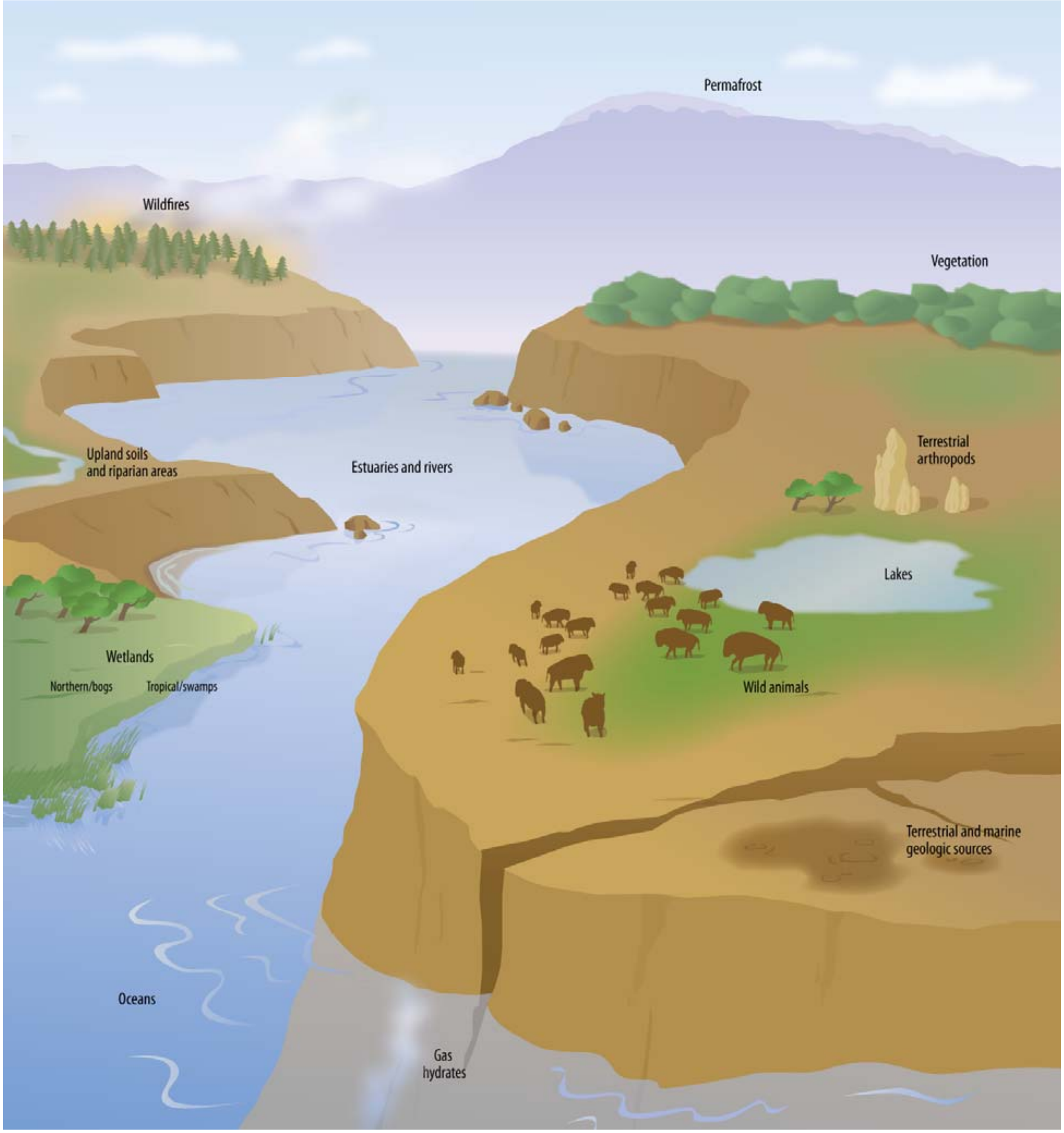
United States Environmental Protection Agency

Office of Atmospheric Programs (6207J)
Washington, DC 20460

EPA 430-R-10-001
April 2010

Methane and Nitrous Oxide Emissions From Natural Sources



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1200 Pennsylvania Ave., NW
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Acknowledgments

This report was prepared under a contract between the U.S. Environmental Protection Agency and Eastern Research Group, Inc. (ERG).

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EPA thanks the following individuals who served as peer reviewers for this report:

- Stephen Del Grosso, USDA Agricultural Research Service
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- Aslam Khalil, Portland State University
- Joel S. Levine, NASA Langley Research Center
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Executive Summary

In 1993, EPA prepared a Report to Congress entitled *Current and Future Methane Emissions from Natural Sources* (U.S. EPA, 1993). That report provided global estimates of current and future emissions of methane (CH_4), a “greenhouse gas,” from natural sources. Much new knowledge has emerged since 1993. For example, the Intergovernmental Panel on Climate Change’s recent Fourth Assessment Report (referred to hereafter as “AR4”) (Solomon et al., 2007) reviewed the scientific evidence and reached the strongest conclusions to date regarding climate change. The AR4 focused largely on anthropogenic (or human-produced) sources, however, and included only a limited assessment of natural source emissions.

This report serves as an update to EPA’s original 1993 report on natural sources. Building on the AR4 and other recent efforts, this report summarizes the latest research and provides global estimates of current and future emissions of CH_4 from natural sources, including emissions from newly identified sources. It also provides global estimates of current and future emissions for nitrous oxide (N_2O), another important greenhouse gas, from natural sources.

ES.1 Introduction

CH_4 and N_2O are “greenhouse gases,” meaning that they trap infrared radiation (heat) from the earth’s surface and increase the temperature of the earth. Without this natural “greenhouse effect,” temperatures would be about 33ºC (60ºF) lower than they are now, and life as we know it today would not be possible.

During the past century, humans have substantially added to the amount of greenhouse gases in the atmosphere through activities such as burning fossil fuels and deforestation. The added gases are enhancing the natural greenhouse effect, and very likely contributing to an increase in global average temperature and related climate changes.

CH_4 and N_2O are emitted from both natural and anthropogenic sources. Natural sources of CH_4 include fires, geologic processes, and bacteria that produce CH_4 in a variety of settings (most notably, wetlands). N_2O is also produced by bacteria. Major anthropogenic sources of these gases include fossil fuel combustion and agriculture. Some sources can be related to both natural and anthropogenic processes. For example, forest and grassland fires, which produce CH_4, can be either human-initiated (e.g., for land clearing) or the result of lightning ignition or other natural causes.

While much attention is currently focused on anthropogenic sources of greenhouse gases, there is ample evidence that emissions of these gases from natural sources have also changed over time. Human activities have significant potential to change emissions from these sources, both directly (e.g., decreased CH_4 from wetlands, due to wetland loss from draining and filling) or indirectly through human-induced climate change (e.g., increased CH_4 emissions from wetlands due to rising temperature, or from wildfires that are more frequent and severe). Therefore, to address greenhouse gas emissions, it is important not only to quantify the current magnitude of natural sources, but also to understand how human activities and climate change affect emissions from these sources.

This report presents many different estimates of CH_4 and N_2O emissions, reflecting the variety of approaches that scientists use to characterize emissions. These approaches generally fall into two categories: “bottom-up” and “top-down.” “Bottom-up” estimates work from a small scale to a larger scale, extrapolating actual measurements of flux (that is, the release or uptake of a gas) to larger scales, or developing a model of the processes controlling fluxes and then applying it to a larger scale. “Top down,” or inverse, methods use atmospheric concentration measurements, atmospheric transport models, and statistical methods to estimate emissions from individual sources.

ES.2 Summary of Natural Source Emissions

This report focuses on identifying and quantifying greenhouse gas emissions from the following natural sources:

- Wetlands
- Upland soils and riparian zones
- Oceans, estuaries, and rivers
- Permafrost
- Lakes
- Gas hydrates
- Terrestrial and marine geologic sources
- Wildfires
- Vegetation
- Terrestrial arthropods and wild animals

Figure ES-1 and Table ES-1 summarize the current global estimates of CH_4 and N_2O emissions from each of these natural sources. The table presents the annual emissions of CH_4 and N_2O in teragrams (Tg)[1] from each source, and compares these emissions to the overall annual flux of these gases into the atmosphere (total global emissions from all sources) as identified in the AR4. Most of the emissions estimates are shown as ranges, which reflect the variety of estimates available in the literature. Point estimates shown here are based on averaging and professional judgment. Following typical conventions, N_2O emissions are presented as Tg of nitrogen (N).

Natural sources of CH_4 are estimated to produce 37 percent of the total CH_4 flux into the atmosphere every year. The largest source of natural CH_4 emissions is natural wetlands, which contribute 170 Tg CH_4/yr (per year). Several other sources contribute substantially as well, including geologic emissions (now estimated at 42 to 64 Tg CH_4/yr), lakes (estimated at 30 Tg CH_4/yr), and vegetation (which potentially contributes 20 to 60 Tg CH_4/yr). For some natural sources, such as wetlands, CH_4 emissions are reasonably well understood, having been quantified over some time. Other sources, such as vegetation and terrestrial and marine geologic sources, are potentially significant, but are newly identified or are in the early research stages of quantification, so their contribution is uncertain.

Natural sources of N_2O are estimated to contribute about 64 percent of the total inputs to the atmosphere. The largest sources of natural N_2O emissions are soils (contributing 6.6 Tg N/yr) and oceans, rivers, and estuaries (contributing 5.4 Tg N/yr). However, there is some controversy as to what fraction of the emissions associated with rivers and estuaries should be considered natural source emissions, as they are driven primarily by anthropogenic contributions of nitrogen to the water bodies (e.g., from agricultural runoff).

Sections ES.2.1 through ES.2.10 summarize what is known about each of the major natural sources of CH_4 and N_2O, including estimates of current and future emissions where available.

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[1] 1 teragram (Tg) equals 1×10^{12} grams or 1 million metric tons.

It is important in reading this report to keep in mind that the earth is a system of interacting components, and change often affects many components as well as their interactions. This report is organized into chapters covering natural sources by type (e.g., wetlands, lakes, oceans, gas hydrates, etc.). However, the earth is a mosaic of these different source types, the boundaries between these source types are sometimes inexact (e.g., between a wetland and the emergent vegetation of a lake margin), and system changes that affect one source can also affect one or more other sources.

The issue of methane in permafrost regions exemplifies this interconnectedness. The projected thawing of permafrost with climate warming may contribute to increased natural source methane emissions to the atmosphere. However, this is a complex system response. There is not a lot of methane frozen into permafrost (unless it is a gas hydrate formation), so permafrost thaw will not release much methane directly. The methane it does release has a reasonable probability of being oxidized as it diffuses through 1 to 100 meters of thawed soil before reaching the atmosphere (see Chapter 5, "Permafrost"). Therefore, the report concludes that permafrost thawing is not likely to be a strong methane source. However, if gas hydrates are associated with permafrost, then thawing permafrost and destabilization of these hydrates may co-occur (though they are not exactly the same thing), releasing methane, potentially in large quantities (see Chapter 7, "Gas Hydrates"). Another consideration is changes in wetland vegetation and moisture status associated with permafrost thawing; this would be an issue for some, but not all, permafrost landscapes. If the landscape gets wetter and the vegetation composition becomes more dominated by sedges, this could lead to increased methane emissions from a wet landscape - at least for years to decades; however, if the landscape gets drier (or stays relatively dry), then methane emissions would probably stay low (see Chapter 2, "Wetlands"). Finally, permafrost thaw can be associated with thermokarst erosion, which can form (or drain) lakes; these lakes can also be methane sources (See Chapter 6, "Lakes"). Each chapter of this report specifies the natural sources addressed by that chapter.

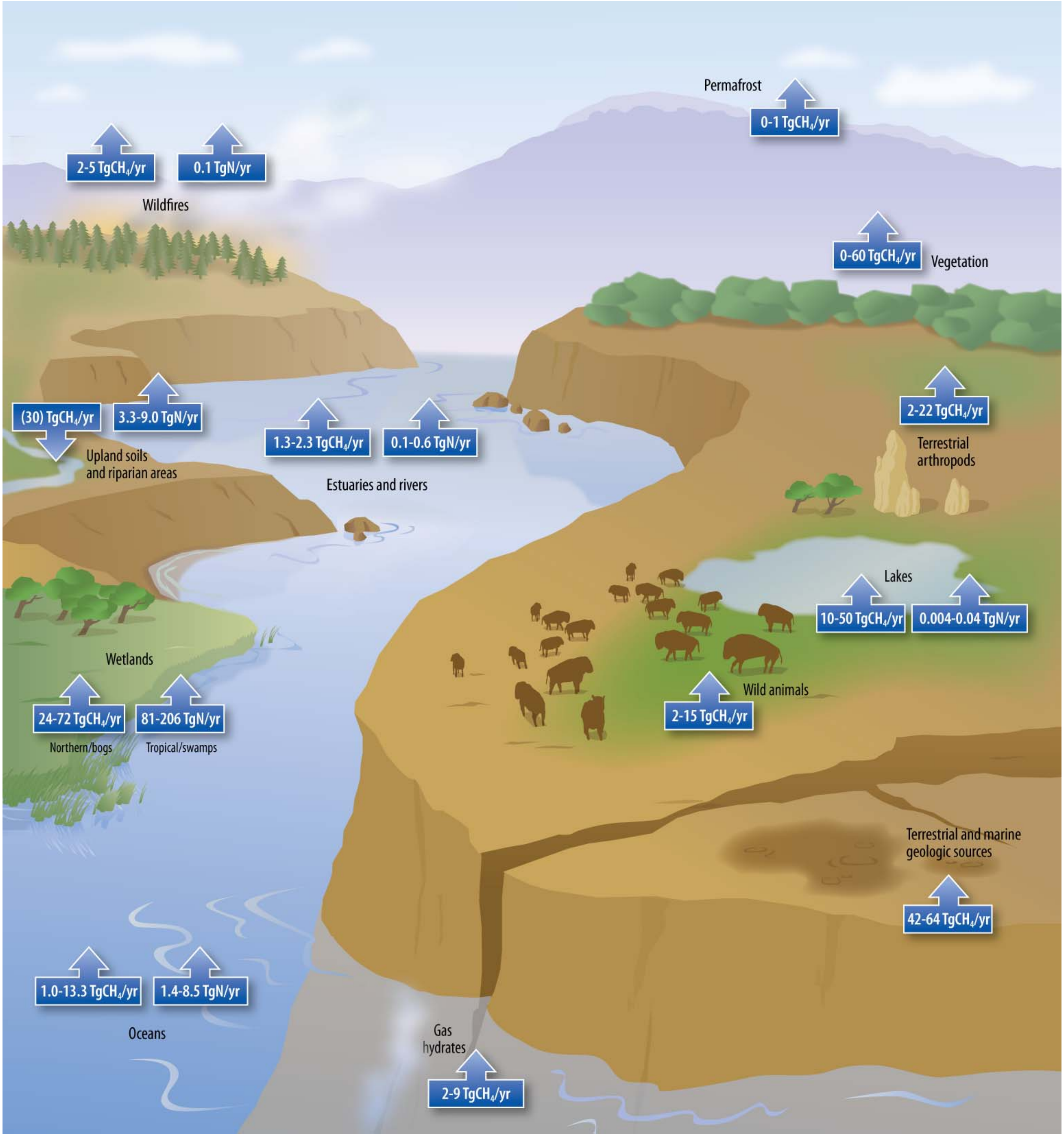

Figure ES-1. Estimated annual emissions of CH_4 and N_2O from natural sources. N_2O emissions are presented as Tg of nitrogen (N). Note that permafrost and any permafrost sources of methane occur mostly at high latitudes, not high elevations. See Table ES-1 for additional detail.

