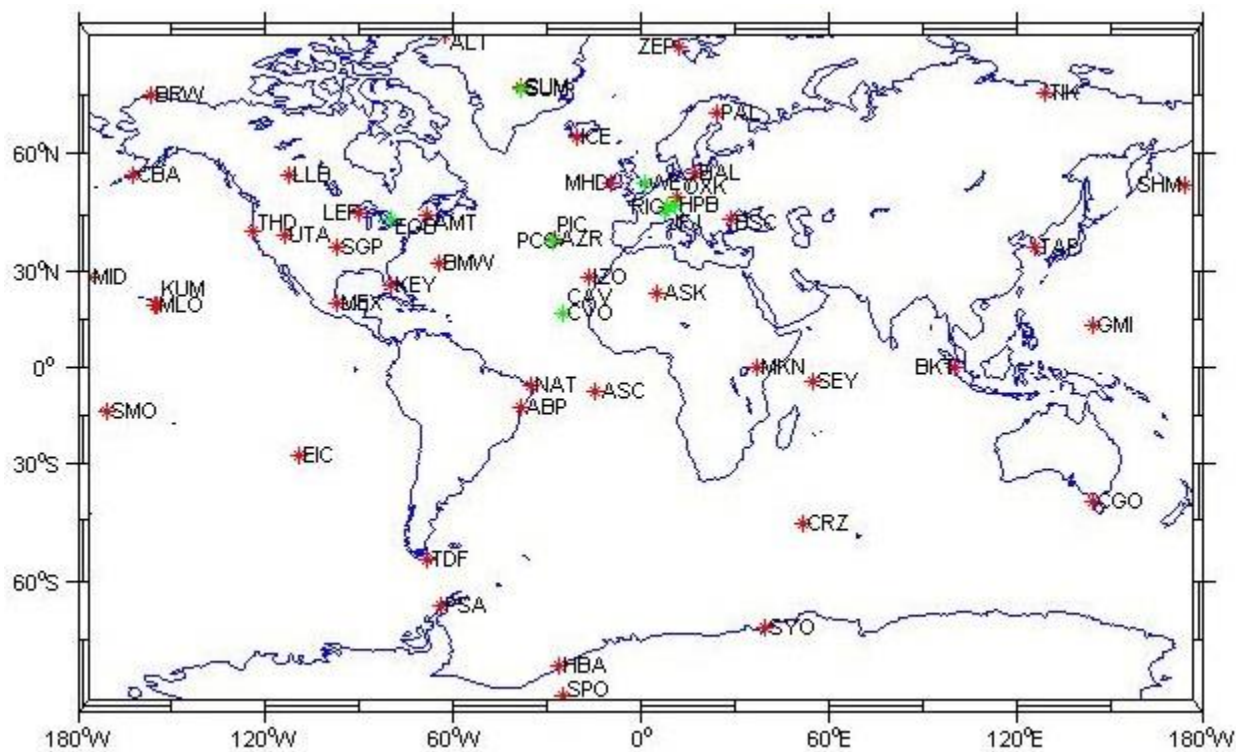


Figure 1: Map of Global Monitoring Sites within the NOAA GAW Network

Depending on site location and accessibility, analyses are typically conducted within 1-9 months after sample collection. The selection of gases that are included relies on their chemical stability during sampling, storage, and analyses, and the ability for detection at their observed levels at clean air background locations. Reported chemical species are NMHCs: ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, hexane, and isoprene. The Gas Chromatography

method used to analyze samples also provides data for propene, benzene and toluene. However, these gases are not currently reported due to high analytical uncertainties.

After completion of all calibration and quality control steps, final data are reported to the NOAA GMD data portal and are then released to the World Data Centre of Greenhouse Gases approximately 18-24 months after sample collection. Data from this program are contributed as a common good for public use in scientific research. These data also support the development and evaluation of coupled chemistry and climate models to help in further deciphering sources and sinks of climate forcing gases (WMO-GAW 1996).

This program addresses the goals set forth at the WMO/GAW Expert Workshop on Global Long-Term Measurements of VOCs held in 2009 as a part of the World Meteorological Organization Global Atmosphere Watch Report. Goals of this research focus on (1) long-term monitoring to derive changes and trends in the atmospheric composition, (2) monitoring to enable analyses of source-receptor relationships and transport processes, as well as (3) photochemical process studies at the respective GAW sites making use of all available GAW data (GAW 2009). This report also sets targets for accuracy and precision in measurements for compounds at all levels, strongly adhered to by INSTAAR.

Literature Review

To include: Ozone, Background of VOCs, Relationship between Methane and Ethane, Ethane's Sources and Sinks, Global Distribution of Ethane, Methane's Sources and Sinks, as well as Global Distribution of Methane.

Ozone

There are many approaches to the study of climate; this work particularly focuses on the measurement of VOCs in the Earth's atmosphere. Volatile organic compounds include saturated, unsaturated, and other substituted hydrocarbons. A hydrocarbon is a compound consisting entirely of hydrogen and carbon, the majority of which are produced naturally when organic matter decomposes, forming crude oil. Human dependence on natural resources such as crude oil has increased the emissions of hydrocarbons in the atmosphere, a significant contribution to the atmospheric warming of the planet. Hydrocarbons, with the exception of methane, have low life spans and concentrations in the atmosphere because they readily react with oxidants in the atmosphere, playing a key role in ozone production in the Earth's troposphere.

Naturally occurring in the stratosphere, ozone is welcomed due to its ability to block the sun's harmful ultraviolet radiation. However, anthropogenic ozone found in the Earth's troposphere can negatively affect other components of the atmosphere. Tropospheric ozone is an indirect result of air pollution caused by fossil fuel emissions. When fossil fuels are burned, nitrogen oxide gas (NO_x) and volatile organic compounds (VOC) are released into the air. VOCs play an important role in the chemistry of the atmosphere by influencing ozone and hydroxyl radical (OH) concentrations, and the conversion rates of nitrogen oxides (NO_x). Elevated levels of VOCs and NO_x have led to an approximate doubling of ozone in the lower troposphere over the past couple of centuries, making tropospheric ozone the third most important anthropogenic greenhouse gas following carbon dioxide (CO₂) and methane (Helmig 2009). Due to ozone's strong oxidizing properties, increases in tropospheric ozone are a concern for living systems on Earth. Ozone stresses and damages vegetation, resulting in a reduction of terrestrial CO₂

sequestration. High rates of photochemical processing take place during the warm months of spring and summer, where NO_x and VOCs are more likely to combine with oxygen and form ozone due to the absorption of light by hydrocarbon molecules (EPA 2000). VOCs also serve as a source of atmospheric secondary organic aerosol (SOA), which influences the solar radiation budget and cloud droplet nucleation. Through these complex interactions, VOCs play an important role in air quality and climate.

Background of VOCs

Though anthropogenic VOC emissions have decreased greatly since the 1980s, emissions from human activities still play a determining role in urban and regional air chemistry. In the atmosphere, VOC lifetimes can span a range from minutes to months. VOCs are removed from the atmosphere through oxidation, as well as through dry and wet deposition to the Earth's surface (Simpson 2012). VOC sources and sinks vary geographically and seasonally, contributing to a fluctuation of atmospheric concentrations. Emission rates of anthropogenic VOCs are relatively constant year-round, suggesting that seasonal cycles are primarily due to changing atmospheric oxidation strength and removal rates of these compounds. The major depletion route of atmospheric VOCs is through oxidation with the hydroxyl radical. Hydroxyl radicals are formed exclusively by a photochemical mechanism, light-induced dissociation of atmospheric ozone and the subsequent reaction of energetic oxygen atoms with water vapor. Consequently, the VOC oxidation strength roughly follows the irradiance of a subset of ultraviolet light (Simpson 2012). Oxidation strength reaches its maximum in regions with high

humidity and in the summer season. Therefore, VOC seasonal cycles and spatial distributions serve as prime indicators for the distribution of hydroxyl radicals.

Relationship between Ethane and Methane

Quantifying and understanding ethane's long-term global decline (Figure 2) provides insight to understanding methane's growth rates. Since ethane has common sources and sinks to methane but a shorter atmospheric lifetime, studying ethane can help constrain studies of methane. Methane is the most abundant hydrocarbon in the remote atmosphere, followed by ethane. Ethane is a precursor to tropospheric ozone and it influences the atmosphere's oxidative capacity through its reaction with the hydroxyl radical, a primary atmospheric sink (Simpson 2012). Methane is a key species in determining the oxidation capacity of the troposphere, ultimately affecting water and ozone budgets (Dlugokencky 1994). As an important trace component of the atmosphere, methane absorbs infrared radiation thus affecting earth's radiation budget.