Table ES-1. Current Methane and Nitrous Oxide Emissions From Natural Sources

Source	Methane (Tg CH_4/year)			Nitrous Oxide (Tg N/year)		
	Emissions Estimate[a]	Range[b]	δ^{13}C (‰)[c]	Emissions Estimate[a]	Range[b]	δ^{15}N (‰)[d]
Wetlands	**170.3**			Negligible		
- Northern/bogs	42.7	24–72	-62			
- Tropical/swamps	127.6	81–206	-58.9			
Upland soils and riparian areas	-30	Not available		6.6	3.3–9.0	-38 to +2
Oceans, estuaries, and rivers	9.1	2.3–15.6	-58	5.4	1.5–9.1	-2 to +12
Permafrost	0.5	0–1		Negligible		
Lakes	30	10–50	-53.8		0.004–0.04	
Gas hydrates		2–9[e]	-62.5			
Terrestrial and marine geologic sources		42-64	-41.8			
Wildfires		2–5	-25	0.1	Not available	
Vegetation		Not a source or 20–60	Not available			
Terrestrial arthropods[f]	20	2–22	-63			
Wild animals	8	2–15	-60.5			
All natural sources	**208**	**See note[g]**	**-57[h]**	**12.1**	**See note[g]**	**8.8[i]**
All sources to the atmosphere (anthropogenic and natural)	566[j]	503–610[k]	-54.5[c]	18.8[l]	8.5–27.7	7[m]
Natural sources as a percent of the total	37%	See note[g]	n/a	64%	See note[g]	n/a

[a] In some cases, a point estimate cannot be provided due to large uncertainty.

[b] Ranges presented here may reflect a compilation of several different estimates. Published estimates vary due in part to uncertainty in estimating the global number of point and diffuse sources and the average annual emissions from each individual source or source area.

[c] Mean value from Whiticar and Schaefer, 2007, and references therein.

[d] Range from Rahn and Wahlen, 2000, and references therein.

[e] The emission estimates for gas hydrates correspond to the flux of methane to the ocean, most of which is likely to be oxidized in the ocean water column.

[f] Estimates for terrestrial arthropods include termites. It is estimated that other arthropods could contribute up to 100 Tg CH_4/year.

[g] Because the relative contributions of emissions from each source to the total budget are not independent of each other (i.e., if one source is at the lower end of its estimated range, another may be at the higher), the ranges cannot be summed.

[h] Lassey et al., 2007.

[i] Based on change from pre-industrial to present as estimated by Röckmann et al., 2003; assuming that pre-industrial emissions are primarily natural.

[j] Mean value for anthropogenic emissions from Wuebbles and Hayhoe, 2002; natural emissions from this work.

[k] Range in total anthropogenic and natural emissions from Denman et al., 2007, and references therein.

[l] Estimates of anthropogenic emissions from Denman et al., 2007; natural emissions from this work.

[m] Observed tropospheric values from Rahn and Wahlen, 2000, and references therein.

ES.2.1 Wetlands

Wetlands are ecosystems in which saturation with water is the dominant factor controlling soil development and the species of plants and animals that occur. Covering about 5 percent of the Earth's surface, they are concentrated in the high latitudes, where frozen soils can inhibit water drainage, and in the tropics, where precipitation rates are high. Bacteria in the moist, anoxic (oxygen-free) wetland soil produce CH_4 as they decompose dead plant material, making wetlands an important CH_4 source. The opposite is true for N_2O. Although bacteria found in wetlands do produce N_2O, flooded conditions tend to favor bacteria that consume N_2O and produce nitrogen gas (N_2).

Emissions of CH_4 and N_2O from wetlands to the atmosphere are a small residual of the much larger amounts produced and consumed in wetland soils. The different types of bacteria in wetlands that produce and consume these gases are affected differently by environmental factors (e.g., temperature, water level, and organic matter supply and characteristics). Therefore, a relatively small environmental change can result in a large change in flux by changing the balance between production and consumption.

Methane

Current Emissions Estimates

The earlier version of this report (U.S. EPA, 1993) estimated total emissions to be 109 Tg CH_4/yr, including 38 Tg CH_4/yr from high latitude wetlands, 5 Tg CH_4/yr from temperate wetlands, and 66 Tg CH_4/yr from tropical wetlands. The 1993 report extrapolated emissions based on measurements of actual gas flux from wetlands, however, so that only a relatively small number of sites represented these diverse ecosystems. Measurements have shown that gas fluxes are highly variable over time (e.g., from day to day, week to week, and year to year). Fluxes also vary from place to place, even within the same wetland. Although there are clear seasonal changes as well as differences between wetland types, the high variability makes large-scale estimates difficult. Average emissions therefore have large uncertainty estimates. High variability occurs because many small-scale factors combine to influence fluxes and small environmental differences can cause large differences in flux. Variability is also high because of the many ways emissions can occur. Bubbling, for example, only happens sporadically but can release large amounts of gas.

In recent years, more sophisticated models have emerged for estimating emissions from wetlands. There are still substantial uncertainties attached to emissions estimates, but using models to calculate emissions also allows estimation of fluxes under changed environmental or climate conditions. The emissions estimates in this report (see Table ES-1) were derived by taking a simple average of the many estimates that have been made since 2004. Flux estimates for high latitude wetlands range from 24 to 72 Tg CH_4/yr, with an average of 43 Tg CH_4/yr. Reported emissions from tropical wetlands range from 81 to 206 Tg CH_4/yr, with an average of 128 Tg CH_4/yr. Overall, these estimates reflect an increase over the figures in the 1993 report, although uncertainties are still quite high. Although the 1993 report suggested that emissions from the tropical latitudes made the greatest contribution to global fluxes, the recent numbers have increased their importance from roughly 61 percent to about 75 percent of the total CH_4 emissions from wetlands worldwide.

Future Emissions Scenarios

Changes in land use and climate will affect CH_4 emissions from wetlands, with the potential for both large increases and large decreases. At high latitudes, changes in climate are thought to be the major factors driving changes in CH_4 emissions. For example, models using altered temperatures and rainfall suggest that emissions from northern wetlands could double by the end of the 21st century. In the tropics, changes in land use, such as draining or filling wetlands for other uses, are believed to be the major driver of change.

Models suggest that sulfur deposited in wetlands by acid rain may decrease CH_4 flux. Changes in wetland plants (for example, in the species present or in their growth rate) can affect emission pathways (movement through soil layers, bubbling, or movement through plants), as well as the quality and quantity of organic material available to be decomposed.

Nitrous Oxide

The available research indicates that wetlands are a negligible source of N_2O. There is some evidence that they may be a small sink (i.e., removing N_2O from the atmosphere) but no global estimates have been made.

If water levels in wetlands drop significantly under altered rainfall patterns, it is possible that these systems may more closely resemble upland soils and may therefore emit N_2O.

ES.2.2 Upland Soils and Riparian Zones

Upland soils are well-aerated, not water-saturated, and generally oxic (that is, containing oxygen), with dry soil conditions. These conditions favor microbial processes that make these soils a sink for CH_4 and a source of N_2O. Natural sources include upland soils associated with forests and grasslands under natural vegetation, but not agricultural lands.

Riparian zones, located at the interface of terrestrial and aquatic environments, are often permanently wet and rich in organic matter, with saturated soil conditions and microbially available carbon that contribute to higher rates of production of N_2O than dry upland soils.

Many interrelated factors determine both the magnitude of emissions of N_2O from upland and riparian soils and the sink strength for CH_4. As the carbon and nitrogen cycles in soils are linked, changes in nitrogen and carbon availability strongly influence the rate of emission or sequestration. Recent studies have found that soil organic carbon content, vegetation type, soil pH, bulk density, and drainage are the major factors influencing N_2O emissions. The strength of soil as a sink for CH_4 depends on oxidation by methanotrophic (methane-using) microbes in the soil, and therefore is influenced by environmental factors that control this oxidation rate. The primary factor is soil diffusivity, which controls the amount of CH_4 transferred into the soil and, therefore, its availability to methanotrophs.

Both upland soils and riparian soils have been significantly impacted by human activities. The arable lands composed of dry upland soils have been cleared for agricultural use, which is responsible for an estimated 80 percent of anthropogenic emissions of N_2O through soil emissions, biomass burning, and animal production. Riparian zones have been significantly impacted by agricultural activities as well. Riparian buffer zones serve as sites for nitrate removal from agricultural runoff, and are often loaded with high levels of nitrogen.

Methane

Current Emissions Estimates

CH_4 sink strength of soils under natural vegetation (including upland and riparian soils) is estimated at 30 Tg CH_4/yr. Process-level (bottom-up) methods of estimating CH_4 budgets (i.e., the balance of sources and sinks) contain significant uncertainties due to the aggregation of local measurements, taken on short time scales and with large spatial variability. While recent strides have been made in collecting and analyzing emissions measurements and the source strength of tropical soils has been characterized, there still exist a lack of field measurements and significant model uncertainties.

Future Emissions Scenarios

Future CH_4 oxidation by soils will depend on the changing human activities on these soils, as well as on climate patterns that are shifting as a result of global climate change. Clearing land for agricultural use has been shown to lead to a decreased capacity for CH_4 oxidation, for example. Global climate models show patterns of temperature and precipitation changes worldwide. As soil moisture is a key determinant of the microbial processes that consume CH_4, these shifting climate patterns will determine the fluxes of CH_4 into the future.

Nitrous Oxide

Current Emissions Estimates

Based on the available data, emissions of N_2O from soils under natural vegetation (including upland and riparian soils) are estimated at 6.6 Tg N/yr.

Many microbiological, chemical, and physical parameters affect N_2O emissions, and complex interactions among these factors make extrapolating global emissions budgets difficult and uncertain. Further, the vast majority of studies in the past have focused on N_2O emissions from agricultural, not natural, soil sources. Since the publication of the AR4, the number of N_2O emissions measurements has been increasing steadily, allowing for improvements in emission models and budgets. However, while recent strides have been made in collecting and analyzing emissions measurements and the source strength of tropical soils has been characterized, there still exist a lack of field measurements and significant model uncertainties.

Future Emissions Scenarios

As with CH_4, future N_2O emissions will depend on changing human activities and climate patterns. Clearing land for agricultural use has been shown to lead to increased N_2O emissions, for example. Because soil moisture is a key determinant of the microbial processes that consume or produce N_2O, shifts in global precipitation and temperature patterns will affect N_2O fluxes in the future.

ES.2.3 Oceans, Estuaries, and Rivers

In water bodies, CH_4 and N_2O are produced by microbial processes that occur both in the water column and in sediments. Ultimately these gases can enter the atmosphere. This report considers a range of aquatic sources, including the deep waters of the open ocean, shallower coastal waters (i.e., on the continental shelves), freshwater rivers, and estuaries where fresh and salt waters mix.

Methane

Sampling conducted in the 1960s and 1970s found that in general, surface aquatic waters are relatively small sources of CH_4 to the atmosphere. Methane production is greater in areas under freshwater and in shallow waters with highly organic sediments. In the open ocean, enhanced CH_4 production and flux can be found in upwelling areas, which are areas where the prevailing winds and currents bring nutrient-rich deep water to the ocean surface. Upwelling areas tend to have higher rates of primary productivity, which in turn leads to more organic material falling to depth, depleting oxygen levels and creating favorable conditions for methane-producing bacteria.

Current Emissions Estimates

CH_4 fluxes from water bodies are typically calculated from surface dissolved concentrations and wind speeds. Because the global flux of CH_4 from oceans, estuaries, and rivers is relatively small, these sources have not been the focus of extensive research, and the available data have geographic and seasonal limitations that add considerable uncertainty to any overall estimates. For example, no data are available for tropical latitudes or upwelling zones.

Open ocean

Open ocean emissions are low and dispersed over large areas, and thus they are difficult to resolve with techniques such as inverse modeling that use changes in atmospheric concentrations to estimate flux. The most recent estimates for the open ocean fall into two groups, with some estimates of less than 1 Tg CH_4/yr and several others around 4 Tg CH_4/yr. For this report an estimate was derived by calculating a simple average of 1.8 Tg CH_4/yr.

Coastal ocean areas

Emissions from the continental shelves are somewhat higher than those from the open ocean, even though these environments cover a much smaller area. This difference likely reflects greater organic inputs and an increase in sedimentary contributions. An average of recent estimates gives a total flux of 5.5 Tg CH_4/yr.

Estuaries and rivers

Estuaries and rivers cover limited areas, yet they contain much biological activity. They are also sites of active mixing, enabling CH_4 produced in adjacent wetlands and shallow-water environments to be rapidly released to the atmosphere. Published global emissions estimates from estuaries and rivers are sparse. Averaging the available estimates for estuaries and adding the only available estimate for rivers results in a total flux of 1.85 Tg CH_4/yr.

Overall, natural CH_4 emissions from oceans, estuaries, and rivers are estimated at 9.1 Tg CH_4/yr (see Table ES-2). Uncertainties are due to sparse data, poor habitat coverage, and lack of any tropical or southern latitude sampling. It is, however, very similar to estimates made since the mid-1970s (10 to 15 Tg CH_4/yr). Although better flux estimates would improve confidence in emissions, it is unlikely that they would change global estimates by more than a few Tg, as natural emissions from oceans, estuaries, and rivers represent only about 2 percent of the total global CH_4 emissions to the atmosphere every year.

Table ES-2. Natural Emissions of CH_4 From Oceans, Estuaries, and Rivers

	Annual Emissions, Tg CH_4/yr	Percent of Total Emissions
Open ocean	1.8	20%
Continental shelves	5.5	60%
Estuaries and rivers	1.85	20%
Total	**9.1**	

Future Emissions Scenarios

Natural emissions of CH_4 from oceans, estuaries, and rivers are expected to remain largely unchanged in the future.

Nitrous Oxide

The oceans are believed to be one of the largest natural sources of N_2O emissions. Estuaries and rivers also contribute N_2O to the atmosphere; however, emissions of N_2O from these other aquatic environments are typically classified as anthropogenic because the majority of nitrogen entering these systems is believed to be associated with human activities such as agriculture.

Current Emissions Estimates

Open ocean

Published estimates of open ocean fluxes generally range from 3 to 6 Tg N/yr. For example, the AR4 estimates natural emissions from oceans at 3.8 Tg N/yr, with a range of 1.8 to 5.8 Tg N/yr. This report combines several recent estimates to calculate an open ocean N_2O flux of 3.2 Tg N/yr, consistent with the AR4 estimate. The most significant recent development in open ocean emissions estimates has been a better understanding of the geographic distribution of fluxes. Earlier reports calculated that the ocean area from 30^{o}S to 90^{o}S made the largest contribution to global emissions (about 45 percent of the total). More recent work has decreased this flux estimate, and inverse modeling results suggests that this region may contribute as little as 7 percent to the global total.

Coastal ocean areas

Because continental shelves receive drainage from rivers and estuaries, they are impacted by humans. Several approaches have been used to estimate emissions, and published estimates vary by about an order of magnitude. By combining these estimates with recent models of natural and anthropogenic nitrogen export from rivers and estuaries, this report estimates that the flux of natural N_2O from the continental shelves is 1.5 Tg N/yr. Enhanced emissions are expected in upwelling zones; however, exact estimates are complicated because upwelling intensity can vary over time and space. Currently, regional/short-term upwelling estimates do not agree with global/annual flux estimates. A simple average of reported global fluxes from upwelling zones is 0.4 Tg N/yr. The estimates for both continental shelves and upwelling areas have substantial uncertainties, but these are unlikely to change estimates by more than 1-2 TgN/yr.

Estuaries and rivers

Estuaries and rivers are highly impacted by human activities and the corresponding changes in continental nitrogen budgets. The AR4 estimates N_2O emissions of 1.7 Tg N/yr from coasts, estuaries, and rivers (with a range of 0.5 to 2.9 Tg N/yr), and assumes that these emissions are entirely anthropogenic. Based on published models, we estimate that the flux of natural N_2O from estuaries is approximately 0.24 Tg N/yr and the natural flux from rivers is 0.09 Tg N/yr, for a total of 0.33 Tg N/yr.