Ethane (C₂H₆)

Ethane occurs as a trace gas in the Earth's atmosphere, currently with an average concentration of 1450 p.p.t.v. (part per trillion per volume) measured at Summit, Greenland. Pre-Industrial concentrations of ethane are likely to have been lower because a significant proportion of the ethane in today's atmosphere originated as fossil fuels. Ethane's production and use in the petroleum industry may result in its release to the environment through various waste streams.

Ethane's primary source is the venting and flaring of fossil fuels, though this does not include the combustion of fossil fuels. Combustion of fossil fuels would not necessarily increase global ethane concentrations, while venting unburned natural gas to the atmosphere does. Of the global ethane budget of 13 Tg/yr-1 (teragrams per year), 8-9.2 Tg/yr-1 is emitted from the production and consumption of fossil fuels. Biomass burning is a relatively minor yet significant contributor at 2.4-2.8 Tg/yr-1. Lastly, biofuels contribute 2.6 Tg/yr-1.

	Emissions (TG/year)
Fossil Fuels	8.0-9.2
Biomass burning	2.4-2.8
Biofuels	2.6
Total	13

Table 1: Ethane Sources and Sinks
Credit: Simpson et al. 2012

Ethane Sources

Ethane is emitted to the atmosphere through the venting and flaring of fossil fuels, as well as through the burning of biomass, both of which are discussed in this section.

Venting and Flaring of Fossil Fuels

Natural gas is found in deep underground natural rock formations or associated with other hydrocarbon reservoirs in coal beds. Ethane is the second most abundant component of natural gas energy sources. Prior to technological advancements in the 1960s, ethane was not separated from methane in the production of natural gas but was simply burnt along with the methane as fuel (Chandra 2006). Today, ethane on its own is economically viable and is a chief petrochemical feedstock. However, if the relative cost exceeds the benefit from extraction, ethane is not extracted from natural gas sources, later affecting quality of natural gas

downstream. As natural gas becomes more economically viable throughout the 21th century, it becomes increasingly less likely that its components will be vented to the atmosphere. The assumption has been made for the purposes of this study that the rising economic value of natural gas and the development of cleaner technologies have led to sharp reductions in the release of light hydrocarbons into the atmosphere. However, it is possible that the decrease in emissions from the natural gas industry have been offset with the venting of ethane in the production and processing of petroleum.

Biomass burning

Biomass burning is a significant source of ethane emissions in the atmosphere. While natural wildfires can contribute to ethane emissions, the largest contributor of biomass burning occurs as a result of humans (Etiope 2009). The combustion of both living and dead organic matter results in VOC emission to the atmosphere. Biomass burning is a common practice in the Southern Hemisphere where deliberate burnings are used to clear out land. As a result of destroying biomass waste in this manner, Southern Hemisphere emissions attributed primarily to biomass burning are estimated at 1.0 Tg/yr-1 (Etiope 2009) though this value could be higher than estimated. Ethane emissions in the Southern Hemisphere are small in comparison to those in the Northern Hemisphere.

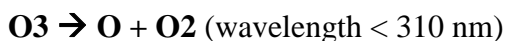
Biofuel

Biofuel is a type of fuel whose energy is derived from biological carbon fixation. Currently, biofuels are gaining attention, driven by factors such as increasing oil prices and the need for energy security. Though considerably better for the environment, biofuels still contribute a significant portion of ethane into the atmosphere. Biofuel emissions are concentrated in the northern mid-latitudes, in direct correlation with the majority of the world's people.

Ethane's Sink

Atmospheric removal rates of ethane play an important role in the composition and chemistry of the atmosphere. Ethane's primary sink is its reaction with the hydroxyl radical (-OH). Many reactions in the atmosphere take place through the formation of radical species, those with unpaired electrons. The electronegativity of these elements makes them extremely volatile in the atmosphere. In this case, the hydroxyl radical, a primary oxidizing and "cleansing" agent in the atmosphere, is formed (Prinn 2003).

The first step is the photo-dissociation of tropospheric ozone, requiring light with wavelengths of less than 310nm, which is considered to be ultraviolet or higher energy.

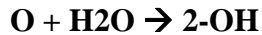


97% of the resulting single oxygen radicals immediately recombine with diatomic oxygen to reform ozone. This reaction requires the interaction of

a third component, which may be any species, although is most likely to be nitrogen.



3% of the remaining oxygen radicals go on to react with water vapor to create the hydroxyl radical.



In this reaction, ethane is destroyed, forming the hydroxide radical.

Ultimately, the resultant radicals may lead to the reformation of tropospheric ozone. Factors increasing water vapor and incident radiation will lead to faster rates of ethane removal (Uherek 2004).



Due to the oxidizing capacity of the hydroxyl radical, ethane is completely broken down in approximately 2-3 months (Simpson 2012). Through this reaction, ethane is a precursor to tropospheric ozone. The magnitude of the ethane sink has a seasonal and latitudinal variation because the atmospheric concentrations of $\cdot OH$ rise during summer months. With the required presence of incident radiation, oxygen, and water vapor, the destruction of ethane is possible. As radiation and water vapor both increase in the tropics during the summer months, $\cdot OH$ concentrations rise and ethane is removed with higher frequency.

Ethane's Distribution

Investigations into the dominant processes that control the abundance of ethane in each hemisphere were done by Dr. Detlev Helmig using the TM5 atmospheric tracer transport model (Simpson 2012). Findings proved that anthropogenic sources were the main driver of the ethane signal in one Alaskan site, with a smaller biomass burning component that peaks during the summer. These model simulations also led to

investigation of recent ethane decline over the past 25 years. It was found to be unlikely that changes in global levels of the hydroxyl radical were responsible for ethane's long-term global decline, because global -OH levels have shown little inter-annual variability and are generally well buffered against changes on inter-annual timescales. Rather, due to the fact that anthropogenic emissions dominate the ethane budget in the Northern Hemisphere, ethane's strong decline was attributed primarily to emission sequestration in the fossil fuel sector, specifically fugitive emissions of natural gas.

In addition to pronounced latitudinal variations, atmospheric ethane concentrations vary both seasonally and inter-annually. Ethane shows a late winter maximum and summer minimum in each hemisphere (Badr 1991). These clear, anti-correlated seasonal signals in each hemisphere

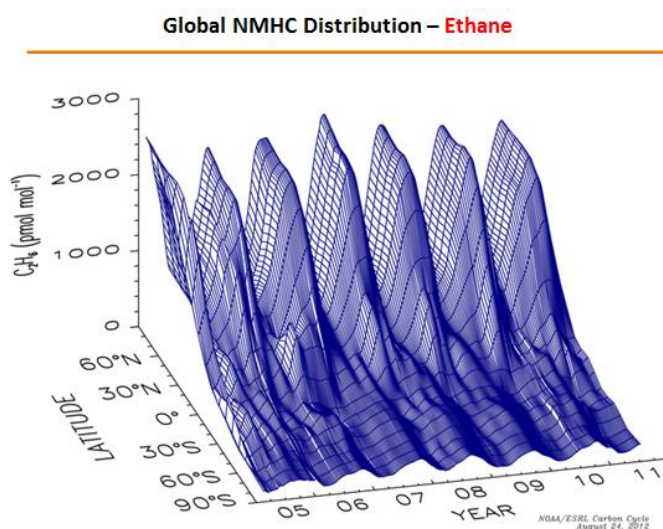


Figure 2: A three-dimensional representation of the latitudinal distribution of atmospheric ethane. Data are from the NOAA/ESRL Carbon Cycle cooperative sampling network.

Credit: Ken Masarie NOAA/ESRL

are principally attributed to enhanced summertime photochemical sinks. These seasonal cycles rule out the possibility that variations are due to a change in anthropogenic sources, contributing to ethane and methane variability. From 1984 to 2010 the average ($\pm 1\sigma$) amplitude of ethane's seasonal signal was much larger in the high Northern Hemisphere than in the Southern Hemisphere, which is consistent with ethane's source distribution (Simpson 2012). The Northern seasonal signal also shows significant inter-annual variability with several large, positive short-term anomalies of up to 30% that typically occur every 3-5 years, and have been linked to fluctuations in biomass burning emissions (Simpson 2012). Global ethane concentration peaked in the 1960s and 1970s, declining significantly since 1984, with the largest decrease at high northern latitudes. Decline in ethane emissions was greatest at high northern latitudes, while a similar trend has occurred at all latitudes within the Northern Hemisphere as confirmed with NOAA GAW data (Figure #). If this decline in global ethane emissions is attributed to a decline in the venting and flaring of natural gas, we can estimate the concurrent decline in methane emissions from fossil fuel sources.

Methane (CH₄)

Methane is an important atmospheric trace gas that controls numerous chemical processes and species in the troposphere and stratosphere. A strong greenhouse gas with significantly adverse environmental impacts, methane is typically found in small amounts in the atmosphere under natural conditions. During the past two centuries, methane has begun to accumulate in the atmosphere and is the cause of much speculation for atmospheric researchers.