Together, the estimated natural N_2O fluxes from oceans, estuaries, and rivers total 5.4 Tg N/yr (see Table ES-3). This figure is at the upper range in uncertainty that the AR4 predicts for oceans, estuaries, and rivers (5.8 TgN/yr); however, the AR4 assumes that all N_2O from coasts, estuaries, and rivers reflects anthropogenic sources only. If total global N_2O emissions are 18.8 Tg N/yr (Table ES-1), then natural emissions from these environments contribute about 29 percent of all N_2O emissions worldwide.

Table ES-3. Natural Emissions of N_2O From Oceans, Estuaries, and Rivers

	Annual Emissions, Tg N/yr	Percent of Total Emissions
Open ocean	3.2	59%
Continental shelves	1.5	28%
Upwelling zones	0.4	7%
Estuaries	0.2	4%
Rivers	0.1	2%
Total	**5.4**	

Future Emissions Scenarios

Like CH_4, natural emissions of N_2O from oceans, estuaries, and rivers are expected to remain largely unchanged. Estimates should become more accurate, however, as the accumulating database of atmospheric N_2O measurements makes it possible to use inverse modeling techniques to determine emissions on smaller time and spatial scales. Greater precision is important because emissions change seasonally and some sources (e.g., upwelling areas) are highly episodic and occur only over relatively small areas.

Overall, it is not expected that possible changes in oceanic emissions of N_2O will greatly affect climate policy. While ocean N_2O emissions do make a significant contribution to global emissions, most of these emissions are from the open ocean and are less susceptible to anthropogenic impacts. Based on the current understanding of emissions, the major controls are fundamental physical oceanic properties (e.g., wind parameters and ocean mixing) that are not easily influenced by human activities.

ES.2.4 Permafrost

Permafrost is soil, sediment, or rock that is continuously frozen (temperature < 0°C) for at least two consecutive years. Permafrost is widespread and nearly continuous in the arctic, but also exists intermittently in the sub-arctic and boreal regions, and at high elevation. EPA's 1993 report included permafrost as a natural source of CH_4, because early results were emerging on CH_4 frozen within permafrost which could be released from the permafrost as it melts.

Methane

Emissions estimates are based on measured concentrations of CH_4 in permafrost and estimates of contemporary permafrost degradation rates. Current CH_4 releases from permafrost are estimated to be 0 to 1 Tg CH_4/yr. The AR4 does not include permafrost as a natural source of CH_4.

There is now strong evidence that permafrost is melting, and that a substantial fraction of permafrost existing now will be melted within the next 100 years due to global climate change. However, it now also seems clear that this permafrost melting will be only a small direct source of CH_4. CH_4 concentrations in permafrost are not high, and as CH_4 is released from melting permafrost, it must pass through the overlying thawed soil before reaching the atmosphere. During this transport, some or most of the CH_4 will be oxidized to carbon dioxide (CO_2) before reaching the atmosphere.

Indirectly, however, thawing permafrost is already impacting CH_4 emissions from other natural sources, particularly lakes and wetlands. Permafrost can contain ice wedges, which are lenses of frozen water that can be up to several meters thick. As permafrost thaws and ice wedges melt, this water can sometimes drain away, leading to ground subsidence or collapse, which in turn can alter drainage patterns. In this process, known as thermokarst erosion, lakes and wetlands can form or can dry up. This process affects CH_4 emission rates from high latitude lakes and wetlands.

Nitrous oxide

N_2O concentrations are estimated to be about 1,000 times smaller than CH_4, although few studies have measured them, and global emissions of N_2O from permafrost are considered negligible. The AR4 does not include permafrost as a natural source of N_2O. Because N_2O concentrations in permafrost are very low, little N_2O is likely to be released on melting.

ES.2.5 Lakes

Lakes and ponds are naturally formed permanent water bodies contained on a body of land. This source category includes natural freshwater lakes but excludes impoundments and reservoirs (water bodies formed by dams), as greenhouse gas emissions from impoundments, reservoirs, and other engineering works are considered to be anthropogenic.

Lakes contribute to both CH_4 and N_2O global emissions, although analysis of this source has been limited to date. CH_4 is produced by the activity of methane-generating bacteria in anoxic sediments, while N_2O is produced by microbial activity in sediments and water as an intermediate product of both an aerobic process called nitrification and an anaerobic process called denitrification.

Methane

CH_4 production rates depend on temperature, organic matter availability (food for the bacteria), and isolation from oxygen; these factors are influenced by climate, lake size and depth, and productivity of microscopic and macroscopic plants and animals, which create organic matter for CH_4 production when they die and sink to the bottom. There are four pathways for CH_4 emissions from lakes: bubbling, diffusion, plant-mediated transport, and seasonal overturning. Bubbling has been determined to be the dominant pathway for CH_4 flux, accounting for more than 90 percent of CH_4 emissions from lakes. Wind speed is an important control on gas exchange between a lake and the atmosphere. Flux rates by all pathways generally increase with increasing wind speed.

Current Emissions Estimates

Based on recent estimates, lakes emit approximately 30 Tg CH_4 to the atmosphere per year. One key uncertainty involves the total surface area of lakes and ponds. The number and total area of large lakes is well known, but the number and total area of small lakes and ponds is not. A recently published estimate suggests that there are about 300 million natural lakes and ponds worldwide, 90 percent of which are smaller than 1 hectare (0.01 km^2). Lakes smaller than 1 km^2 constitute about 40 percent of the total global lake surface area. Because small lakes and ponds generally emit more CH_4 per unit area than large lakes, uncertainties about total surface area are a major factor in the overall uncertainty of the estimate.

Future Emissions Scenarios

Climate warming impacts on permafrost and the development of thermokarst lakes could substantially affect future CH_4 emissions from lakes. It is estimated that emissions from lakes north of 45°N will eventually decrease, due to lake area loss and permafrost thaw. Before this long-term decline, though, would come a period of increased CH_4 emissions associated with thermokarst lake development in the zone of continuous permafrost. CH_4 emission rates from northern lakes could rise as high as 50 to 100 Tg CH_4/yr during this transitional period, which would last hundreds of years.

Nitrous Oxide

Because nitrification and denitrification are highly sensitive to oxygen availability, oxygen concentrations are an important factor controlling the balance between the two processes. Lake oxygen concentration is affected by water temperature, water depth, and the rate at which oxygen is consumed by organisms living in lake water and sediments. The amount of nitrogen available as ammonium (for nitrification) and nitrate (for denitrification) is also an important control on N_2O production.

Current Emissions Estimates

Lakes are generally considered a weak source of N_2O to the atmosphere (estimated at 0.004-0.04 Tg N_2O/yr). Accordingly, few data have been collected. Global emissions from lakes are likely to be much smaller than emissions from other natural N_2O sources such as soils, oceans, and estuaries.

Future Emissions Scenarios

No estimates of future N_2O emissions from lakes have been published. Increased nitrogen loading and increased temperatures may cause an increase in N_2O fluxes from lakes, but total N_2O flux from lakes is likely to remain a very small fraction of total global N_2O emissions from natural sources.

ES.2.6 Gas Hydrates

Gas hydrates are ice-like crystals formed between water and a gas molecule under high pressure and ambient temperatures. Gas hydrates can store large amounts of the gases that they trap, and are stable within a specific range of temperature and pressure known as the hydrate stability zone. Large quantities of CH_4 are currently trapped in hydrate form, occurring mainly on continental shelves and to a lesser extent below permafrost regions.

Current Emissions Estimates

Under current conditions, the CH_4 emissions from gas hydrates are small (estimated at 2 to 9 Tg CH_4/yr); however, the potential for significant CH_4 release from gas hydrates warrants close examination of this source. A significant fraction, if not all, of these emissions are expected to be oxidized in the ocean water column.

Since 1993, there has been limited discussion of the current flux of CH_4 from gas hydrate reservoirs. Oceanic and onshore continental reserves are believed to be stable at present, which means that they are not currently emitting CH_4. Offshore continental shelf reserves are currently unstable, however, and are believed to emit CH_4. Estimates assume that the CH_4 being liberated from the gas hydrate form is released into the atmosphere. It is possible, however, that some or all of this gas is not actually emitted to the atmosphere—that, instead, it is oxidized or absorbed within the sediment or dissolved into the water column.

Future Emissions Scenarios

Due to their proximity to the Earth's surface (< 2,000 meters) and the sensitivity of the hydrate stability zone, gas hydrates will likely be affected by climate change. Pressure on hydrates is expected to change as a result of sea level rise and the melting of polar ice caps; however, temperature changes are likely to have a far more significant effect. CH_4 emissions from this source are likely to increase as temperature rises. Based on recent research, it is estimated that the increase in methane emissions due to an increase in ocean temperatures may be sufficient to overcome oxidation in the water column and result in significant atmospheric methane emissions. The magnitude of the methane emissions expected to reach the atmosphere due to release from methane hydrates upon ocean warming is, however, uncertain.

ES.2.7 Terrestrial and Marine Geologic Sources of Methane

CH_4 and other hydrocarbons can seep naturally from geologic sources deep within the Earth's crust. Some geologic CH_4 emissions are produced via what is known as macroseepage, which includes relatively large localized emissions from identified geologic features and events such as mud volcanoes and localized vents. Emissions can also result from diffuse soil exhalation or degassing in volcanically active or other geothermal regions, and from microseepage in petroliferous or hydrocarbon-containing sedimentary basins. Sources include both marine (underwater) and terrestrial (land-based) faults.

Current Emissions Estimates

Previous estimates of natural sources have either ignored this source or only evaluated "traditional" but actually minor sources such as high temperature magma-producing volcanoes. More recent estimates include emissions from mud volcanoes, other macroseepage locations, terrestrial microseepage, and submarine seeps.

Submarine estimates are extremely uncertain, particularly when estimating the proportion of emissions that are absorbed by ocean water before reaching the surface. In contrast, estimates of onshore emissions can be based on direct measurements and standard emission factor concepts applied to point sources (for individual features such as mud volcanoes) and more diffuse area sources (for microseepage). "Bottom-up" emissions estimates for both marine and terrestrial sources generally lie in the range of 32 to 74 Tg CH_4/yr. This range largely reflects uncertainty in estimating both the global number of sources and the proportion of emissions that actually reach the atmosphere, rather than being absorbed by ocean water. Recent isotopic constraints on the budget suggest a narrower range of 42 to 64 Tg CH_4/yr, based on the total burden of "fossil" (radiocarbon-free) methane in the atmosphere.

Future Emissions Scenarios

Relatively few climate- or human-related factors are believed to be capable of influencing emissions of CH_4 from geologic sources. Some reports suggest decreased emissions associated with large-scale extraction of oil and gas, and increased emissions following deglaciation events and the corresponding increase in seismic activity (i.e., post-glacial rebound). While geologic CH_4 emissions have almost certainly changed in the past and are likely to continue to change in the future, these mechanisms are too speculative to use as a basis to estimate even the potential direction of future changes in geologic CH_4 emissions.

ES.2.8 Wildfires

Wildfires are fires in forests, grasslands, savannas, and shrublands. They can either be ignited by lightning strikes or started accidentally by humans, but do not include deliberate controlled burns for land-clearing activities. As they burn, wildfires release a number of greenhouse gases, particulates, and other air pollutants. When combustion is complete—for example, in dominantly flaming fires—the carbon in biomass is generally converted to CO_2 and the nitrogen is converted to oxidized forms such as N_2O. When combustion is incomplete, particularly in smoldering fires, some carbon is released in the form of carbon monoxide (CO) and CH_4.

Although emissions from wildfires may be virtually indistinguishable from controlled burns, an important distinction must be made between natural fires (induced by lightning or accidentally started by humans) and anthropogenic fires (deliberately human-initiated). Almost 90 percent of all biomass burning is considered to be deliberate or planned anthropogenic burning. Much of it occurs in the tropics, where savanna and forest fires are driven by land clearing for agriculture and the need for fuelwood. Prescribed burning for forest management and agricultural waste burning is also prevalent in temperate-boreal regions such as the boreal forests of Canada and the temperate forests of the eastern U.S.

Methane

Current Emissions Estimates

Wildfire emissions of CH_4 are estimated to range from 2 to 5 Tg per year. This range depends on the frequency and strength of wildfires, which in turn are determined by a number of factors, including type of vegetation burned, influences from weather (e.g., wind, humidity, temperature) and climate (e.g., large-scale climatic patterns such as El Niño), and influences from humans (e.g., settlement, transportation, and recreation patterns).

As noted above, it is extremely difficult to distinguish between the burned areas from natural wildfires and those from anthropogenic fires, which makes it difficult to quantify wildfire CH_4 emissions relative to the global total from all biomass burning. Estimates of wildfire CH_4 emissions are currently based on the assumption that about 10 percent of global biomass burning is natural, although this proportion is likely to vary from year to year.

Future Emissions Scenarios

Future climate change is likely to lead to enhanced frequency of weather conditions associated with high wildfire risks in many regions of the world. Climate change could affect multiple elements of wildfires, including fire behavior, ignition, fire management, and vegetation fuels. The complex interactions between each of these factors will determine future spatial and temporal distribution of wildfires and their emissions.

Currently, no scenarios for future CH_4 emissions from global wildfires exist in the literature. Efforts are, however, directed toward developing models that can predict or forecast wildfire events and can therefore be used to estimate emissions.

Nitrous Oxide

Current Emissions Estimates

N_2O emissions depend not only on the amount of biomass burned, but also on the nitrogen content of this biomass and the type of fire (smoldering versus flaming), which can vary from one ecosystem to another. Based on the limited emission factors available, EPA estimates global wildfire N_2O emissions to be approximately 0.1 Tg N/yr, although no reference for this value is available in the peer-reviewed literature. Given the methodological problems associated with estimating the amount of biomass burned in wildfires, a valid statistical error analysis of the emission estimates cannot be performed.

Future Emissions Scenarios

No scenarios for future N_2O emissions from global wildfires exist in the literature.

ES.2.9 Vegetation

Plants have long been recognized as important conduits for CH_4 emissions, transporting CH_4 from anaerobic soils and sediments to the atmosphere. However, it is only recently that plants themselves have been considered a possible source of CH_4 production. In 2006, it was reported that plants emit CH_4 through an unidentified process under aerobic conditions, and that this previously unrecognized source could add up to as much as 62 to 236 Tg CH_4/yr, or 10 to 40 percent of global CH_4 emissions. A significant plant CH_4 source could help explain a number of gaps in the understanding of current and past global CH_4 budgets, including an apparent large unidentified CH_4 source in the tropics.

Current Emissions Estimates

The initial estimate of the size of a possible plant CH_4 source has since been revised downward in a number of analyses that have either scaled emission rates measured in the laboratory by estimates of global plant production ("bottom-up" estimates) or worked backward from global budgets to determine how large a plant CH_4 source could be reconciled with current estimates of other CH_4 sources ("top-down" estimates). The range of greatest agreement among these estimates is about 20 to 60 Tg CH_4/yr. However, few studies have attempted to measure direct CH_4 emissions from plants, and those reports include a finding of no significant emissions. Given this finding and the uncertainties regarding the underlying mechanism, a best estimate of global plant emissions must also include the possibility of zero emissions—i.e., that plants are in fact not a direct source of CH_4.

Future Emissions Scenarios

The recently proposed aerobic plant CH_4 source has not yet been incorporated into simulations of future CH_4 emissions. However, future plant emissions would likely depend on changes in the distribution of different vegetation types, as well as changes in environmental factors that might control emission rates. Current estimates attribute 35 to 50 percent of global plant emissions to tropical forests, with the second largest source, tropical savanna and grasslands, contributing about 20 percent. These estimates suggest that future plant emissions will depend largely on changes in climate and land use in the tropics.