The level of methane has risen from about 700 ppb in 1750 to around 1774 ppb in 2005 (Hidore 2010). Pre-industrial levels have nearly doubled in the 20th century, now reaching 1880-1900 ppb in 2012 according to research at INSTAAR. This current level is the highest in at least the past 650,000 years with much of its increase occurring since 1960 (Badr 1991). Each methane molecule is about 21 times as efficient at absorbing Earth's radiation as carbon dioxide (CO₂). On a global basis, methane is now second to CO₂ in volume of emissions, accounting for about 23% of greenhouse gases (Hidore 2010).

Methane's potential impact on earth systems makes it increasingly more important to monitor and predict. Methane rises in the atmosphere, passing through the troposphere to the stratosphere. In the stratosphere the sun breaks down methane, oxidizing its hydrogen, producing two water molecules (Dlugokencky 1994). Water vapor is not normally present in any significant amounts above the troposphere and is a contributor to ozone production. Estimates show that a doubling of methane in the atmosphere should increase water vapor in the stratosphere by approximately 30% (Hidore 2012). Enough water vapor exists to produce clouds made up of water and ice crystals in the cold temperature found at heights of approximately 82 km. These clouds reflect Earth radiation back to the surface, compounding the warming of the surface.

Methane Sources

There are many sources of methane, 80% of which are biological and 50% that are anthropogenic (Badr 1991). This overlap occurs because many biological sources of methane are

controlled and perpetuated by man. An example of this is the bacterial production of methane in rice fields through agricultural production.

Anthropogenic sources of methane emission include fossil fuel use, biomass combustion, landfills, and agriculture, including rice cultivation and animal husbandry. Biogenic emissions of methane include bacterial production in wetlands as well as gas hydrates within oceans and permafrost.

Origin	CH ₄ Emission		
	Mass (Tg/a)	Type (%/a)	Total (%/a)
Natural Emissions			
Wetlands (incl. Rice agriculture)	225	83	37
Termites	20	7	3
Ocean	15	6	3
Hydrates	10	4	2
Natural Total	270	100	45
Anthropogenic Emissions			
Energy	110	33	18
Landfills	40	12	7
Ruminants (Livestock)	115	35	19
Waste treatment	25	8	4
Biomass burning	40	12	7
Anthropogenic Total	330	100	55
Sinks			
Soils	-30	-5	-5
Tropospheric OH	-510	-88	-85
Stratospheric loss	-40	-7	-7
Sink Total	-580	-100	-97
Emissions + Sinks			
Imbalance (trend)	+20	~2.78 Tg/(nmol/mol)	+7.19 (nmol/mol)/a

Table 2: Methane Sources and Sinks

Credit: Houweling et al. (1999)

Fossil Fuel Use/Industry/Mining

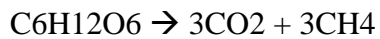
Similar to ethane, the majority of methane emissions arise from the fossil fuel industry. The largest contributions come from the venting and flaring of natural gas as well as leakage from gas processing and distribution pipes. Additionally, pockets of methane that have been trapped between layers of coal during its formation can be released. Methane within the coal itself is also released during the mining of coal. Of the global methane budget, fossil fuel emissions account for 110 Tg/yr-1.

Biomass Burning

Biomass combustion releases 40 Tg/yr-1 of methane into the atmosphere each year. Though biomass burning results mainly in the production of carbon dioxide, methane and other VOCs are released in the event of incomplete biomass combustion. Therefore, methane emissions from biomass burning are dependent on the completeness of combustion and the carbon content of the fuel used (ECI 2008).

Biological Production of Methane

Methanogenic bacteria generate methane by breaking down organic matter anaerobically, releasing carbon dioxide and methane according to the reaction:



Cellulose and bacterial action → release carbon dioxide and methane

As this process involves the action of bacteria, the rate of methane production is strongly dependent on temperature. Maximum methane production is experienced at temperatures between 37° and 45°C (ECI 2008). Further increases in global temperature may enhance bacterial methane production, reinforcing the greenhouse effect.

Agriculture/Rice Cultivation/Animal Husbandry

Agricultural practices also result in significant methane emissions. The two major sectors are rice production and the rearing of livestock. Wetland areas called “paddies” where rice is typically cultivated are essentially man-made wetland areas. Rice paddy soil is completely waterlogged for 4 months each year, creating an artificial wetland. These areas are characterized by high moisture content, oxygen depletion and high organic substrate and nutrient levels. As such, they provide ideal conditions for methanogenic bacteria and result in substantial emissions of methane, approximately 40 Tg/yr-1, essentially 100 grams of methane per 1kg of rice (ECI 2008). Ruminant animals such as cattle, sheep and goats produce methane as part of their natural digestive processes. Food is broken down by bacteria in the rumen, aiding in digestion as the animal’s own stomach enzymes are insufficient to break down plant polymers. These bacterial processes then yield methane, carbon dioxide and ammonia as gaseous byproducts. As the world population increases, livestock and rice cultivation efforts have increased in scope to feed the growing number of inhabitants.

Landfills

Landfill sites also provide an anaerobic environment where methanogenic bacteria break down waste into organic materials. Depending on the composition of the waste, methane gas emissions can vary. The amount emitted to the atmosphere depends on the design and operation of the landfill site. The Clean Air Act of 1996 placed regulations on landfill emissions resulting in a significant decrease in air pollution. However, the Clean Air Act still allows for the venting

and flaring of methane gas. As methane gains in economic value, Methane Utilization Projects are implemented in many U.S. landfills. In these projects, the recovered methane is used as on-site fuel to generate electricity or it is sold to energy consumers (EPA 1999).

Termites

Methane is also produced by the digestive processes of termites in the amount of 20 Tg/yr-1, approximately 5% of emissions worldwide. This value is unlikely to change as termite populations are not expanding, despite greater availability of biomass due to deforestation (ECI 2008). These emissions are significant but for the purposes of this study treated as background emissions, as this source is likely to remain constant.

Wetlands

Wetlands are the largest source of natural methane emissions, as methane is produced by the anaerobic decomposition of organic matter covered by water. The boreal wetlands organically produce anaerobic bacteria, which emit methane gas. Measurement of wetland methane emissions are difficult to calculate due to influence from agricultural sectors.

Methane Gas Hydrates

Though methane gas hydrates are not considered sources or sinks, they are the largest store of methane on the planet, accounting for 53% of all fossil fuels on earth (Englezos 1987).

They are a crystalline solid mixture of water and methane, essentially methane trapped within ice. These hydrates are found in ocean floor sediments and arctic permafrost.

Oceans

Although methane hydrates are contained within the earth's oceans, they represent a large potential source of emissions. As surface water is supersaturated in dissolved methane, through molecular diffusion methane is then released to the atmosphere at 15 Tg/yr. This figure can vary greatly because oceans are a large carbon sink, and are dependent on the amount of carbon in the atmosphere. As carbon is absorbed into the surface water, hydrocarbons are molecularly diffused into the ocean. As time passes and the water is circulated, upwelling currents are brought to the surface, which deposit methane back into the atmosphere. Methane is also produced naturally along the continental shelf and tidal flats as organic matter decomposes. The CH₄ oxidation in sediment and H₂O controls CH₄ flux to the atmosphere from water ecosystems. Currently, 60-90% of new methane emissions are oxidized in lakes and seas, respectively (Badr 1991). This oceanic release to the atmosphere is nearly immediate, on the order of 2-3 years (Nisbet 1989).

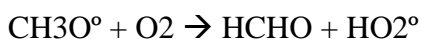
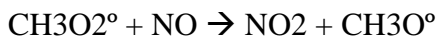
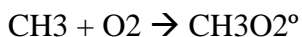
Permafrost

In latitudes from about 50° to 60° in the northern hemisphere, much of the land surface is covered in permafrost. Permafrost is ground that is frozen year-round to a considerable depth. Methane hydrates contained in the Arctic tundra are trapped within the frozen, solid structure of the hydrate. In the summer the surface melts, but it does not melt deep enough to thaw all of the

soil as the permafrost provides a barrier for gases beneath and water above. The amount of methane gas trapped in this hydrates are unknown and require further research (Hidore 2006).