ES.2.10 Terrestrial Arthropods and Wild Animals

Termites and other terrestrial arthropods produce CH_4 as a result of microbial degradation of ingested organic matter. CH_4 is also produced by enteric fermentation, a normal digestive process that occurs in ruminant animals such as bison, deer, elk, mountain goats, and sheep, as well as in some smaller rodent species. In the 1993 report, EPA cited termites as a contributor to natural CH_4 emissions, but did not discuss this source. It also did not consider contributions from any other terrestrial arthropods or from enteric fermentation in animals. Note that enteric fermentation also occurs in cattle and other domesticated ruminants; however, emissions from livestock are considered anthropogenic, so this report estimates emissions from wild animals only.

Current Emissions Estimates

In the years since the publication of the 1993 report, additional investigation of CH_4 emissions from termites has resulted in more refined estimates of emissions from the various termite species, and has suggested that some CH_4 may be oxidized in termite mounds prior to atmospheric release. The factors that determine the magnitude of emissions of CH_4 from terrestrial arthropods include the species of arthropod, including the specific type of termite. The highest rates of CH_4 are produced by arthropods with methanogenic (methane-producing) bacteria, which are found in many species of termites. Other terrestrial arthropods have been studied to assess whether they generate CH_4 and should be included in any estimates of global emissions. Based on this new research, termites and other terrestrial arthropods continue to be a small but not insignificant contributor to global CH_4 emissions, producing an estimated 2 to 22 Tg CH_4 per year.

Estimates of emissions from wild animals range from 2 to 15 Tg CH_4/yr.

Future Emissions Scenarios

Emissions from terrestrial arthropods (including termites) and wild animals are not expected to change substantially in the future. Changes to land use, which alter the type of plants available for wild ruminants, could affect the diets of these animals and subsequently their rate of enteric fermentation. As human activity encroaches on wildlife ecosystems, wild animal populations will likely decrease due to habitat unavailability. The habitats for terrestrial arthropods and wild animals are also linked to climate effects, resulting in shifting ecosystems (e.g., in more northern environments) or drought, which are likely to decrease populations. Currently, no scenarios for future CH_4 emissions from this source exist in the literature.

ES.3 Future Needs

It continues to be difficult to estimate contributions from natural sources, and uncertainties can be large, as evidenced by the large ranges associated with the emissions estimates. Additional research focused on improving our understanding of the processes that result in CH_4 and N_2O emissions should improve current flux estimates and help refine future estimates under altered environmental conditions. High uncertainty in some sources is a result of a lack of basic data – flux measurements may be sparse from some geographic regions and/or seasons. For a number of sources such as wetlands, uncertainties are high in part because these are highly dynamic systems that respond to short-term climate and weather variability with changed emissions. This source of uncertainty will always be present. A number of sources currently rely on inventory-type data to extrapolate small-scale measurements. While this is reasonable for some sources (for example, the number of mud volcanoes is unlikely to change quickly or drastically), this means that they are largely static estimates. Even if modeled, these flux estimates will be limited by the spatial and temporal resolution of the data used for their extrapolation. Reliance on inventory or long-term average data also means that it is difficult to fully take advantage of the accumulating data base of atmospheric mixing ratios and isotopic signatures. These data are highly dynamic and this short-term variability is a crucial part of their utility in inverse modeling approaches. These techniques have proven that they can both help to constrain “bottom up” estimates and provide a way to integrate highly variable natural systems.

For wetlands, the major natural source contributing to CH_4 emissions, research in tropical areas remains sparse and incomplete. Increased work linking emissions to environmental controls, long-term studies to capture seasonality and inter-annual variability, and work on the importance of episodic emissions will help resolve difficulties in modeling these systems. In addition, more work should examine the relationships between CH_4 flux and net primary productivity (the rate at which biomass is produced, for example by photosynthesis), since these relationships appear to be habitat-specific. Because emissions to the atmosphere are a function of the competing processes of CH_4 production and consumption, both processes and their responses to environmental controls must be understood across the landscape. Episodic emissions, which may release a sizeable fraction of annual flux, remain difficult to measure and include in models. Failure to adequately incorporate these fluxes, however, can yield inaccurate and misleading results.

For upland soils and riparian zones, the major natural source contributing to N_2O emissions, more field measurements and improvements in global emissions models are needed. While field measurements of N_2O have increased steadily in the past several years, coverage of global vegetation zones remains incomplete. More measurement data are needed, especially for the dry tropical forest, savanna, tundra, and temperate ecosystems not affected by nitrogen deposition. These measurements should be carried out over extended periods, to help improve our understanding of the complex factors that impact emissions as well as to assess natural variability.

There are many additional areas where research would help improve flux estimates. These are discussed in more detail in the source-specific chapters, but we briefly list a number of them here, where uncertainties are notably high. They include:

- Data from tropical and southern latitude oceans, estuaries, and rivers, as well as estimates of upwelling sources.
- Improvements to permafrost models to account for lateral water movement, dynamic vegetation algorithms, and detailed soil physics.
- Data to quantify lake fluxes, particularly in the Arctic, boreal region, and tropics.
- Better quantification of CH_4 reserves stored as gas hydrates, as well as better estimation of the rate of CH_4 absorption into oceans and CH_4 oxidation in the water column.
- Rates of CH_4 from seeps and mud volcanoes oxidized in sediments, as well as better quantification of the source locations (e.g., number of mud volcanoes, frequency of eruption).
- Activity data for wildfires, including area and amount of biomass, burned area estimates associated with natural wildfires, and additional research on emissions related to different “fuels” (i.e., different types of vegetation).
- Confirmation or rejection of vegetation as a source of CH_4.
- Research that better quantifies the oxidation of CH_4 through termite mounds, confirmation of CH_4 from non-termite terrestrial arthropods, and activity data for arthropods and wild animals.

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Chapter 1. Introduction

Methane (CH_4) and nitrous oxide (N_2O) are important greenhouse gases, present in the atmosphere, that are produced in part by natural sources. Greenhouse gases prevent heat emitted by the Earth from escaping to space (Figure 1-1). The natural greenhouse effect is necessary to life as we know it. It maintains the Earth's surface temperature at an average of 15ºC, 33ºC warmer than it would be otherwise (NOAA, 2007). Because greenhouse gases can absorb infrared radiation, changes in their atmospheric concentrations can alter the energy balance of the climate system. Increases in greenhouse gas concentrations in the atmosphere produce a net increase in the absorption of energy by the Earth, leading to climate change such as a warming of the Earth's surface—as has been observed in recent decades (U.S. EPA, 2007).

What is climate change?

Climate change, as defined in the IPCC's Fourth Assessment Report, refers to a change in the state of the climate that can be identified (e.g., by using statistical tests) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer (Solomon et al., 2007b).

The previous version of this report (U.S. EPA, 1993) provided global estimates of current and future CH_4 emissions from natural sources. Since the release of that report, there has been significant new research on a number of previously identified sources (e.g., wetlands), newly identified potential sources (e.g., vegetation), and the contribution of N_2O from natural sources. This report provides a summary of the latest research, and presents global estimates of current emissions of both CH_4 and N_2O from natural sources, as well as global estimates of future changes in those emissions where data are available.

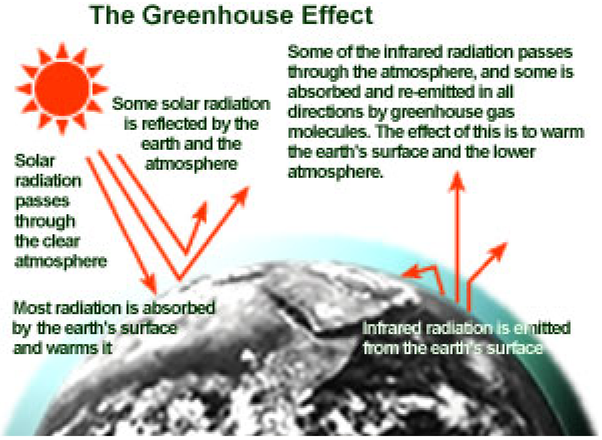

Figure 1-1. The Greenhouse Effect

1.1 Importance of Methane and Nitrous Oxide as Greenhouse Gases

Long-lived greenhouse gases such as CH_4 and N_2O are chemically stable and persist in the atmosphere over time scales of a decade (in the case of CH_4) to centuries or longer (for N_2O). For this reason, emissions of these gases have a long-term influence on climate. These gases become well-mixed throughout the atmosphere much faster than they are removed, and their global concentrations can be accurately estimated from data at a few locations (Solomon et al., 2007a).

1.1.1 Methane

The chemical lifetime of CH_4 from removal through reactions with the hydroxyl radical (OH) is estimated at 9.6 years (Folland et al., 2001). Once emitted, however, CH_4 actually remains in the atmosphere for what is known as a "perturbation lifetime" of approximately 12 years before removal and ultimate conversion to carbon dioxide (CO_2), mainly by chemical oxidation in the lower atmosphere, or troposphere (Solomon et al., 2007b). The longer perturbation lifetime of CH_4 is primarily a result of feedbacks between CH_4, OH, and its byproduct CO which is also removed by reactions with OH. Minor removal processes include reaction with chlorine in the marine boundary layer, a soil sink, and stratospheric reactions. Increasing emissions of CH_4 reduce the concentration of OH, a feedback that may increase the atmospheric lifetime of CH_4 (Solomon et al., 2007b). As OH also reacts with other short-lived pollutants including volatile organic compounds (VOCs) and tropospheric ozone, changing emissions of VOCs and ozone precursor species are also likely to affect CH_4 lifetime (Wuebbles et al., 2000).

CH_4 is one of several greenhouse gases responsible for increased radiative forcing on the climate system (see box on "Radiative forcing"). Over a period of 100 years, each molecule of CH_4 has 25 times the direct global warming potential of a molecule of CO_2 (Solomon et al., 2007b). Ice core records indicate that, over the last 650,000 years, atmospheric CH_4 concentrations have varied from lows of about 400 parts per billion (ppb) during glacial periods to highs of about 700 ppb during interglacial periods. Atmospheric CH_4 has increased by about 1,000 ppb since the beginning of the industrial era in the late 1700s, representing the fastest changes in this gas over at least the last 80,000 years. In 2005, the global average abundance of CH_4 measured by NOAA in both hemispheres was 1,774.62 ± 1.22 ppb, more than double its pre-industrial value (Forster et al., 2007).

Radiative forcing is a measure of how the energy balance of the Earth-atmosphere system is influenced when factors that affect climate are altered. Radiative forcing is usually quantified as the "rate of energy change per unit area of the globe as measured at the top of the atmosphere," and is expressed in units of watts per square meter (W/m^2). When radiative forcing from a factor or group of factors is evaluated as positive, the energy of the Earth-atmosphere system will ultimately increase, leading to a warming of the system. In contrast, for a negative radiative forcing, the energy will ultimately decrease, leading to a cooling of the system. As of 2005, atmospheric CH_4 and N_2O are the second- and third-largest contributors to radiative forcing among greenhouse gases, after CO_2 (IPCC, 2007):

CO_2	$+1.66\ W/m^2$
CH_4	$+0.48\ W/m^2$
N_2O	$+0.16\ W/m^2$

1.1.2 Nitrous Oxide

Like CH_4, N_2O is a long-lived greenhouse gas responsible for increased radiative forcing on the climate system. N_2O has an atmospheric lifetime of about 114 years, and over a 100-year period, each molecule of N_2O has a direct global warming potential 298 times that of a single molecule of CO_2 (Solomon et al., 2007b). Ice core data for N_2O have been reported extending back more than 2,000 years from the present. These data show relatively little change in mixing ratios over the first 1,800 years of this record. Since the beginning of the industrial revolution, however, N_2O levels exhibit a relatively rapid rise. Since 1998, atmospheric N_2O levels have steadily risen, reaching 319 ± 0.12 ppb in 2005 (Forster et al., 2007).

1.2 Sources of Methane and Nitrous Oxide

To understand the role of natural sources of CH_4 and N_2O, it helps to be familiar with a few key concepts that describe the movement of gases into and out of the atmosphere. The atmosphere is considered a reservoir, where each of these gases resides for a specific lifetime. Other reservoirs include oceans and soils. Material can be transferred from one reservoir into another—a process described as a flux. Fluxes into a reservoir such as the atmosphere are known as sources, while fluxes out are called sinks. Each reservoir also has an overall budget, which represents the balance sheet of all sources and sinks.

This report examines the flux of CH_4 and N_2O into the atmospheric reservoir, with a particular focus on natural sources. Because sources of CH_4 and N_2O to the atmosphere are essentially processes that release gases into the air, this report will use the term "emissions" to describe the actual movement of these gases into the atmosphere.

1.1.1 Methane

A large portion of CH_4 emissions can be linked to the biological process of anaerobic decomposition, in which bacteria break organic matter down in the absence of oxygen. Methanogens are a specialized group of microbes that break down certain molecules, such as hydrogen (H_2) and CO_2, to produce CH_4 through the process of methanogenesis. Some of this CH_4 can be partly or completely oxidized by another group of bacteria, called methanotrophs, while the remainder can ultimately enter the atmosphere. Microbial production of methane occurs in a variety of settings, some deemed natural and others attributed to anthropogenic activities. For example, methanogenesis can occur both in natural wetlands (a natural source) and in human-influenced wetlands such as rice paddies (an anthropogenic source). Methanogenesis also takes place in other water bodies, submerged sediments, landfills and waste treatment facilities, and the digestive systems of certain animals—some domesticated (an anthropogenic source) and some wild (a natural source).

Other natural sources of CH_4 include wildfires and geologic processes. Other anthropogenic sources include natural gas handling, biomass burning, and fossil fuel combustion.

Scientists use several methods to determine the relative contributions of different sources to the atmosphere (see Section 1.3 for more detail on methods). For example, the relative abundance of the three principal isotopes of carbon (stable ^{12}C, stable ^{13}C, and unstable or radioactive ^{14}C) can indicate which processes are producing CH_4. This is because microbes producing CH_4 discriminate against the heavier isotopic form, ^{13}C, resulting in CH_4 that is depleted in ^{13}C. In contrast, combustion processes (wildfires, biomass burning) do not discriminate. Fossil fuel sources of CH_4 (coal, oil, natural gas hydrates, geological sources) release ancient carbon that lacks radioactive ^{14}C, while more modern CH_4 contains ^{14}C. Information on the isotopic signature of the hydrogen in CH_4 has also been used to characterize sources. In theory, weighting individual source isotopic signatures by their fluxes and accounting for fractionation by sink processes should yield the isotopic signature of atmospheric CH_4, but the signatures of many sources overlap and signatures can change seasonally. The addition of isotopic data however, can be a powerful constraint on possible source budgets.

Methanogens are microorganisms (Archaea) that produce methane as a metabolic byproduct in anoxic conditions. Methanogens are anaerobic; most are rapidly killed by the presence of oxygen. There are over 50 described species of methanogens.

Methanotrophs are bacteria that are able to grow using methane as their only source of carbon and energy. They can grow aerobically or anaerobically and require single-carbon compounds to survive. Under aerobic conditions, they combine oxygen and methane to form formaldehyde, which is then incorporated into organic compounds.

By analyzing ice cores, scientists can compare present-day methane concentrations and sources with historical (i.e., pre-industrial) records (Chappellaz et al., 2000). This has been helpful in estimating how natural sources respond to changes in the environment before there was a significant anthropogenic input. Changes in ^{14}C isotopic ratios in ice cores can also help evaluate natural fossil CH_4 sources such as geological sources.

The total flux of CH_4 into the atmosphere from all sources is currently 566 teragrams[2] of CH_4 per year (Tg CH_4/yr), which is more than double the pre-industrial value (Solomon et al., 2007b). Based on analysis of known CH_4 sources, observed isotopic abundances, and budget modeling, the Intergovernmental Panel on Climate Change (IPCC) estimates that the significant increase in atmospheric CH_4 levels observed over the last two centuries is primarily due to increasing anthropogenic emissions of CH_4, which are currently approximately 1.5 to 2.5 times the magnitude of natural emissions (Forster et al., 2007). In this report, we reach a similar estimate by adding together the best estimates for the main

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[2] 1 teragram (Tg) equals 1×10^{12} grams or 1 million metric tons.

natural source categories, which suggest that natural sources contribute 208 Tg CH_4/yr to the atmosphere, or 37 percent of total global emissions. The remainder comes from anthropogenic sources, the largest of which are livestock, landfills, and natural gas systems (U.S. EPA, 2007).

1.1.2 Nitrous Oxide

Global production of N_2O is attributed largely to microbial processes. Bacteria produce N_2O through nitrification and denitrification, which are key processes within the natural nitrogen cycle (Figure 1-2). Nitrification is the main source of N_2O under aerobic conditions, while denitrification dominates under anoxic conditions.

In nitrification, bacteria oxidize nitrogen through a two-step aerobic process. Two groups of nitrifying bacteria are responsible: those that oxidize ammonium (NH_4) to nitrite (NO_2) and those that oxidize NO_2 to nitrate (NO_3). This multi-step process produces some N_2O as a byproduct or as an alternate product of ammonium oxidation. In denitrification, bacteria reduce oxidized inorganic forms of nitrogen. This process may form N_2O as an intermediate byproduct, or it may consume N_2O. Therefore, the process of denitrification can be either a source or a sink for this gas, depending on environmental conditions such as oxygen levels, nitrogen levels, pH, and temperature (Sorai et al., 2007; Capone, 1991).

Microbial sources and sinks of N_2O can be considered either anthropogenic or natural, depending on the setting. Anthropogenic sources of N_2O largely relate to agricultural soils, especially production of nitrogen-fixing crops and forages, the use of synthetic and manure fertilizers, and manure deposition by livestock. Natural sources reflect microbial processes in uncultivated soils, oceans and other aquatic systems, and possibly wetlands.

Other anthropogenic sources that produce N_2O include fossil fuel combustion (especially from mobile sources), industrial processes, wastewater treatment and waste combustion, and biomass burning (U.S. EPA, 2007).

Global estimates of N_2O emissions from natural sources have utilized top-down approaches that rely on atmospheric mixing ratios to estimate natural sources and sinks of N_2O (Prather et al., 2001; Crutzen et al., 2008). For example, Prather et al. (2001) estimated that the net pre-industrial flux of N_2O was 10.2 TgN/yr).

The total flux of N_2O into the atmosphere from all sources is currently estimated at 18.8 Tg per year as nitrogen (Tg N/yr), which represents an increase since the pre-industrial era (Solomon et al., 2007b). This increase primarily reflects human activities, particularly agriculture and associated land use change. The IPCC estimates that about 60 percent of all N_2O emissions come from natural sources, but individual source estimates remain subject to significant uncertainties (Forster et al., 2007). In this report, we estimate that natural sources contribute 12.1 Tg N/yr to the atmosphere, or 64 percent of the total of all emissions worldwide.

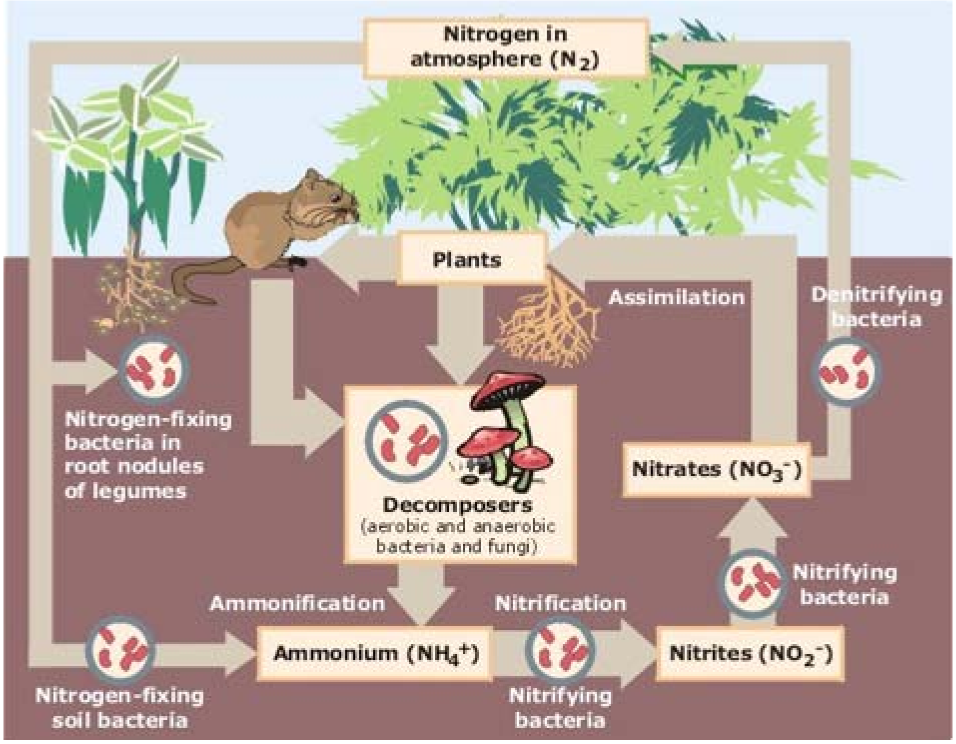

Figure 1-2. The Nitrogen Cycle

1.2 Overview of This Report

This report focuses on identifying and quantifying CH_4 and N_2O emissions from the following natural sources:

- **Wetlands.** Chapter 2 of this report discusses wetlands, which are ecosystems where saturation with water is the dominant factor controlling soil development, as well as the species of plants and animals that are present. Wetlands are transitional areas, at the interface between upland environments and aquatic systems, and are thought to cover about 5 percent of the Earth's surface. Because saturated soils create anoxic conditions, wetlands are an important natural source of CH_4, which is produced by anaerobic microbial processes. Wetlands are believed to be negligible sources of N_2O, though, and may at times act as minor sinks.
- **Upland soils and riparian zones.** Chapter 3 addresses upland and riparian soils. Upland soils are well aerated and generally oxic. These dry soil conditions favor microbial processes which make them a sink for CH_4 and a large source of N_2O. Natural sources include upland soils associated with forests and grasslands under natural vegetation, but not agricultural lands. Riparian zone soils are often permanently wet and rich in organic matter, with saturated soil conditions and microbially available carbon that contribute to higher rates of production of N_2O than dry upland soils.
- **Oceans, estuaries, and rivers.** Chapter 4 of this report considers a range of aquatic sources, including the deep waters of the open ocean, shallower coastal waters (i.e., on the continental shelves), freshwater rivers, and estuaries where fresh and salt waters mix. Microbial processes that produce CH_4 and N_2O can occur both in sediments and in the water column. The oceans are believed to be one of the two largest natural sources of N_2O to the atmosphere, as well as a minor natural source of CH_4. Continental shelf areas, estuaries, and rivers also contribute emissions of CH_4 and N_2O. These water bodies typically have higher organic inputs and nutrient levels than the

open ocean, and because they are relatively shallow, mixing is active and can transport gases produced in the sediments into near-surface water where it can be released to the atmosphere. However, there is some controversy as to how much of the N_2O emissions associated with rivers and estuaries should be counted as natural source emissions, because they are largely driven by anthropogenic contributions of nitrogen to these water bodies.

- **Permafrost.** Permafrost is soil, sediment, or rock that is continuously frozen (temperature < 0°C) for at least two consecutive years. As discussed in Chapter 5, CH_4 and N_2O can be frozen within permafrost, and thus permafrost represents a stock of CH_4 and N_2O than can be released upon thawing. Gas hydrates, which can co-occur with permafrost but which also are common in non-permafrost regions, are discussed separately in Chapter 7, "Gas Hydrates."
- **Lakes.** Chapter 6 addresses lakes and ponds, which are naturally formed permanent water bodies contained on a body of land. This report excludes impoundments and reservoirs, since gas emissions from water bodies formed by dams and other engineering works are considered to be anthropogenic. Lakes contribute to natural emissions of CH_4, but appear to be a minor source of N_2O.
- **Gas hydrates.** As described in Chapter 7, gas hydrates are ice-like crystals formed between water and gas molecules such as CH_4 under high pressure and ambient temperatures. Large quantities of CH_4 are currently trapped in hydrate form, occurring mainly on continental shelves and to a lesser extent below permafrost regions. Under current conditions, global CH_4 emissions from gas hydrates are small; however, the potential for significant CH_4 release from gas hydrates warrants close examination.
- **Terrestrial and marine geologic sources.** Chapter 8 discusses natural seeps of CH_4 and other hydrocarbons from geologic sources deep within the earth's crust. Geologic CH_4 emissions can be produced via what is known as "macroseepage," which includes relatively large localized emissions from identified geologic features and events such as mud volcanoes and localized vents. Emissions also can result from "microseepage" in volcanically active or other geothermal regions. Sources include both marine (underwater) and terrestrial (land-based) faults.
- **Wildfires.** Wildfires are fires in forests, grasslands, savannas, and shrublands. This report includes fires ignited by lightning strikes or started by humans, but not controlled burns. As Chapter 9 explains, wildfires release a number of greenhouse gases, particulates, and other air pollutants as they burn. Incomplete combustion or smoldering of biomass, consisting of both living and dead organic matter, is the primary source of emissions of CH_4 from wildfires. Wildfires also produce N_2O, with the amount produced depending on the nitrogen content of the biomass burned.
- **Vegetation.** Chapter 10 addresses direct CH_4 emissions from vegetation, including upland tropical forests and other unflooded ecosystems. It has not been previously considered a potential source of CH_4, because drier soils act as an oxidative sink for CH_4. However, recent findings suggest that such ecosystems may be a significant unrecognized source of CH_4 although the existence and magnitude of this source remains to be confirmed.
- **Terrestrial arthropods and wild animals.** Chapter 11 of this report discusses the production and emission of CH_4 by termites and other terrestrial arthropods as a result of microbial degradation of ingested organic matter, as well as CH_4 emissions caused by enteric fermentation in wild ruminant animals such as bison, deer, elk, mountain goats, and sheep, and also in some smaller rodent species.

It is important to note that there can be both ambiguity in source definitions (e.g., are small ponds in natural wetlands a wetland source or a lake source?), and a mixture of sources (e.g., co-location of permafrost, gas hydrates, and geologic sources). Field studies may include flux measurements that have contributions from more than one of the sources listed here. This is discussed further in the chapters on each source.

It is also important to keep in mind that the earth is a system of interacting components, and change often affects many components as well as their interactions. This report is organized into chapters covering natural sources by type (e.g., wetlands, lakes, oceans, gas hydrates, etc.). However, the earth is a mosaic of these different source types, the boundaries between these source types are sometimes inexact (e.g., between a wetland and the emergent vegetation of a lake margin), and system changes that affect one source can also affect one or more other sources.

The issue of methane in permafrost regions exemplifies this interconnectedness. The projected thawing of permafrost with climate warming may contribute to increased natural source methane emissions to the atmosphere. However, this is a complex system response. There is not a lot of methane frozen into permafrost (unless it is a gas hydrate formation), so permafrost thaw will not release much methane directly. The methane it does release has a reasonable probability of being oxidized as it diffuses through 1 to 100 meters of thawed soil before reaching the atmosphere (see Chapter 5, “Permafrost”). Therefore, the report concludes that permafrost thawing is not likely to be a strong methane source. However, if gas hydrates are associated with permafrost, then thawing permafrost and destabilization of these hydrates may co-occur (though they are not exactly the same thing), releasing methane, potentially in large quantities (see Chapter 7, “Gas Hydrates”). Another consideration is changes in wetland vegetation and moisture status associated with permafrost thawing; this would be an issue for some, but not all, permafrost landscapes. If the landscape gets wetter and the vegetation composition becomes more dominated by sedges, this could lead to increased methane emissions from a wet landscape - at least for years to decades; however, if the landscape gets drier (or stays relatively dry), then methane emissions would probably stay low (see Chapter 2, “Wetlands”). Finally, permafrost thaw can be associated with thermokarst erosion, which can form (or drain) lakes; these lakes can also be methane sources (See Chapter 6, “Lakes”). Each chapter of this report specifies the natural sources addressed by that chapter.

1.3 Summary of Methods

This report builds on information provided in EPA’s 1993 report (U.S. EPA, 1993) as well as the Intergovernmental Panel on Climate Change’s Fourth Assessment Report, or AR4 (Solomon et al., 2007b). The 1993 EPA report focused primarily on natural wetlands and other fossil sources (including gas hydrates and permafrost) as contributors to the global CH_4 budget, but briefly acknowledged other sources such as termites, ocean and freshwater systems, and non-wetland soils. The 1993 report did not include any estimates of these other CH_4 sources, however, nor did it address natural sources of N_2O. Although several of the major greenhouse gases occur naturally, the AR4 attributes increases in their atmospheric concentrations over the last 250 years largely to human activities. Therefore, the majority of research discussed in the AR4 focused on anthropogenic sources, and the AR4 includes only a limited assessment of natural source emissions.

Scientists use a variety of approaches to characterize emissions. These approaches generally fall into two categories: “bottom-up” calculations and “top-down” or inverse modeling. Bottom-up estimates are based on an estimate of activity (e.g., population contributing to the source) combined with an emission factor reflecting the amount of emission per unit of activity. The estimate also can include direct emission measurements from individual sources or other variables that contribute to the calculation of an emission factor (e.g., temperature, geographic location) (Olivier, 2002). Although conceptually simple, bottom-up methods contain numerous uncertainties. First, point measurements taken at a limited number of locations and times must be assumed to be representative of global emissions. These point measurements must be extrapolated to larger scales which can introduce significant error and most extrapolations are performed using inventory-type data (e.g., population size, burned area, or vegetation type) which tends to be a "snap-shot" of conditions. As data coverage improves, however, researchers are focusing more attention on the need to understand and predict temporal and spatial variations in those emissions. Such variations are particularly important for biogenic sources such as wetlands, whose emissions can vary by several orders of magnitude depending on the location, time of day, season, or year. Although these uncertainties continue to produce a range of values in the emission estimates for individual sources, bottom-up ranges also can be constrained by top-down analyses.

Inverse modeling methods use atmospheric concentration measurements, atmospheric models, and statistical tools to estimate emissions from individual sources. This method requires initial *(a priori)* emissions information distributed over time and space (Olivier, 2002). Such analyses use observed spatial and temporal changes in atmospheric mixing ratios and isotopic abundances as input to mass-balance or more sophisticated three-dimensional chemical transport models of the atmosphere. In the case of CH_4, data on abundances and isotopic ratios are usually taken from ground-based observing stations and ice core samples, although satellite observations are also being incorporated into more recent analyses (e.g., see Frankenburg et al., 2006). The isotopic composition of atmospheric CH_4 provides particularly valuable information, as it reflects the relative strength of bacterial versus nonbacterial and modern versus fossil sources of CH_4, as well as differentiating among various formation pathways (Cicerone and Oremland, 1988; Conny and Currie, 1996; Whiticar, 2000).

Mass-balance modeling approaches use spatial and regional variations in isotopic composition as well as hemispheric and global averages as input to box models. Atmospheric observations are compared with the flux-weighted composition of total emissions plus the fractionation effects of sinks, taking into account the effects of atmospheric transport. In this way, the magnitudes of individual sources as well as entire budgets have been estimated (e.g., Khalil and Rasmussen, 1983; Stevens and Engelkemeir, 1988; Cicerone and Oremland, 1988).

Three-dimensional chemical transport models in combination with knowledge of sources and sinks perform calculations that match modeled estimates of concentrations and isotopic composition with observed abundances. Because the model should ultimately agree with observations, the initial conditions can then be evaluated and changes made if needed. Uncertainties in sources and sinks can be reduced through this process and the relationships between emissions, atmospheric chemistry, and the climate system better quantified. Numerous studies (e.g., Fung et al., 1991; Hein et al., 1997) have used this approach, while others have developed new inversion methods (Brown, 1995; Kandlikar and McRae, 1995; Kandlikar, 1997; Houweling et al., 1999). These analyses, combined with multi-box and source-specific studies, produce comprehensive budgets of sources and sinks.