Methane Sinks

Methane shares in ethane's removal from the atmosphere through its reaction with the hydroxyl radical (-OH). Atmospheric removal rates of methane play an important role in the composition and chemistry of the atmosphere. Many reactions in the atmosphere take place through the formation of radical species, those with unpaired electrons. The electronegativity of these elements makes them extremely volatile in the atmosphere. In this case, the hydroxyl radical is formed, and is a primary oxidizing and "cleansing" agent in the atmosphere (Prinn 2003). The reaction between methane and the hydroxyl radical is as follows:



Due to the oxidating capacity of the hydroxyl radical, methane is completely broken down in approximately 8.4 years. Through this reaction methane is a precursor to tropospheric ozone. Reactions between methane and the hydroxyl radical initiate a chain of possible reactions that produce other species, such as carbon monoxide, nitrogen dioxide and hydroperoxide, which can then be removed from the atmosphere (ECI 2008). The magnitude of this sink has a seasonal and

latitudinal variation because the atmospheric concentrations of -OH rise during summer months. With the required presence of incident radiation, oxygen and water vapor, the destruction of methane is possible. The magnitude of this sink has a seasonal and latitudinal variation because the atmospheric concentrations of -OH rise during summer months. With the required presence of incident radiation, oxygen and water vapor, the destruction of ethane is possible. As radiation and water vapor both increase in the tropics during the summer months, -OH concentrations rise and methane is removed with higher frequency.

Methane Statistics

There is evidence that the rates of emissions from known sources have increased along with the growth of human population. The 1% annual increase in the total rate of methane emissions approximately corresponds to the rises in the emissions from individual sources during the 1970s (Badr 1991). If this tendency persists, the methane contributions from these sources will be respectively 160 and 170 million tons per year by the year AD 2020.

Methods

Description of the NOAA Glass Flask Method, based on “Sampling, Storage and Analysis of C2-C7 NMHC from the US NOAA Cooperative Air Sampling Network Glass Flasks”, written by Jacques Hueber in 2008.

The NOAA network flasks are prepared from borosilicate glass. Flask volumes vary from 2.2 to 2.5 liters. A single valve connects to a glass tube extending almost to the bottom of the flask. Another valve is located to the side of the top end of the flask. This design facilitates complete replacement of the fill-gas with sample air during the filling process. The outside of the flasks is coated with a light-proof polymer to minimize potential photochemical degradation reactions and to avoid shattering in case of accidental breakage. Flask treatment and conditioning measures take place before flasks are shipped to measurement sites. Flasks are evacuated to ~10 Pa at room temperature and then sealed for 24 h to check for leaks. Flasks are then filled to 1000 hPa with synthetic air containing 330 ppm CO₂ and shipped to the sites. The filling of the flasks with this artificial air allows identification of insufficiently purged samples that return from the network sites. Portable Sampling Units (PSU) are used at all surface flask sampling sites. The air sample is usually taken from ~5m above ground through tubing attached to a telescoping pole. Air is drawn through the tubing at a flow rate of 5–7 liters/ min⁻¹ by a pump and is then pushed through a pair of flasks in series for 5–8 min. Depending on the location and weather conditions, network flasks can be filled under a wide range of humidity resulting in highly variable amounts of water vapor in the collected air samples. Samplers used in humid environments are equipped with a thermoelectric water condenser to reduce the sample dew point to ~10 °C and to prevent water condensation in the flasks at lower temperatures. A pressurized leak check is performed, the flask valves are closed, and the flasks are then shipped to Boulder for analysis. Flasks are shipped in the dark in cardboard containers at ambient temperature and are kept in these same conditions after arrival in Boulder until their analysis occurs.

Analysis technique consists of a Gas Chromatography system run by the University of Colorado's Institute of Arctic and Alpine Research. A custom-made flask manifold, a sample extraction, and GC inlet system were specifically tailored towards the requirements of this. After sample drying to a dew point of $-10\text{ }^{\circ}\text{C}$, NMHC were pre-focused on a peltier cooled micro-adsorbent trap and analyzed by GC-MS using an $\text{Al}_2\text{O}_3/\text{KCl}$ -deactivated PLOT column. Quantification is done by flame ionization detection. This manifold accommodates 12 flasks and 2 standard inlet ports. Each flask could be individually accessed from the manifold using pneumatically controlled shut-off valves. The entire system is computer-controlled and automated using LabView software. During routine operation the manifold was purged with 100 ml of sample air before concentrating a 500 ml sample.

A compressed ambient air reference was used for regular instrument calibrations. This reference gas was calibrated against numerous gravimetrically prepared hydrocarbon standards in the NOAA Earth System Research Laboratory, Boulder. The NOAA calibration scale has previously been found to be on average within 2% agreement with that of several other laboratories in the US, Canada, and Europe. This reference gas and in-house generated NMHC-free synthetic air (NMHC < 5 ppt per compound) were analyzed regularly, typically twice daily, for a period of more than 1 year. Compound specific carbon response factors were calculated as weekly averages and used for quantification of NMHC in all described experiments, and later in the network sample analysis. Response factors were further cross-referenced ~once per month to a NIST-traceable 2,2-dimethylbutane (DMB) standard (Scott Specialty Gases, Longmont, CO, USA, Table 2). Additional comparison experiments with two other ambient air reference gases, one multicomponent NMHC standard, and one halogenated VOC standard were conducted to

further compare the calibration scale and to confirm peak identifications. The accuracy error of these reference gases is estimated to be $\leq 5\%$.

The internal pressure of the sampling flasks varies notably upon arrival at INSTAAR's laboratory. The flask pressure depends on the filling pressure (which varies according to the ambient pressure/elevation at the site) and on the amount of sample that has been withdrawn during the previous analyses. The air from the flask was then extracted and analyzed in 200 ml aliquots. This smaller sample volume was chosen in order to achieve a good number of data points over the investigated pressure range. Measurements of these extractions were bracketed by injections of 200 ml samples of the reference gas that were introduced directly from the cylinder. In summary, these findings show that potential biases in the quantification of NMHC resulting from the variability in the sample pressure and from the varying amount of sample that has been withdrawn in the prior analyses steps are well below the uncertainty bounds of this analysis. Depending on their ambient air mixing ratios, C2-C7 NMHC is measured with accuracy and repeatability errors of $<10\text{-}20\%$. Saturated NMHC showed less than 5% changes in their mixing ratios in glass flask samples that were stored for up to 1 year. A series of blank experiments showed negligible contamination from the sampling process and from storage of samples in these glass flasks ($<10\text{pptv yr}^{-1}$). Our laboratory was audited by the World Calibration Center for Volatile Organic Gases in 2008 and 2011 and found to meet all quality criteria defined by the WMO-GAW program for Reactive Gases on both occasions.

The repeatability of the flask analysis was determined from several experiments. The precision values (standard deviation) were calculated from multiple analyses of the same air sample from different flasks. Repeatability was also determined from NMHC results in pairs of

flask samples that were collected concurrently at network sites. The standard deviations in experiments reflect the precision of the chromatographic analysis. Multiple measurements of the reference gases and standards with sample introduction directly from the gas cylinders generally resulted in a relative standard deviation of 1–10%. The median value of all such measurements was 3% for saturated C₂–C₅ NMHC, and 5% for all compounds. When flask filling and sample extraction were included, the repeatability of the analysis degraded to some extent, but not largely.

A deterioration of the analytical precision is expected for the full procedure, as analytical errors are also expected to arise from the sampling process, storing and shipping of samples, as well as from the analyses steps prior to the NMHC quantification from the network flasks. The paired sampling/analysis of flasks allows for an evaluation of these contributions. For this purpose we determined the relative standard deviation (by dividing through the mean mixing ratio value from both analyses) between single extractions from each of the two flasks that were filled together at a network site. Not unexpectedly, the relative precision of these analyses improves with increasing mixing ratio. The median precision error was typically <5% above 100 pptv; at levels <100 pptv the median precision error increased to 5–10%. The WMO-VOC quality objective defines a desired precision of ± 15 pptv for mole fractions <100 pptv, and 5% for ethane–pentanes at levels >100 pptv. Most median repeatability values fall below these thresholds, but that for ethane 34% of the data exceeded the target. A contributing factor that reduces the precision in the ethane analysis is the more difficult peak integration as ethane is the earliest analyte peak in the chromatogram eluting close to the injection peak. Results for C₃–C₅ NMHC measurements met the GAW data quality guideline for precision in 87% (propane), 85%

(iso-butane), 89% (butane), 91% (iso-pentane), and 91%(n-pentane) of all cases. These data were used to define a data rejection criterion based on the repeatability of the analysis from flask pairs.

Validity of the data was confirmed by the inter-comparison of flask results with in-situ NMHC measurements. In April 2006, NOAA began the collection of flask samples at the Deutscher Wetterdienst Hohenpeissenberg WMO-GAW station. Variable measurement procedures were standardized as much as possible, for example wind speed and height of sample intake. The in-situ GC systems collected an air sample over a 15-min sampling time. The flask sampling was synchronized with the in-situ sampling during this time. Consequently, as the samples analyzed by both laboratories are not strictly identical, this test cannot be seen as a classic inter-comparison experiment, nonetheless these results are still very valuable for evaluation of the flask method. The Hohenpeissenberg flask samples were subjected to the same handling and analytical practices as for flasks from all other NOAA network sites, including the prior analyses for greenhouse gases and stable isotopes before being analyzed for NMHC. Except for n-hexane, all other compound data series display a general good agreement, with both measurements showing identical behavior in the seasonal cycle, and the flask measurements also capturing some of the short-term variability that is more evident in the higher resolution in-situ data. It is obvious that results vary by compound and concentration, with better agreement seen at the higher levels. In general, good agreement is found for most of the light alkanes. Another indicator for the degree of agreement are the regression line slopes that were calculated for each compound (using a two-sided best linear fit to allow for minimizing of errors in both variables). These calculations resulted in slope/intercept (pptv)/R²-values of 1.03/0/0.99 for ethane. The average analytical uncertainty (P > 95) for C₂–C₇NMHC in the Hohenpeissenberg in-situ

measurements for mixing ratios >100 pptv was determined to be ~7%. Using the above detailed results for the flask accuracy and precision measurements for C2–C5 NMHC, and considering that flask are analyzed as pairs (n = 2), we estimated an uncertainty of ~12% for the flask analysis (at P > 95). This is mostly due to the fact that at lower mixing ratios even relatively small absolute deviations will cause large relative errors exceeding the agreement window. This observation supports the choice of absolute error margins, rather than percentage deviations, as data approach the detection limit (as done in the GAW guideline).

In conclusion, these experiments define conditions and possibilities for NMHC monitoring from whole air glass sampling flasks following the particular protocols that are used in the NOAA global greenhouse gas monitoring network. NMHC recoveries from the flasks did not show sensitivity towards the sample pressure. Extensive tests on the accuracy and precision of this analysis demonstrated that more than 94% of results for saturated C2–C5NMHC, and for isoprene, benzene, and toluene met WMOGAWVOC data quality goals. These experiments demonstrate the feasibility to study regional and global distributions of most C2–C7 NMHC using infrastructure and sampling protocols within existing and operational glass flask sampling programs. In particular, these results showed that C2–C5 alkanes, isoprene, benzene, and toluene can be analyzed in the remaining sample after completion of the greenhouse gas analyses from the NOAA network flasks, with analytical uncertainties of these data in most cases meeting GAW VOC guidelines. This ongoing project will provide the scientific community with global scale NMHC measurements for detailed investigation of atmospheric chemistry processes.

The data acquired through the NOAA Glass Flask Sampling Project for VOC GAW after quality control measures, are uploaded to the NOAA Earth Science Research Laboratory database and are accessible for public use as well as aid in research on a global scale.

Result Curve Methods to Create the Graphs used in this Thesis

The record at each site is a combination of three signals: a long-term trend, a nonsinusoidal yearly cycle, and short-term variations from several days to several weeks that are due to local and regional influences on the compound concentration (Thoning 1989). Once the data have been selected for background conditions, additional filtering is applied to remove variations with magnitudes up to several parts per million (ppm), in order to investigate phenomena that occur over time scales longer than a few weeks. The objective is to remove the short-term fluctuations from the record, then separate the long-term trend and annual cycle data. Filtered data are objectively selected data identified as values that are representative of well-mixed air at the latitude of sampling site, and which are not affected by some known local phenomenon. A statistical approach is used for rejecting certain data; the assumption is that the concentration of a compound in well-mixed air should change by only a small amount over several days (Thoning 1989). This assumption is based on the fact that at very remote monitoring sites, such as South Pole, Antarctica, the variability within an hour and hour-to-hour is very small ($<0.1\text{ppm}$) (Gillette et al. 1987). When concentration changed by more than 0.25ppm , the sample data is flagged for removal as called for by Peterson et al. [1982, 1986]. Data is then rejected based on two criteria: instability of the compound concentration, and large changes in the compound concentration from one sample to the next (Thoning 1989).

The method used to filter data points uses the fast Fourier transform (FFT) algorithm to convert the data set from the time domain into the frequency domain, apply a low-pass filter in the frequency domain to separate the features of interest, then perform an inverse FFT to convert the filtered data back into the time domain (Thoning 1989). The FFT also requires that the number of points used be an integral power of 2. Therefore the data must be "zero padded" to obtain the required number of points. This is done by first removing from the data the mean and a linear trend which passes through the first and last data points, so that the data sets approximately centered around zero and begins and ends with zero. The data record is then extended by 1 or 2 years on each end by repeating the first and last years of data, with the provision that the added data begin and end each year at zero. This extrapolation was included to minimize any end effects that occurred during the filtering process. An equal number of points with zero value are then added at each end of the data until the required number of points is obtained. The dataset is then converted in to the frequency domain using the fast Fourier transform algorithm.

The smoothed curve is computed by filtering averages with a low-pass filter. The transformed data are multiplied by a low-pass filter function which retains only the desired frequencies in the data. The short-term variations due to the high-frequency part of the spectrum can be removed by applying a low-pass filter with an appropriate cutoff frequency, which is defined as the frequency at which the filter attenuates the amplitudes of the cycles by one half. The transfer function of the filter used is a decreasing exponential, referenced in the Thoning et. al report, "Atmospheric Carbon Dioxide at Mauna Loa Observatory and Analysis of the NOAA GMCC Data," published in 1989. As uniform atmospheric mixing in the northern hemisphere

occurs within 2-3 months, any frequencies higher than about 6 cycles yr⁻¹ should be removed from the record and frequencies lower than this should be relatively unchanged. As a result, the data record is much smoother after filtering owing to the removal of the high-frequency portion of the record. The long-term trend can be separated from the record by again, applying a low-pass filter, but this time removing periods of one year and shorter. The long-term trend then consists of cycles with periods longer than one year in length. An inverse FFT is then calculated to convert the data back to the time domain. The mean and linear trends removed previously are then added back into the data to arrive at the final filtered data set.

The seasonal cycle of the chemical has the same basic shape from year to year, with small but significant variations. For example, the peaks of the cycles can vary from a sharp point to a more rounded shape, and the “shoulder” during the chemical’s rise in the beginning of the year is sometimes missing or reduced in size. By subtracting the trend values from the smoothed values, the de-trended annual cycle remains. This assumes that the annual cycle is made up of the entire band of frequencies between 1 cycle yr⁻¹ and the frequencies retained by the smoothing filter, not just of the fundamental and harmonic frequencies. Peak amplitude uncertainty is 0.32 ppm, uncertainty for each individual amplitude value 0.22ppm.

The Growth Rate trend line is the result of fossil fuel combustion, changes in the amount of carbon held in standing biomass and soils, and global-scale phenomenon such as El Nino, which can cause inter-annual variations in the chemical’s growth rate. Time variation of the chemical’s growth rate can be determined by computing the derivative of the filtered point trend line. The resulting curve then has the statistical uncertainty of 0.16 ppm yr⁻¹. The upward slope

of a trend line implies that the growth rate is due to anthropogenic emissions, as biogenic emissions and sinks are consistent on a year-to-year basis.

Statistical Uncertainty

Filtering with this method in the frequency domain is functionally equivalent to convolution filtering in the time domain. That is, filtering in the frequency domain can be visualized as a weighted moving average process in the time domain. The formulation of the filter in the time domain can be used to facilitate estimation of the statistical uncertainty associated with the filtering time series. The theory of error propagation shows that the statistical uncertainty or variance for each value is small enough that other errors, such as calibration and measurement errors, as well as uncertainties due to data selection, become significant at this level. It is difficult to determine a precise value for these other non-statistical errors. A conservative approach assigns the same uncertainty of 0.11 ppm for both filtered and trend data (Thoning 1989). Because the extrapolated data at the ends of the actual record will differ somewhat from the true values, there is a larger uncertainty in an empirical manner, based on different extrapolation techniques and using different lengths of the record.

Discussion

This section includes a review of current research, data and results from this thesis, as well as conclusions and recommendations.

Current Research

A study done by Isobel Simpson in 2012 on the topic of ethane and methane was greatly beneficial to my research. Several assumptions from the Simpson study were validated with NOAA data and used as a basis for this research; (1) as the logarithm of VOC concentrations in air parcels declines linearly during their atmospheric transport, ratios of VOC pairs with similar source emission ratios can be used as an indicator of their atmospheric oxidation rate, and (2) A graph of atmospheric ethane mixing ratio versus methane growth rate reveals a remarkably

strong correlation between the two gases over the past 25 years (Figure 3) (Simpson 2012).