Bottom-up and top-down methods each have advantages and disadvantages. For example, bottom-up methods require accurate activity data and emission factors, while top-down methods require the development of models which may have many unknowns. Top-down methods can provide comprehensive coverage, but cannot easily attribute emissions to specific activities in specific regions. Inventories of anthropogenic greenhouse gas emissions typically use bottom-up methods.

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Chapter 2. Wetlands

Wetlands are ecosystems where saturation with water is the dominant factor controlling soil development and the species of plants and animals that are present (Cowardin et al., 1979). Because water saturation is a defining characteristic of wetlands, these areas are an important natural source of CH_4, which is produced by bacteria requiring oxygen-free conditions. Wetlands are believed to be a negligible source of N_2O and may at times act as a minor sink.

Researchers have known for some time that wetlands produce CH_4 (Koyama, 1963; Swain, 1973). However, interest in measuring emissions from wetlands accelerated in the mid- to late 1970s as the atmospheric importance of these releases became clear (Ehhalt, 1974; Baker-Blocker et al., 1977; Harriss and Sebacher, 1981; Harriss et al., 1982). A large database has accumulated over the last 30 years. These data were summarized for the period before 1993 in the earlier version of this report (U.S. EPA, 1993*)*. The wetlands flux review portion of that publication was published by Bartlett and Harriss (1993).

The measurement of wetland CH_4 flux remains an area of very active research and the flux database from diverse wetland types continues to grow. The focus of work, however, has moved beyond the initial phase of assessing source magnitude as understanding has increased. Most of the current work examines environmental controls and processes. Although the most recent IPCC report (AR4) does not calculate wetland CH_4 fluxes, work cited in the report estimates emissions ranging from 100 to 231 Tg CH_4/yr. If the total CH_4 flux from all sources is roughly 566 Tg CH_4/yr (see Table ES-1), then wetlands may contribute 18 to 41 percent.

Measurements of the flux of N_2O from wetlands are much sparser. Initial work demonstrated that emissions are relatively low; efforts, therefore, have focused on ecosystems that are more important globally. Estimates of the wetlands flux of N_2O are not included in the AR4.

2.1 Description of Emission Source

Wetlands are transitional areas at the interface between upland, terrestrial environments and aquatic systems. They are distinctly different from both terrestrial and aquatic environments, but depend on them both. The global area of wetlands has been estimated at 5.2 to 5.86×10^6 km^2 and they are thought to cover about 5 percent of the Earth's surface (Matthews and Fung, 1987; Prigent et al., 2007).

Although topography (the lay of the land and its elevation) is not the defining characteristic of wetlands, it is an important factor contributing to their presence, since it can control where water goes and how long it remains. The water itself may come from precipitation, subsurface flow from ground water, or surface flow from a surrounding watershed or water body such as an ocean, river, or lake. Characteristics of the water from these different types of sources can determine wetland type (for example, saline or fresh, low nutrient or high, active water flow or still and stagnant).

The presence of water in wetlands creates significant physiological problems for both plants and animals, and adaptations to it have resulted in distinctive communities. The line between wet and dry environments is often a gradual one, and water saturation may occur on a constant, seasonal, daily, or even sporadic basis and still be the dominant factor defining a landscape.

Wetlands are diverse and can be classified in many different ways. The U.S. National Wetlands Inventory uses a combination of water depth (deepwater vs. shallow water), landscape location (marine, estuarine, riverine, and lacustrine or bordering lakes), and vegetation to classify habitats. The colloquial terms "marsh," "swamp," "fen," "bog," "muskeg," and "pocosin" identify environments largely on the basis of vegetation. Wetlands are found from the tundra to the tropics and on every continent except Antarctica. In the tropics, where rainfall is strongly seasonal, many wetlands (such as varzea or flooded forests) also occur seasonally. At high latitudes, although the amount of precipitation is often relatively low, frozen soils inhibit drainage over large regions and create a landscape of abundant wetlands and shallow standing water.

Vegetation characteristics and water dynamics, used to classify wetlands, are also useful for characterizing CH_4 and N_2O emissions, because they integrate many environmental factors that affect the production of the gases. Major controls on soil conditions include organic inputs (the quantity and quality of vegetative material) and the balance between aerobic and anaerobic soil environments, which is largely controlled by the presence or absence of water.

Although some wetlands in the United States have been constructed for water processing, environmental, or management reasons, they will not be discussed here due to their human origin and ecological differences from natural systems. Riparian zones, usually defined as the interface between uplands and flowing water, occur in many forms (grassland, forest, unvegetated) and may or may not be wetlands. If they are vegetated by plant communities characteristic of water-saturated soils, they are included in this report's definition of wetlands and are addressed in this chapter. Other types of riparian zones are addressed in Chapter 3, "Upland Soils and Riparian Areas."

2.2 Factors That Influence Emissions

Both CH_4 and N_2O are produced by bacteria in wetland soils and are therefore affected by a suite of environmental variables. Emission of both gases is a function of the balance between their production and consumption, which are carried out by different functional groups of bacteria. Environmental controls may affect these groups differently, resulting in non-linear responses to small changes. For example, bacteria producing CH_4 (methanogens) have been found to be more sensitive to temperature than those oxidizing CH_4 (methylotrophs and methanotrophs). This means that a change in temperature may change the balance between production and consumption, and thus change emissions. Flux to the atmosphere is commonly a small residual of the larger amounts of the gases that are produced and consumed in the soil. This means that the potential is present for large changes in flux in response to what may appear to be minor environmental change.

Whalen (2005) recently summarized wetland biogeochemical controls on CH_4 emissions and grouped these into process-level and ecosystem-level factors.

2.2.1 Process-Level Controls

Process-level controls include organic material quality and quantity, temperature, and pH. All of these affect how rapidly and well bacteria grow. Bacterial responses to controls are frequently non-linear, as demonstrated by the classic logarithmic Q_{10} temperature response model (the reaction rate change for a $10^{o}C$ temperature change).

The presence of water inhibits the diffusion of O_2 (here water is considered an ecosystem-level control; see Section 2.2.2). Because methanogens require oxygen-free conditions to grow, soils saturated with water provide this critical condition for methanogenesis to occur. Once anaerobic conditions have been established, however, organic matter supply and temperature have been shown to be primary controls (Valentine et al., 1994; Coles and Yavitt, 2002).

Since N_2O is an intermediate product of nitrification and denitrification (see Chapter 1), controls on its atmospheric release are also complex. As for CH_4, interactions between different functional groups mean that changes in environmental parameters have multiple effects. Rates of nitrogen cycling overall are impacted by soil fertility and texture, available N (NO_3, NO_2, or NH_4), and oxygen, needed for respiration (Groffman, 1991). Davidson (1991) has proposed a conceptual model of the controls on N_2O release from soils that has been widely used. Known as the "hole-in-the-pipe," this model uses the analog of water flowing through a leaky pipe for the flow of N in soils during organic matter decomposition. The sizes of the holes in the "pipe" are analogous to the relative rates of nitrification and denitrification. In fertile soils, flow through the pipe is large, as are the "leaks." The converse is true in infertile soils, and neither gas is produced in large amounts. In dry soils, where O_2 is present, the nitrification "leak" is greater and NO, which is more oxidized than N_2O and N_2, is the dominant gas. In wetter soils, with less soil O_2, denitrification is dominant and more N_2O is produced. In very wet soils, denitrification also dominates, but proceeds all the way to the most reduced end product, N_2. Testing this model against observations from a wide range of sites suggests that it can help explain both the amount of N gases released as well as their relative proportions (Davidson and Verchot, 2000).

Reported Q_{10} temperature coefficients for methanogenesis (see Whalen, 2005, and cited references) are relatively high, indicating a strong response to temperature change by methanogens. Bacteria oxidizing CH_4 appear to have a somewhat weaker response. Although laboratory studies have suggested that optimal pHs for many methanogens and methanotrophs lie in the neutral range, many wetland soils are acidic and both functional groups appear to tolerate what may be sub-optimal conditions. Moore and Roulet (1995) suggest that pH is a secondary control on production and oxidation of CH_4.

CH_4 oxidation by bacteria occurs in a wide variety of soils and environments, including those of wetlands. Bacteria can consume CH_4 from both the soil and from the air. The uptake of atmospheric CH_4 is largely determined by its rate of diffusion into the soil and, less critically, temperature. Controls on diffusion rates in soils are physical—primarily moisture content and soil texture. Rates of CH_4 uptake vary over a much more limited range than do CH_4 emissions, which is consistent with the greater importance of physical controls. The uptake of atmospheric CH_4 largely takes place in the surface of well-drained soils such as forests rather than wetlands. The role of well-drained soils as a sink for atmospheric CH_4 is discussed in more detail in Chapter 3. Subsurface CH_4 oxidation, however, is an important process in wetlands, where it consumes a significant portion of the CH_4 produced. Understanding controls on emissions therefore requires assessing both CH_4 production and CH_4 oxidation.

Recent work has suggested that nutrient inputs (sulfur and nitrogen) may affect CH_4 emissions. These studies have focused on the atmospheric deposition of sulfate (SO_4) by acid rain and the wet and dry deposition of N. Because SO_4 may also be used by bacteria to decompose organic material, its addition can alter carbon flow pathways, reducing the energy flow through methanogenesis and therefore reducing emissions. For example, this competitive interaction and its effect on emissions has been observed in salt marshes, where natural SO_4 inputs from seawater decrease fluxes (Bartlett et al., 1987). Field experiments suggest that reductions due to atmospheric deposition may be substantial, up to 40 percent of controls (Dise and Verry, 2001; Gauci et al., 2002). Examining a gradient in SO_4 deposition, Vile et al. (2003) found that CH_4 production decreased as deposition rates increased. Gauci et al. (2005) followed the response of emissions after the addition of a pulse of SO_4. They report that emissions were suppressed for at least 5 years and estimate that as many as 10 years may be required for recovery to previous levels.

Although it might be expected that chronic N additions to wetlands would also decrease CH_4 emissions since NO_3 is also used during bacterial organic decomposition, field simulations suggest that effects are relatively small (Dise and Verry, 2001). Zhang et al. (2007), however, report significant increases in CH_4 flux over a range of N additions. They suggest that this increase is most likely an indirect effect of the N-induced increase in plant biomass. Effects on N_2O emissions are unknown, but would not be expected to be large since water saturation (and the low O_2 levels as well as slowed diffusion it creates) appears to be the major control on emissions rather than N inputs. Sensitivity to N inputs is likely to depend upon a wetland's nutrient status.

The complex and non-linear response of bacteria to process-level controls means that at larger scales where these variables can be highly dynamic, fluxes can be highly variable both in time and space. This has created significant difficulties in attempting to derive large-scale flux estimates.

2.2.2 Ecosystem-Level Controls

At the ecosystem level, the most important control on emissions of CH_4 and N_2O is the presence of water and the position of the water table. For N_2O, this single variable appears to be the dominant control on whether a site is a small source or a sink, since wetland systems appear to be poised at near-equilibrium with respect to the atmosphere. The process of denitrification is thought to dominate in wet soils (more than 60 percent water-filled pore spaces), producing a greater fraction of N_2O than NO (Davidson, 1991). However, water-saturated soils (more than 80 percent water-filled pore spaces) slow diffusion, which enhances N_2O consumption, resulting in little release to the atmosphere. For saturated wetland soils, therefore, N_2 becomes the dominant gas released (Davidson, 1991). Under moderately wet conditions, N_2O may be produced by denitrifiers and some fraction may diffuse to the atmosphere before consumption occurs. It may also remain in the soil and be released if soils dry (Davidson et al., 1993). This may happen seasonally, as in seasonal wetlands and lakes in the tropics, or as a consequence of drought. Wetting and drying cycles have been shown to enhance N_2O emissions and bacterial responses to wetting appear to be rapid (Davidson et al., 1993; Venterink et al., 2002). Nitrogen dynamics in seasonal wetlands in the tropics undergo annual transitions between nitrification-domination and denitrification-domination (Koschorreck and Darwich, 2003). Koschorreck (2005) reports high rates of N_2O flux during the transition between flooded, anaerobic soils and dry, aerobic conditions.

For CH_4, the presence of water serves as the primary and required condition in wetlands. There is essentially no flux and there may even be uptake from the atmosphere in its absence. In the Great Dismal Swamp, for example, a lack of rainfall transformed much of the system from a strong source to a sink as the water level fell (Harriss et al., 1982). If the system is wet, then other variables such as organic quality and quantity come into play. Summarizing work over a 12-year period in northern wetlands with high water tables, Christensen et al. (2003) found that temperature and substrate availability combined to explain virtually all of the variation in annual emissions. Wetlands located in riparian zones receive water, C, and nutrients from both adjacent water bodies and from upland downslope surface or subsurface flows (Itoh et al., 2007). Under high flow conditions, the rapid resupply of oxygenated water may suppress methanogenesis even through soils are water-saturated.

The climatic setting as well as the plant species present in a wetland exerts important controls on emissions at larger scales. Plants have been shown to affect CH_4 emissions both directly and indirectly. Species differ in the amount of biomass they produce as well as how easily that biomass may be decomposed. In addition, some wetland plant species can move gases produced in sediments such as CH_4 through stem and leaf gas spaces and release them to the atmosphere (Sebacher et al., 1985). There is evidence that N_2O may also be transported and released to the atmosphere by some plants (Mosier et al., 1990; Rusch and Rennenberg, 1998; Chang et al., 1998; Yan et al., 2000; Kreutzweiser et al., 2003).

Net ecosystem CO_2 exchange (NEE, a measure of plant primary productivity) and CH_4 exchange have been found to be correlated in some wetlands (Whiting and Chanton, 1993; Christensen et al., 2000) and this relationship has been used as a basis for modeling fluxes at large scales (Walter and Heimann, 2000). Labeling studies, which mark organic material with low levels of radiation, indicate that much of the CH_4 released to the atmosphere has come from recently produced organic material, rather than from older soil organic material (King and Reeburgh, 2002; Megonigal et al., 1999). In fact, King et al. (2002) estimate that more than 75 percent of average CH_4 flux from tundra wetlands is derived from recently fixed carbon.

Recently, von Fischer and Hedin (2007) used a radioactive tracer technique to explore hypotheses about controls on CH_4 fluxes at the landscape scale. Their study evaluated the relative importance of three mechanisms in controlling emissions: (1) fluxes were controlled by bacterial CH_4 oxidation; (2) fluxes were controlled by substrate availability, the amount of C mineralization; and (3) fluxes were determined by the relative C flow through methanogenic vs. non-methanogenic decomposition pathways (nitrification/denitrification, aerobic decomposition, SO_4 reduction). In contrast to the work indicating a strong link between emissions and C supply (Whiting and Chanton, 1993), they found that rates of C mineralization did not explain variations in fluxes at these large scales. Rather, they found that surprisingly small changes in C flow between mineralization pathways resulted in large differences in CH_4 production and subsequent flux. On average, if more than 0.04 percent of total C mineralization was through methanogenic pathways, soils were net sources of CH_4. This result indicates that CH_4 production is highly sensitive to soil redox status and the development of anaerobic microsites where energy flow can be diverted to methanogenesis. Such microenvironments could develop due to differences in C supply, nutrients, or moisture. von Fischer and Hedin suggest that while ecosystem C supply may constrain CH_4 production from a mass-balance perspective, it is the fine-scale biophysical factors that create the high variability that has been observed in emissions within and across environments and which must be included in models.

Redox (short for **reduction/oxidation**) describes the relative oxidation status of a soil. Soils with a low redox status have little available oxygen, which limits the types of reactions that can take place.

2.2.3 Methane Emission Pathways

Emissions to the atmosphere from wetlands occur through a variety of mechanisms (Figure 2-1): by diffusion across the soil or water interface, by ebullition (bubbling) when concentrations are high and exceed saturation levels, and by plant-mediated transport, as noted above. The relative importance of these pathways can vary between habitats as well as over the course of a season, as production and soil concentrations change seasonally and plants mature and die. In a number of wetland types, ebullition has been found to release a significant fraction of total emissions (Bartlett et al., 1988; Marani and Avala, 2007; Happell and Chanton, 1993). Assessing the importance of ebullition can be difficult, however, because it is episodic and may release a considerable volume of gas in a very brief period. If sampling was not occurring at this time, emissions may be significantly underestimated.

Wetland plants can also serve as important transport pathways to the atmosphere. By moving rapidly through the air spaces in plant stems and leaves, CH_4 can bypass the near-surface unsaturated layer where most CH_4 oxidation occurs and thus a greater fraction of production may be released to the atmosphere. Transport through plants can be by diffusion, following the air pressure gradient produced by the plant during respiratory consumption (Garnet et al., 2005), or by bulk flow, pressurized ventilation. Although not all plant species transport CH_4 (Sebacher et al., 1985; Chanton and Dacey, 1991), transport through plants may make a major contribution to total emissions. For example, Whiting and Chanton (1992) estimated that 90 percent of the CH_4 flux from a sub-arctic fen was plant-mediated. Oquist and Svensson (2002) found that plants functioned as important controls on emissions, but species acted in different ways in the wetlands they investigated.

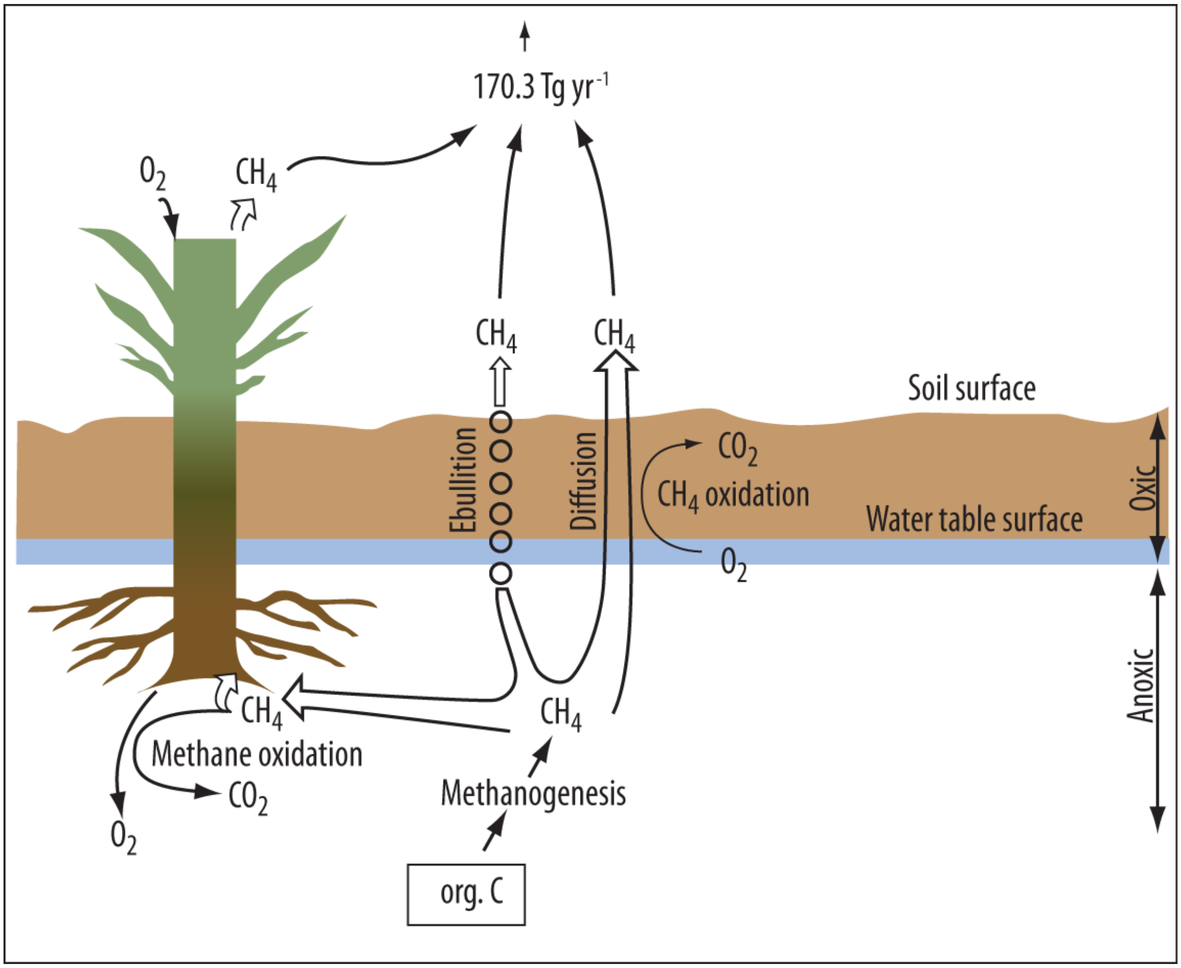

Figure 2-1. Conceptual model of CH_4 cycling in wetland and upland environments, showing plant-mediated transport, bubbling, and diffusion. Adapted from Whalen, 2005.

The importance of plant-mediated N_2O fluxes is difficult to evaluate, since only a few wetland species have been investigated. Rice plants, particularly under flooded conditions, appear to be an important pathway for N_2O release from paddy soils (Yan et al., 2000). Emissions of N_2O have been reported from both the prop roots and pneumatophores (specialized root structures used for air transfer) of several mangrove species (Kreutzwieser et al., 2003; Krithika et al., 2008). Black alder, a common European tree in wetlands, develops internal air spaces in response to flooding, as do a number of other trees found in wetlands. These air spaces were found to enhance the transport of both CH_4 and N_2O from soils (Rusch and Rennenberg, 1998) and the authors suggest that this may be a common phenomenon in wetland tree species.

The variety of transport mechanisms to the atmosphere, their high spatial and temporal variability, and their dependence upon small-scale environmental factors complicate efforts to derive larger-scale flux models. They also add significant uncertainty to flux estimates and can be a large source of error if flux measurement techniques create artifacts.

2.3 Current Global Methane and Nitrous Oxide Emissions From Wetlands

This section discusses the techniques used to make global flux estimates from wetlands and then review current estimates. The majority of this discussion focuses on CH_4 fluxes because of their global importance and because few large-scale estimates of N_2O from wetlands have been made. However, the techniques used for global flux estimation are fully applicable to N_2O.

An **empirical** model just uses observations to make estimates. For example, summer emissions might be found to contribute 90 percent of annual emissions. It implies no deeper understanding.

A **process** model uses an understanding of the underlying processes that control flux to make estimates. For example, fluxes might be modeled using soil temperature, as a result of the control of bacterial growth by temperature.

2.3.1 Techniques for Making Global Estimates

This section discusses three techniques for making global estimates of CH_4 and N_2O emissions from wetlands: surface flux extrapolation, process modeling, and inverse modeling. Each approach has strengths and weaknesses.

2.3.1.1 Surface Flux Extrapolation

Surface flux extrapolation uses actual emission measurements to calculate a global estimate. Although the scale of possible measurement approaches ranges from less than 1 m^2 (using chambers) to perhaps 100 km^2 (using eddy correlation towers), all estimates of surface flux must be extended in time and space beyond actual observations. The implicit assumption is that the measurements are representative of the true flux and that measurement error is small relative to true variability. For wetlands, however, extrapolating flux is complex because of non-linearities in the processes affecting emissions and high surface heterogeneity on a range of scales. Wetland vegetation can serve as an indicator or integrating variable for environmental parameters that are more difficult to measure over large scales (i.e., nutrient status, frequency, depth, and length of inundation, salinity, organic content). Therefore, it has often been used as a way to organize, characterize, and extrapolate emissions. Vegetation is also a parameter that can be remotely sensed.

Scaling up wetland flux measurements by using vegetation and moisture or water level relies on inventory databases of these variables. These databases may be sources of significant error to the resulting flux estimate (Frey and Smith, 2007). They are also commonly static, lacking the dynamics required for estimating biological processes. The increasing sophistication of satellite sensors of land cover and inundation offers significant improvement in temporal and spatial resolution of these variables. Melack et al. (2004) used seasonal synthetic aperture radar measurements to improve regional flux estimates from the Amazon Basin. Prigent et al. (2007) have recently developed a multi-satellite method combining passive microwave land surface emissions, active microwave backscatter measurements, and visible and near-infrared reflectances to derive the first monthly estimates of inundated area for the years 1993 through 2000 at global scales. The inclusion of seasonal variability in fluxes, however, usually involves either an empirical model or the development of a process-based model.

2.3.1.2 Process Modeling

Although there are still knowledge gaps, it is likely that major improvements in estimating flux will require approaches in addition to simply adding to the flux database. The extrapolation of flux measurements has provided the basis for initial global estimates, but it is clear that measurements cannot be made in every environment under all conditions. Enough is understood about the dynamics of CH_4 in natural systems to permit the development and testing of process-based models, and over approximately the last 10 years these models have increased in number and complexity. Refining and improving models, in combination with increasing the spatial and temporal resolution of the data used for their extrapolation, should yield improved flux estimates.

Process-based models use an understanding of emissions and their environmental controls to calculate fluxes. Because estimates are not based on actual measurements, there are additional sources of uncertainty. A critical assumption is that the model actually captures the variables driving fluxes and that its formulation realistically reflects the all of the important variables and flux responses. Currently many process models are dependent upon the use of the NEE/CH_4 flux relationship described by Whiting and Chanton (1993), which does not appear to be applicable to all wetlands and may be species-specific (Strom and Christensen, 2007).

As for extrapolating flux measurements, process models depend on the databases of environmental drivers such as temperature, inundation, and primary productivity (for those using the NEE/CH_4 relationship). An additional difficulty is the inclusion of the high spatial and temporal variability characteristic of natural systems. This variability contains much of the information of interest for dynamic flux estimations and for predictions under altered climate conditions. Currently, high variability creates correspondingly high uncertainty in emissions. Although it is unlikely that all of this variability can be resolved, improved statistical methods to include small-scale heterogeneity in models should reduce the uncertainty. A technique known as nested sampling has been used with success in several recent measurement programs.

2.3.1.3 Inverse Modeling

The concentration of CH_4 in the atmosphere at any one time and place is a function of its sources and sinks, modified by mixing and transport. Knowledge of how concentrations vary at multiple scales thus can provide data on the factors that control its distribution. The addition of atmospheric concentrations as a constraint on flux is a powerful tool. Inverse modeling attempts to optimize flux estimates given knowledge of these distributions. Inverse (“top down”) models incorporate atmospheric observations, a model of atmospheric transport, and prior estimates of source distributions and magnitudes. Sources are then evaluated to determine if they can “account” for observations and are adjusted, if required, to be more consistent. Difficulties can arise in a variety of ways. Discriminating between co-located sources is a challenge, and inadequate observations can bias results. Complex meteorology and topography are difficult to simulate. If transport models have errors, these may be misinterpreted as source/observation mismatches. Errors in initial assumptions about sources (spatial distribution, magnitude, variability, or even types) can make model interpretation difficult. The spatial and temporal integration of various data sets can also introduce errors. Inverse techniques, however, have increased in sophistication and power over the past 10 years and offer a way to integrate highly variable emissions over large scales and to bring other data sources to bear on the problem of estimating emissions. An increasing database on isotopic ratios of atmospheric CH_4 is a valuable addition to inverse modeling, since these data can be used to help discriminate between source types. Over the last several years, measurements of CH_4 mixing ratios from satellites have been added to the observations available, significantly enhancing data coverage.

2.3.2 Global Wetland Methane Emissions

This subsection summarizes global wetland CH_4 emissions developed using each of the three techniques described in Section 2.3.1. The first global estimates from wetlands were made by extrapolating flux measurements, which gave the initial indication of their significance to the global budget. As the databases of flux, atmospheric measurements, and the variables needed for flux extrapolation has grown, our ability to make more sophisticated estimates has increased.

2.3.2.1 Estimates Based on Flux Measurements

Table 2-1 summarizes existing CH_4 flux measurements and their extrapolation to a global scale from the first version of this report. These estimates are in agreement with other bottom-up estimates based on the existing flux database, shown in Table 2-2. These estimates reduced the initial Matthews and Fung (1987) calculation of the relative importance of northern wetlands as more data became available. Note that although uncertainties are not explicitly estimated, they are known to be large. All estimates are static, since the databases on temperature and ecosystem area used for extrapolation are based either on long-term means or a combination of compiled literature sources. Small-scale flux variability, differences within ecosystem types, as well as possible year-to-year differences are included in error bars on mean fluxes.

Table 2-1. Wetlands Methane Emissions (Tg CH_4/Year), From Bartlett and Harriss (1993) and U.S. EPA (1993)

Ecosystem	Non-Forested Swamps	Forested Swamps	Non-Forested Bogs	Forested Bogs	Alluvial Formations	Annual Emissions
Tropical	31	27	0.5	2.4	5.0	66
Temperate	1.5	1.6	0	2.1	0.3	5
All northern						38
Boreal	1.4	0.5	4.9	12.6	0	20
Arctic	0.2	0.1	4.9	8.9	0	14
Well-drained tundra						4
Total	**34.1**	**29.2**	**10.3**	**26**	**5.3**	**109**

Table 2-2. Global Wetland Methane Flux Estimates Made by Extrapolating Flux Measurements (Tg CH_4/Year)

Global Estimate	Climate Zone			Total	Comment
	High Latitude (N of 50^{o}N; S of 50^{o}S)	Temperate (50–30^{o}N; 30–50^{o}S)	Tropical (30^{o}N–30^{o}S)		
Matthews and Fung, 1987	65	14	32	111	First global estimate, based on relatively few measurements
Aselmann and Crutzen, 1989	25	12	43	80	Uses a different wetland area database than Matthews and Fung (1987)
Bartlett et al., 1990	39	17	55	111	Significant increase in number of tropical emissions
Fung et al., 1991	35		80	115	Same formulation as Matthews and Fung (1987) but more measurements and compares fluxes to atmospheric concentrations
Bartlett and Harriss, 1993	38	5	66	109	Earlier version of this report

Estimates of global wetland emissions based on flux extrapolation range from 80 to 115 Tg CH_4/yr but are not independent of one another, since several use the same area and inundation databases. Bartlett and Harriss (1993) calculated emissions using two different wetlands area estimates and demonstrated that although global emissions were similar, there were significant smaller-scale differences in geographic distribution and between wetland types. Excluding the early Matthews and Fung (1987) calculations, northern wetlands were extrapolated to release 30 to 35 Tg CH_4/yr, an average of 33 percent of the global total; temperate systems emitted 5 to 17 Tg CH_4/yr (10 percent); and tropical systems emitted 50 to 70 Tg CH_4/yr (59 percent). After about 1993, few global flux estimates were made by extrapolating measurements, since the database of atmospheric observations had grown, providing an additional constraint on estimates (Fung et al., 1991), and knowledge of the processes controlling fluxes had permitted the development of large-scale process-models (Cao et al., 1996).

2.3.2.2 Estimates Based on Process Models

Much of the more recent process and inverse modeling simulations is based on the work of Fung et al. (1991). Later work uses the geographic and seasonal distributions of CH_4 sources reported there and updates emissions from other sources. For this reason, wetland emissions are commonly broken down into the bog (forested and non-forested, largely located in the high latitudes) and swamp (forested and non-forested, dominating tropical wetland areas) categories used by Fung and co-workers.