The Simpson et al. study showed variations between methane and ethane in only three instances:

latitudinal, seasonally, and inter-annually. The study concluded that emissions for both ethane and methane were in decline, although concentrations were far more

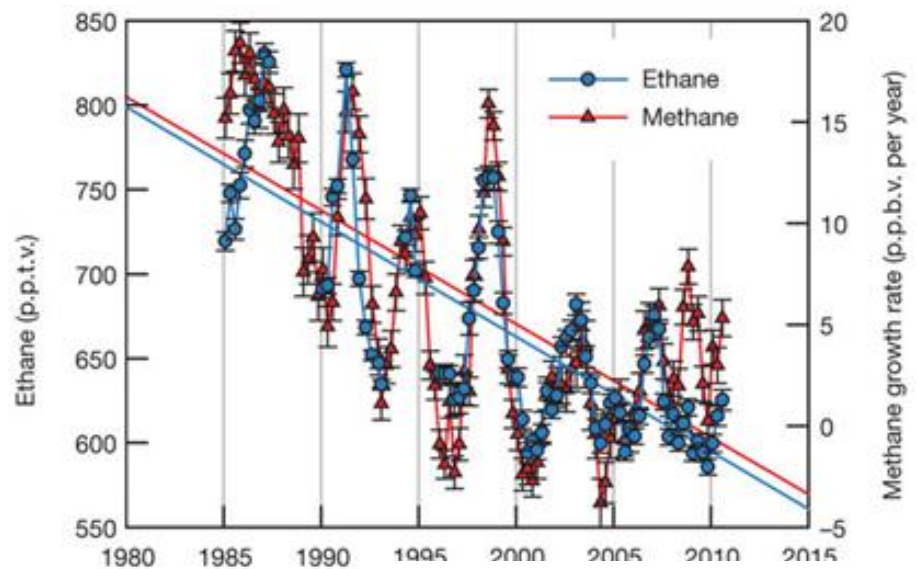


Figure 3: Methane measurements, co-sampled with ethane from the UCI Global Monitoring Network display strong correlation over past 25 years.

Credit: Simpson 2012

significant in the northern hemisphere. This resulted in the conclusion that the decreasing fugitive emissions were then due to the decreased venting and flaring of natural gas (Simpson 2012). The suspected contributors for this decrease in venting and flaring were determined as a result of regulations putting restrictions on venting and flaring, and increases in oil prices making the capture of natural gas at oil fields more economically feasible. Simpson noted that there is the possibility that the decrease in emissions from natural gas industry could have been offset by the production and processing of petroleum, associated with the venting of ethane and methane in production.

Due to their shared sources, ethane and methane have corresponding anthropogenic emission rates, making the compounds easily comparable. After determining this, Dr. Simpson postulated the theory that mass-based MERs can be used to determine the source of methane emissions. Kinetic reactions with hydroxyl radicals in the atmosphere occur at different rates for both ethane and methane. Ethane's atmospheric lifetime before being broken down by hydroxyl radical is only 2 months, whereas methane's atmospheric lifespan is nearly 9 years. With its lengthy atmospheric lifetime, methane concentrations respond much more slowly to changes in emissions than those of ethane. Therefore any change in methane emissions will not be available in data records for another 9 years, while a change in ethane emissions is noticeable within a short timeframe. Though not equivalent, methane's atmospheric growth rate correlates strongly with changes in its emissions (Simpson 2012). Therefore, methane's growth rate is then a more time-sensitive indicator of fluctuations in methane emissions. In a mass-based comparison of the two compounds, the growth rate of methane is compared to ethane's absolute emission values in

parts per trillion per volume. Using University of California at Irvine (UCI) data through the spring of 2010, the Simpson study concluded that methane emissions were in decline.

Data and Results

Curious about the increase in methane growth from 2007 pictured in Simpson's MERs, I investigated further. Correlations show agreement between UCI data used in the Simpson study and NOAA GAW data at several latitudinal bands and sampling sites (Figure 4, Simpson 2012).

As UCI data ends in early 2011, this correlation validates the use of NOAA GAW recent measurements through 2013.

Though the Simpson study concludes that methane emissions may be decreasing, I believe more recent NOAA GAW data display trends that may alter Simpson's conclusion.

Due to the fact that methane and ethane are emitted from fossil fuel sources with characteristic emission ratios, the NOAA GAW long-term ethane record can be used to quantitatively investigate methane's changing growth rate. In order to compare trends of the two compounds, methane growth rates were compared to ethane's absolute concentration in the atmosphere. Recall, the correlation

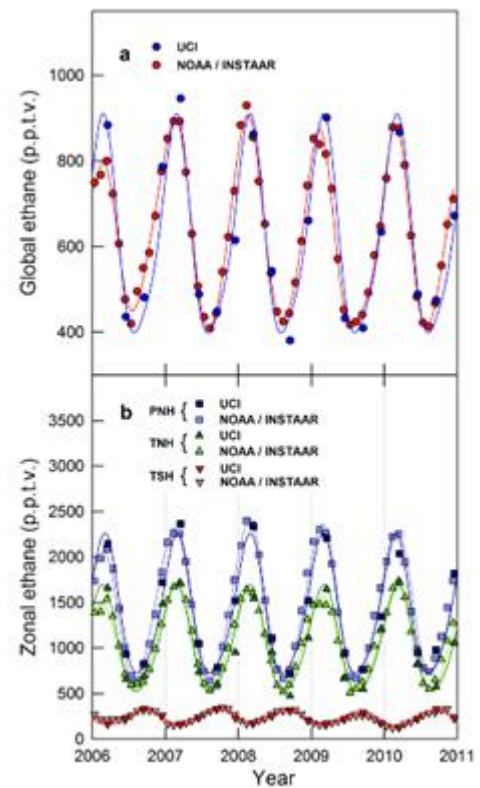


Figure 4: Agreement of UCI data and NOAA GAW data at several latitudinal bands and sampling sites.

Credit: Simpson 2012

between methane's emissions and growth rate as discussed previously.

Though I could confirm a decline in ethane concentrations, methane growth rates have not paralleled these trends at all sites. Referencing NOAA GAW data through 2013, my assumption is that methane growth rates are increasing at several Arctic sites. NOAA's longest term methane record at Mauna Loa, Hawaii has been continuous since 1983 and has exemplified many varying trends over the years. From the onset of the program, methane increases until 1999, when a slight decrease appears through 2005. At this time methane begins to increase again, a trend exhibited through current 2013 data. In analysis of data from Summit, Greenland, it seems likely that methane emissions may be trending upwards. Given increasing summer minimums and winter maximums, I predict that methane emissions may be increasing at Summit, Greenland (Figure 5).

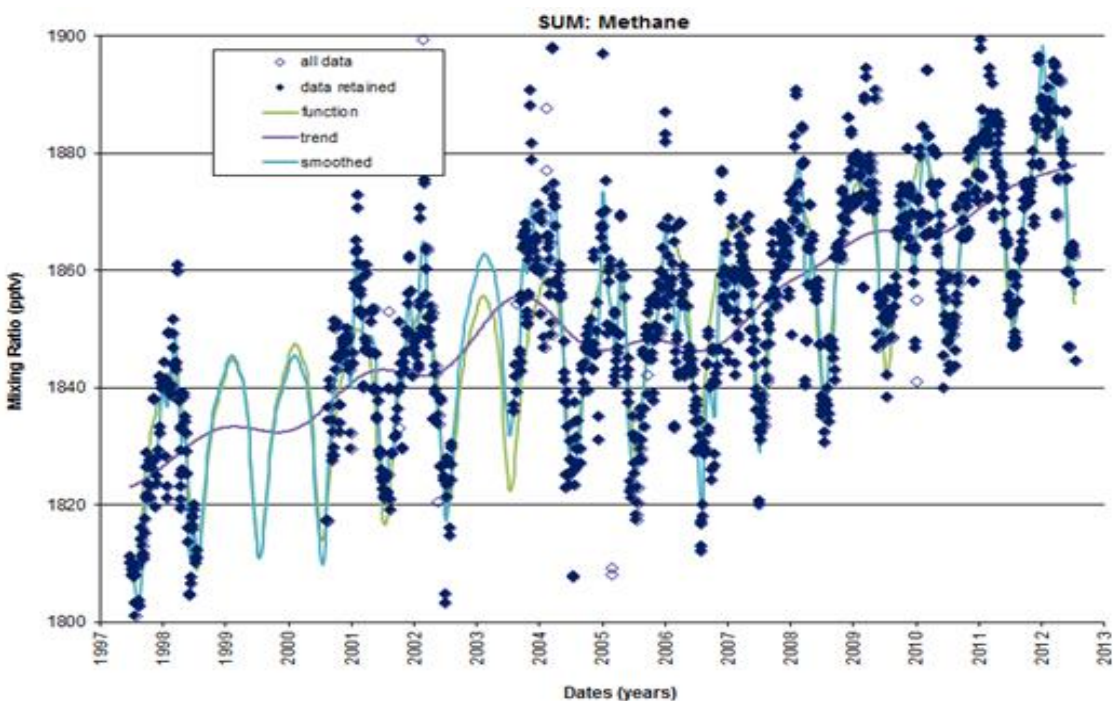


Figure 5: Methane mole fraction at Summit, Greenland site display increasing summer minimum and winter maximums.

Multiple sites within NOAA’s Global Monitoring Network show that while methane emissions appear to be increasing, this is not always matched with an increase in growth rate. Growth rates are increasing primarily in Arctic sites, as tropical sites do not show increases in growth rate trends. Figure 6 shows the increase in methane’s growth rate in recent samples from the Greenland Ice Sheet.

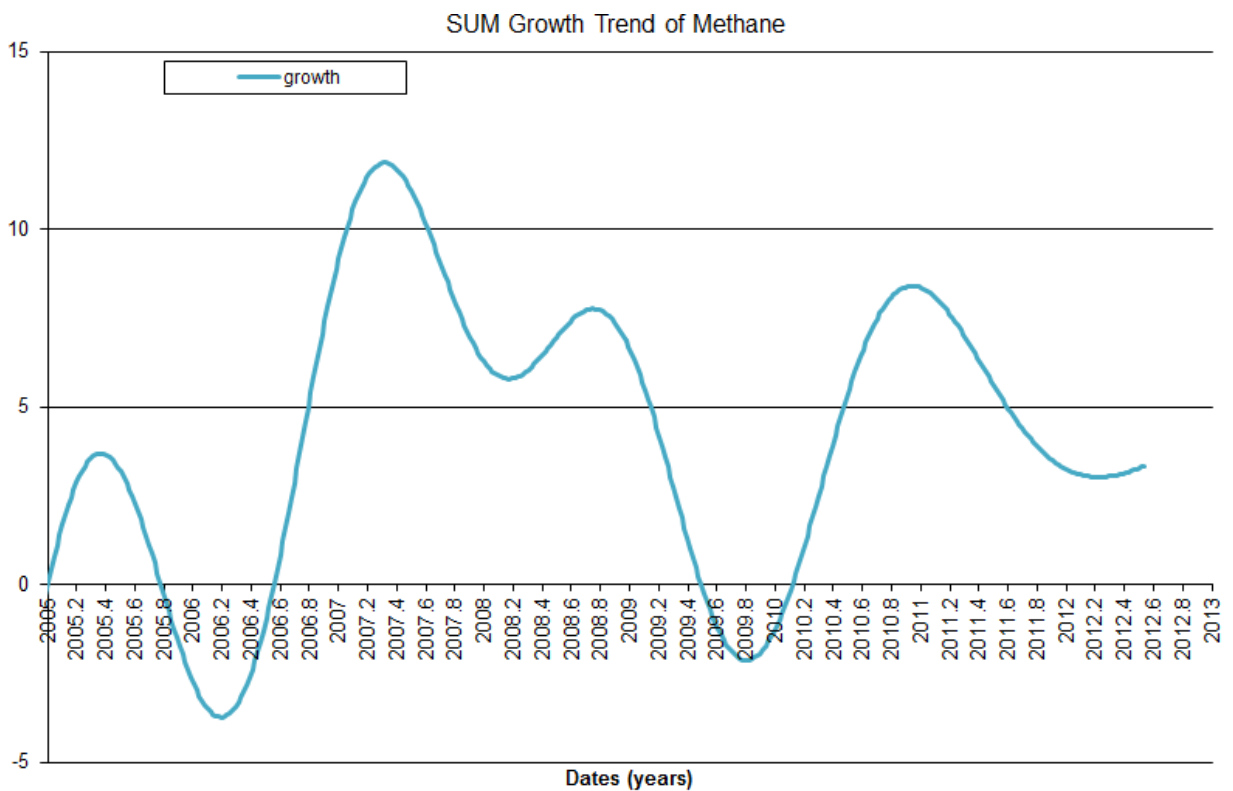


Figure 6: Shows the Increasing Growth Rate of Methane at Summit, Greenland.

Mass-based MERs display a disparity between ethane and methane’s trends. Due to their shared anthropogenic sources, if increases in methane emissions were contributed by fossil fuel

sources then this same trend could be expected in ethane data. However, this is not the case. Due to this constraint, contributions to increasing methane emissions from ethane's shared anthropogenic sources can be eliminated; increased methane emissions would not have been caused by the venting and flaring of fossil fuel or biomass burning. Seasonal cycles rule out the possibility that variations are due to a change in anthropogenic sources, contributing to ethane and methane variability. Increases in methane emissions cannot be from a change in hydroxyl radical sinks either, as it would similarly effect ethane concentrations in the atmosphere. Since the average concentration of hydroxide radical is relatively constant, it is unlikely that changes in hydroxide radical concentration are the cause of decline in ethane concentration (Simpson 2012).

Political awareness of global warming has resulted in sequestration measures targeting anthropogenic fossil fuel emissions. The concurrent decline in fossil fuel use validates the dismissal of anthropogenic methane sources as the origin of increasing methane emissions today. Although unlikely, it is possible that methane could have been emitted by leakage from gas processing and distribution pipes or in the mining of coal. In the past, with considerably less value than oil, natural gas was often vented to the atmosphere during the collection of oil. Due to rising oil prices and increasing value of natural gas resources, the venting and flaring of natural gas is not as common. Though flaring still occurs in areas lacking the infrastructure to capture the resource, it is irrational to assume that the increase in methane emissions has been contributed in this manner. Methane's increasing economic value makes it a profitable resource to conserve. Seasonal cycles of methane rule out the possibility that variations are due to a change in anthropogenic sources as well.

If not due to anthropogenic sources, the increase in methane emissions may then be from any of its biological sources: agricultural practices, landfills, termites, wetlands or gas hydrates. As biological sources typically remain consistent on a year-to-year basis, it is unlikely that an increase in emissions would be found in many of these sources. Despite the world's growing population, emissions from agricultural practices do not appear to be the cause of methane's increased emissions. Rice Agriculture emissions in Asia have been reduced by approximately half ($51 \pm 18\%$) over the past three decades associated with increases in nutrient application and reductions in water use (Kai 2011). Methane emissions from ruminants could potentially be the cause of increases in methane growth rates. The U.S. Food and Agriculture Organization states that agricultural methane output could increase 60% by 2030 (Times 2009). To create the amount of increased emissions seen in NOAA GAW data, the livestock agriculture industry would have needed to grow exponentially more than it has to meet the amount of emissions seen. Increasing growth rates were again, seen primarily at Arctic locations, where agriculture is not prevalent. Still a possibility, the analysis of carbon isotopes within atmospheric methane would result in a conclusive answer. Additionally, termite and landfill emissions are both negligible sources of methane emissions and were treated as background emissions, as this source is likely to remain constant.

Possible contributions to the increased atmospheric concentrations of methane then point to emissions from methanogenic bacteria. The link between land and water, wetlands are one of the most productive ecosystems in the world. Found at many latitudes, wetlands are an ideal home for methanogenic bacteria. Methane production from bacterial sources is strongly dependent on temperature. Maximum methane production is experienced at temperatures

between 37° and 45°C, which is common at tropical latitudes (Hidore 2006). Consequently, the increase in methane emissions could likely be from wetland sources. Of the NOAA GMD sites that could possibly contribute to wetland methane emissions, none showed an increase in methane growth rates and were thusly eliminated as contributors.

As increasing methane growth rates were primarily found at Arctic measurement locations, it seems likely that methane gas hydrates could be the cause. The destabilization of gas hydrates poses another potential contribution to increased methane emissions. Found in arctic permafrost as well as in ocean sediment, methane hydrates present a considerable environmental threat if released into the atmosphere. Should global temperatures increase, these hydrates will become unstable and release the methane gas that is now contained. As global warming is most rapid in sub-arctic regions, melting of the permafrost may already be taking place in some areas and releasing methane into the atmosphere. As high latitudes are experiencing warmer weather, temperature rise at the surface of permafrost leads to convection, warming the permafrost even more quickly and accelerates microbiological decomposition. This destabilization of methane hydrate solids will continue to contribute to emission levels. The release of methane in sub-polar regions is self-perpetuating; if methane is released into the atmosphere, it will lead to still more warming and more methane release. Further increases in global temperature may enhance bacterial methane production, reinforcing the greenhouse effect. Increased methane emissions will continue to warm the Earth's atmosphere, increasing water vapor, ultimately contributing to the further rise of methane concentrations. As these biological sources are awakened by positive feedback (warming) there is theoretically no limit to how quickly emissions can rise.

On longer timescales, methane gas hydrates dissolved in ocean sediment will resurface. With record-high fossil fuel use contributing to an increase VOC emissions, these molecules will dissolve into our oceans to resurface years from now where a tipping point of climate change could then occur. The study finds layers of increased methane concentrations near the surface ocean over the remote Arctic Ocean, with little or no enhancement of carbon monoxide levels. This indicates a non-combustion source of the methane (Kort 2012). If my hypothesis holds true that the recent increase in methane emissions is due to the destabilization of methane hydrates then positive feedback loops that will perpetuate the increase of methane in the atmosphere are already accruing.

Conclusions and Recommendations

Of these possible biogenic sources, methane emissions from Arctic permafrost seem the most likely contributor to increasing growth rates. This is my conclusion, as data revealed increasing growth rates primarily from Arctic sites. In 2012, INSTAAR launched its own in-situ measurements at Summit, Greenland to monitor NMHCs more closely. Though it is still early to conclusively see trends in the data, the value of this research lies in the validation of overall data trends within other sampling networks. Investigation into the interaction between methane hydrate destabilization and climate change at short and long time scales, particularly in the Arctic is increasingly important.

Bibliography

Aydin, M., et al. Recent decreases in fossil-fuel emissions of ethane and methane derived from firm air. *Nature*. Vol. 476. August 2011.

Badr, O. Probert, D. O'Callaghan, P.W. *Origins of Atmospheric Methane*. Applied Energy, Cranfield Institute of Technology. Elsevier Science Publishers Ltd. 189-231. (1991).

Benedict, Manson. Webb, George. Rubin, Louis. *An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and their Mixtures I. Methane, Ethane, Propane and n-Butane*. AIP Journal of Chemical Physics. Volume 8, Issue 4. (1939).

Boissard, C. Bonsang, B. Kanakidou, M. Lambert, G. TROPOZ II: Global Distributions and Budgets of Methane and Light Hydrocarbons. *Journal of Atmospheric Chemistry*. Vol. 25; 115-148. 1996.

California Environmental Protection Agency, Air Resources Board. *The Physics and Chemistry of Ozone*. Office of Environmental Health and Hazard Assessment. 2000.
<http://www.fraqmd.org/OzoneChemistry.htm>

Dlugokency, E. Steele, L. Lang, P. Masarie, K. *The Growth Rate and Distribution of Atmospheric Methane*. *Journal of Geophysical Research*. 1994.

Dlugokency, E. Masaire, K. Lang, P. Tans, P. Steele, L. *A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992*. *Geophysical Research Letters*. 1994.

Dlugokency, E. Masarie, K. Tans, P. *Is the amplitude of the methane seasonal cycle changing?* Elsevier Science. 1997.

Dlugokency, E. Bruhwiler, J. White, W. Emmons, L. *Observational Constraints on recent increases in the atmospheric CH₄ burden*. *Geophysical Research Letters*. 2009.

Environmental Change Institute: School of Geography and the Environment. Climate Science of Methane. (2008).

<http://www.eci.ox.ac.uk/research/energy/downloads/methaneuk/chapter02.pdf>

Englezos, P. et al. Kinetics of Formation of Methane and Ethane Gas Hydrates. *Science Direct*. Volume 42, Issue 11. (1987)

<http://www.sciencedirect.com/science/article/pii/000925098787015X>

Environmental Protection Agency. U.S. Methane Emissions 1990-2020: Inventories, Projections, and Opportunities for Reductions. September 1999.

<http://www.epa.gov/outreach/reports/02-landfills.pdf>

Fleming, Zoë L. Monks, Paul S. Manning, Alistair J. Review: Untangling the influence of air-mass history in interpreting observed atmospheric composition, *Atmospheric Research*, Volumes 104–105, February 2012, Pages 1-39, ISSN 0169-8095, 10.1016/j.atmosres.2011.09.009

Gillette, D., Komhyr, W., Waterman, L. S., Steele, L. P., Gammon, R. H. The NOAA/GMCC continuous CO₂ record at the South Pole, 1975-1982. *Journal of Geophysical Research*, Vol. 92, 1987.

Helmig, D., D. M. Tanner, R. E. Honrath, R. C. Owen, and D. D. Parrish. Nonmethane hydrocarbons at Pico Mountain, Azores: 1. Oxidation chemistry in the North Atlantic region, *J. Geophys. Res.*, 113, D20S91, (2008),doi:10.1029/2007JD008930.

Helmig, D., Bottenheim J., Galbally I. E., Lewis A., Milton M. J. T., Penkett S., Plass-Duelmer C., Reimann S., Tans P., and Theil S. Volatile Organic Compounds in the Global Atmosphere. *Eos Trans. AGU*, 90(52), Feature. (2009).

Henderson, Mark. Methane's impact on global warming far higher than previously thought. *Times Environment*. October 2009.

Hidore, Oliver, Snow. *Climatology. Textbook for Principles of Climate*. 2006.

Ito, Tomoyasu. Lunsford, J. (1985) Synthesis of ethylene and ethane by partial oxidation of methane over lithium-doped magnesium oxide. *Nature* 314; 721-722.

Kai, Fuu Ming. Tyler, Stanley. Randerson, James. Blake, D. Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources. *Nature*, Vol. 476. August 2011.

Kimmerer, T. Kozlowski, Theodore. (1982) Ethylene, Ethane, Acetaldehyde, and Ethanol Production by Plants under Stress. *Plant Physiology*. Volume 69, number 4.

Kort et al. Atmospheric observations of Arctic Ocean methane emissions up to 82° north. *Nature Geoscience*, Vol. 5. May 2012.

Liu, S. Trainer, M. Fehsenfeld, F. Parrish, D. ozone production in the rural troposphere and the implications for regional and global ozone distributions. *Journal of Geophysical Research*. 2012.

Nisbet, E. G. Some Northern Sources of Atmospheric Methane: Production, History, and Future Implications. *Canadian Journal of Earth Science*. 1989.

Pollmann J., Helmig D., Hueber J., Plass-Duelmer C., and Tans P. Sampling, storage, and analysis of C2-C7 non-methane hydrocarbons from the US National Oceanic and Atmospheric Administration Cooperative Air Sampling Network glass flasks. *J. Chromatogr.*, 1188, 75-87. (2008).

Pollmann J., Helmig D., Hueber J., Tanner D., and Tans P. Evaluation of adsorbent materials for cryogen-free trapping-one stage-GC analysis of atmospheric C2-C6 non-methane hydrocarbons. *J. Chrom.*, 1134, 1-15. (2006).

Pozzer A., Pollmann J., Taraborrelli D., Jöckel P., Helmig D., Tans P., Hueber J., and Lelieveld J. Observed and simulated global distribution and budget of atmospheric C2-C5 alkanes. *Atmos. Chem. Phys.* 10, 4403-4422. (2010)

Prinn, Ronald. The Cleansing Capacity of the Atmosphere: Annual Review of Environment and Resources. Vol 28; 29-57. November 2003.

Rudolph, J. The Tropospheric Distribution and Budget of Ethane. Journal of Geophysical Research. Vol. 100, No. D6. June 1995.

Simpson, I. J., Rowland, F. S. Meinardi, S., Blake, D. R. Influence of biomass burning during recent fluctuation in the slow growth of global tropospheric methane. Geophysics. Vol. 33. 2006. ***ASK DH

Simpson I.J., Andersen M.P.S., Meinardi S., Bruhwiler L., Blake N.J., Helmig D., Rowland F.S., and Blake D.R. Long-term decline of global atmospheric ethane concentrations and implications for methane. Nature 488, 490-494. (2012).

Tanner, D., Helmig D., Hueber J., Goldan P. Gas chromatography system for the automated, unattended, and cryogen-free monitoring of C2 to C6 non-methane hydrocarbons in the remote troposphere, Journal of Chromatography A, Volume 1111, Issue 1, 7 April 2006, Pages 76-88, ISSN 0021-9673, 10.1016/j.chroma.2006.01.100. (2006).

Thoning, K. Tans, P. Komhyr, W. Atmospheric Carbon Dioxide at Mauna Loa Observatory and Analysis of the NOAA GMCC Data, 1974-1985. Journal of Geophysical Research, Vol. 94, No. D6. June 20, 1989.

Uherek, Elmar. Oxidation in the Lower Atmosphere. ESPERE. 2004.

http://www.atmosphere.mpg.de/enid/42b8abcc2fd3257968e27086bf463ab7,0/1__Oxidants__Observation/_oxidation__OH_radicals_24y.html

United States Environmental Protection Agency. Available and emerging technologies for reducing greenhouse gas emissions from municipal solid waste landfills. June 2011.

Wahlen, M. et al. Carbon-14 in Methane Sources and in Atmospheric Methane: The Contribution from Fossil Carbon. Science. Vol. 245. May 1989.

World Meteorological Organization. A WMO-BMBF Workshop on VOC. Establishment of a World Calibration/Instrument Intercomparison for VOC to Serve the WMO Global Atmosphere Watch (GAW) Programme. World Meteorological Organization & Global Atmosphere Watch Report No. 111, 1996.

World Meteorological Organization. A WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds (VOCs), 2009. World Meteorological Organization Global Atmosphere Watch Report No. 171.

Worton, D. Sturges, W. Reeves, C. Newland, M. Evidence from firm air for recent decreases in non-methane hydrocarbons and a 20th century increase in nitrogen oxides in the northern hemisphere. Elsevier Journal. 2011.