Global wetland emissions estimated from process models vary more widely than do those based on flux extrapolation. This is in part due to the different approaches taken and to the use of different ways to estimate the environmental factors used for model extrapolation. Global estimates range from 92 to 260 Tg CH_4/yr, but the majority fall into the range of 140 to 160 Tg CH_4/yr—somewhat greater than those calculated from measurements, although uncertainties are quite large (Table 2-3). Note that the Gedney et al. (2004) estimate includes rice paddies and so is not directly comparable to strictly natural wetlands.

Northern ecosystems in particular have been a focus of modeling efforts, so a greater number of estimates have been made from these systems. As shown in Table 2-3, modeling calculations range from 20 to 72 Tg CH_4/yr, for high latitudes. Note, however, that some authors calculate fluxes on the basis of wetland types (i.e., bogs vs. swamp), which correspond to broad latitude classes, but are not an exact match. Tropical (or swamp systems) are calculated to have greater emissions than northern wetlands, and range from 41 to 195 Tg CH_4/yr. For those estimates that include both northern and tropical wetlands, the global contribution from northern systems ranged from 15 to 49 percent and averaged 31 percent. Tropical or swamp systems were calculated to contribute 44 to 85 percent and averaged 64 percent. These relative ecosystem contributions are similar to those calculated from flux measurement extrapolations.

Estimates published by Walter et al. (2001) are relatively high (65 Tg CH_4/yr for bogs and 195 Tg CH_4/yr for swamps). This is believed to be due to the flux database upon which the model was based, rather than a problem with the model structure, and the model has been used in other work yielding estimates more similar to others reported in the literature (Shindell et al., 2004). Emissions calculated by Harder et al. (2007) for high latitudes are also relatively high (72 Tg CH_4/yr, making up 49 percent of the global total), but it is difficult to determine how they were estimated other than that a variety of literature sources were used. The only estimate of temperate wetland emissions from process modeling is that of Cao et al. (1996). At 25 Tg CH_4/yr, it is high in comparison to those derived from measurement extrapolation.

Table 2-3. Global Wetland Methane Flux Estimates Made by Extrapolating Process Models (Tg CH_4/Year)

Global Estimate	Climate Zone			Total	Comment
	High Latitude (N of 50°N; S of 50°S)	Temperate (50–30°N; 30–50°S)	Tropical (30°N–30°S)		
Cao et al., 1996	25	25	41	92	
Christensen et al., 1996	20 (±13)				Modeled using NPP and flux as a fraction of heterotrophic respiration
Lelieveld et al., 1998	54 (bogs and tundra)		91 (swamps)	145 (115–175)	
Walter et al., 2001	65		195	260	
Houweling et al., 2000				147	From a pre-industrial budget using ice core data and a CTM
Kaplan, 2002				140	Christensen et al. (1996) structure, BIOME4 model; much larger estimated wetland area
Shindell et al., 2004	24		133	156	Based on Walter model; northern = 32°N–90°N; tropical = 32°N–32°S
Gedney et al., 2004				297	Includes rice paddies
Zhuang et al., 2004	57				Uses Terrestrial Ecosystem Model (TEM); N of 45°N
Zhuang et al., 2006	36				Uses TEM
Harder et al., 2007	72		74	146	Based on Fung et al. (1991) but revised by combining many sources
Bergamaschi et al., 2007	62		113		Uses Kaplan wetland areas, Christensen model, and a global vegetation model—a priori model input; total flux specified = 174.5

Most process models employ a relationship between CH_4 flux and a measure of plant productivity as the core structure that relates flux to environmental controls (Walter et al., 2001). Christensen et al. (1996) use BIOME2 modeled net primary productivity (NPP) estimates, as moderated through calculations of heterotrophic soil respiration, to estimate flux. Several models attempt to include all three transport pathways of CH_4 to the atmosphere. This requires inputs and/or calculations of vegetation type, density, root distribution, and soil CH_4 distributions. Zhang et al. (2002) have modified a well-known model of soil carbon and nitrogen dynamics (DNDC) to include functions unique to wetlands. Their Wetlands-DNDC model uses the Walter methanogenesis process model and includes water table changes, the growth of mosses as well as vascular plants, and anaerobic soil processes.

In addition to the models referenced in Table 2-3 that have been used to derive large-scale flux estimates, a number of models have been developed that focus on regional or ecosystem-specific estimates. These include those of Frolking and Crill (1994), Potter (1997), Grant and Roulet (2002), Frolking et al. (2002), and Kettunen (2003). Potter et al. (2006) use the NEP:CH_4 relationship in combination with a model to estimate NEP, and a land cover database to calculate U.S. wetland emissions at 5.5 Tg CH_4/yr.

2.3.2.3 Estimates Based on Inverse Modeling

After the initial work of Hein et al. (1997) and Houweling et al. (1999), improvements in inverse modeling techniques have led to a number of recent global CH_4 budgets, as shown in Table 2-4. Early estimates from wetlands are believed to be high due to an overestimate of the magnitude of the OH sink (Wang et al., 2004). As Table 2-4 illustrates, variability in emission estimates is still high, although values are broadly similar to those generated from process models. Estimated flux from bogs or high-latitude wetlands is relatively consistent and ranges from 21 to 47 Tg CH_4/yr, with an average of 35 Tg CH_4/yr. Estimated flux from swamps or tropical wetlands is higher and more variable, ranging from 81 (an estimate believed to include a contribution from co-located rice areas) to 206 Tg CH_4/yr. Swamp estimates average 144 Tg CH_4/yr. Wetlands classified as bogs are calculated to contribute 9 to 29 percent of the global total, averaging 20 percent, while swamp systems contribute 56 to 89 percent, averaging 78 percent of total emissions.

The increasing database of atmospheric observations, sampled both at the ground surface and from satellites, has permitted the calculation of interannual (year-to-year) variability in flux. This is an important capability since emissions have a strong response to variation in environmental drivers. Variability in wetlands emissions (driven by decreases in temperature and other variables), for example, has been suggested as an important factor in slowing the growth rate of atmospheric CH_4 in the early 1990s (Hogan and Harriss, 1994; Wang et al., 2004). The large increase in atmospheric CH_4 observed in 1998 has also been attributed to variability in wetland emissions (Chen and Prinn, 2006). These authors estimate that from year to year, wetland fluxes (and perhaps co-located rice agriculture) may increase as much as 19 Tg CH_4/yr or decrease 15 Tg CH_4/yr, a significant fraction of total global emissions. Bousquet et al. (2006) suggest that between 1991 and 1993, wetland emissions decreased by 24 ± 6 Tg CH_4 due to a decrease in solar radiation after the eruption of Mt. Pinatubo. They find that emissions from wetlands are the dominant source contributing to the interannual variability in emissions, explaining 70 percent of the global changes in growth rate over the last 20 years.

Table 2-4. Global Wetland CH_4 Flux Estimates Made by Inverse Modeling (Tg CH_4/Year)

Global Estimate	Climate Zone			Total	Comment
	High Latitude (N of 50°N; S of 50°S)	Temperate (50–30°N; 30–50°S)	Tropical (30°N–30°S)		
Hein et al., 1997	44 ± 7 (bogs)		192 ± 19 (swamps)	237 (±20)	
Houweling et al., 1999	31.4 (90–45°N) 0 (45–90°S)		48.4 (45–0°N) 65.1 (0–45°S)	145 (±41)	As cited in Dentener et al. (2003)
Wang et al., 2004	27 ± 3 (bogs and tundra)		149 ± 10 (swamps)	176	
Mikaloff Fletcher et al., 2004	21 ± 14 (bogs) 4 ± 4 (tundra)		206 ± 44 (swamps)	231	1998–1999
Chen and Prinn, 2006	34		81	143–148	Includes a contribution from Southeast Asia rice; interannual wetland variability = +19 and -15 Tg CH_4/yr
Bousquet et al., 2006	43 ± 8 (bogs and tundra)		104 ± 12 (swamps)	147 (±15)	Long-term mean for 1984–2003
Bergamaschi et al., 2007	47		161	208	Model constrained by satellite and surface observations

2.3.2.4 Summary of Methane Emissions From Wetlands

The range in calculated CH_4 flux from wetlands is summarized in Table 2-5 according to the techniques used to make the calculations. Uncertainties are not included here, but often range from roughly 10 to 75 percent. This chapter's analysis derives a "best guess" wetlands emissions estimate by taking an average of process and inverse model estimates published since 2004. Calculations made by the extrapolation of flux measurements are not included, since this technique has been largely superseded. Uncertainties in these averages are based only on the range in estimates. Table 2-5 suggests that calculated emissions from northern wetlands have fallen as the modeling techniques have improved and that the overall magnitude of emissions from wetlands, illustrated by summed averages and ranges, has increased.

Here we estimate that wetlands release on the order of 170 Tg CH_4/yr. The majority (75 percent) of emissions are from swamp systems located largely in the tropics. Estimates of these emissions range widely, however. If global emissions of CH_4 from all sources are roughly 566 Tg CH_4/yr (see Table ES-1), then wetlands contribute about 30 percent. Interannual variability, driven largely by climate variability, is high. Using the estimates of interannual variability derived by Chen and Prinn (2006) and Bousquet et al. (2006) of 15 to 19 Tg, the wetlands contribution may vary by ±3 percent from year to year.

Table 2-5. Summary of Estimated Wetland CH_4 Fluxes by Technique (Tg CH_4/Year)

Approach	Northern/Bogs	Tropical/Swamps	Total
Flux extrapolation	31–48[a] avg = 38 (37%)	49–80 avg = 65 (63%)	80–115 sum of avgs = 103 n = 4
Process modeling	20–72[b] avg = 44 (31%)	41–133 avg = 90 (64%)	92–156 sum of avgs = 134 n = 8 (bogs); 5 (swamps)
Inverse modeling	21–47 avg = 36 (20%)	81–206 avg = 144 (78%)	145–237 sum of avgs = 180 n = 6
Current best guess (process and inverse modeling since 2004)	24–72 avg = 42.7 (25%) std. dev. = 16.6; n = 10	81–206 avg = 127.6 (75%) std. dev. = 44.0; n = 8	170.3 range = 105–278 by summing minima and maxima

[a] For flux extrapolation, temperate emissions are split equally between bogs and swamps. Values in parentheses indicate percentage contribution to wetland total emissions.

[b] Walter et al. (2001) estimates excluded.

2.3.3 Global Wetland Nitrous Oxide Emissions

There are very few global estimates of the N_2O released from wetlands, and wetlands are not included in N_2O budgets as significant sources. Bouwman et al. (1993) modeled global N_2O based on the input of organic matter, soil fertility, moisture status, temperature, and oxygen level and concluded that wetlands appeared to make only a minor contribution. A number of measurements have been made of emissions from coastal mangrove swamps, some of which received outside N inputs from sewage or bird droppings. Corredor et al. (1999) calculate global emissions from mangroves ranging from 0.004 to 0.17 Tg N/yr. Similar magnitude fluxes were measured by Allen et al. (2007) over nearly an annual period. Barnes et al. (2006) calculated that coastal mangrove systems release 0.076 Tg N/yr and find that these systems make only a minor contribution to global fluxes. Emissions of N_2O were measured from intertidal mud flats in the Dutch Scheldt estuary by Middelburg et al. (1995). They calculated a small global estuarine intertidal flux of 0.0013 Tg N/yr. 18.8 Tg N/yr (see Table ES-1), If the total N_2O to the atmosphere is 18.8 Tg N/yr (see Table ES-1), then these wetland systems would contribute 0 to 1 percent. Working in the Hudson Bay Lowlands, Schiller and Hastie (1994) also report low emissions. Overall, the authors found that these wetlands acted as a small source to the atmosphere and calculate that N_2O emissions from the Hudson Bay Lowlands would contribute on the order of 0.0005 to 0.005 percent to global N_2O emissions. Open fens released the majority of the regional N_2O emissions, while treed fens and bogs had the lowest flux. Although the Third IPCC Assessment Report (Ehhalt et al., 2001) includes a source called “tropical wet forest” which is a major source to global emissions, this category would be more accurately titled “tropical humid forest” and is not actually wetland. Wetlands are not included as a source of N_2O in the most recent IPCC report (Denman et al., 2007).

The possibility that wet soils may at times act as a sink for atmospheric N_2O was suggested a number of years ago based on laboratory measurements (Blackmer and Bremner, 1976). Scattered measurements have found that this occurs in a variety of wetlands (Keller et al., 1986; Regina et al., 1996; Schiller and Hastie, 1994). Schiller and Hastie, for example, found that about 34 percent of their measurements in the Hudson Bay Lowlands showed atmospheric uptake. Chapuis-Lardy et al. (2007) summarize measurements of N_2O uptake. They suggest that low NO_3 availability and conditions in soils that slow diffusion, such as the water-saturated soils of wetlands, promote N_2O consumption. If a small soil sink for N_2O is a widespread occurrence in wet soils, understanding its magnitude and dynamics would improve global budget estimates. In summary, wetlands appear to contribute negligibly to atmospheric N_2O; their role as a sink can not be currently estimated, but is likely to be small in comparison to the stratospheric sink.

2.4 Future Emission Scenarios

This section focuses on possible future emissions of CH_4. Because wetlands do not appear to be a significant global source of N_2O, no work has been undertaken to estimate how these emissions may change. In general, changes in soil moisture would be expected to have the greatest impact on N_2O fluxes by changing the relative proportions of NO, N_2O, and N_2. If wetlands act as a small, diffuse sink for atmospheric N_2O, it is possible that climate changes may alter the magnitude and timing of this part of the budget.

Before the Industrial Revolution, natural wetlands were the dominant source of CH_4 to the atmosphere (Brook et al., 2000; Etheridge et al., 1998). The increase in human population has decreased the relative importance of wetland sources by both increasing anthropogenic sources of CH_4 and decreasing the wetlands source through drainage and land use change. Both direct and indirect changes in wetland fluxes will continue because many of the controls on flux—such as temperature, rainfall, and vegetation type—are among those expected to change under projected altered climate regimes. The process model developed by Walter et al. (2001) suggests, for example, that a ± 1°C change in temperature may change CH_4 emissions by ± 20 percent and that a ± 20 percent change in precipitation may change emissions by ± 8 percent. The response of emissions to climatic change will vary with latitude. The complex link between climate and wetland CH_4 emissions may also be a positive feedback mechanism accelerating changes in climate (Woodwell et al., 1998; Monson and Holland, 2001). High-latitude wetlands store a considerable fraction of the global soil C pool as a result of the relatively small long-term imbalance between C production and decay. Understanding the sensitivity of this pool to changes in environmental conditions is crucial to understanding the effects of global climate change.

A number of studies have attempted to model the response of wetlands to climate change. These simulations commonly use a process model to estimate current emissions, re-run the model under altered environmental conditions, and then compare subsequent results. Climate models have indicated that there may be large changes in temperature and moisture patterns in the high latitudes over the next 100 years. Because temperature is also the major driver of northern seasonal cycles, much of this work concentrates on boreal wetland responses. The response of wetland CH_4 emissions to changes in climate has also been investigated by examining the link between climate and atmospheric CH_4 in the past through ice core records.

Working on a regional scale, Zhuang et al. (2007) have attempted to model Alaskan CH_4 fluxes and simulate changes in response to the region's expected changes in climate over the 21st century. They calculate that emissions from wet soils will be enhanced more than will oxidation in dry tundra and forest soils. As a result, projected CH_4 emissions from northern wetlands nearly double by the end of the century. In the context of the overall carbon budget (CO_2 and CH_4), it is estimated that in Alaska, net CH_4 emissions will be greater than C sequestration and that there will be a positive feedback between radiative forcing due to changes in wetland C cycling and climate change.

Work on estimated changes in wetland CH_4 emissions is summarized in Table 2-6. Studies to date indicate that emissions will be strongly affected by projected climate scenarios. Altered climate conditions impact emissions in both direct ways (e.g., temperature and precipitation change) and indirect ways (e.g., CO_2 fertilization effects on plant productivity, vegetation change, permafrost thaw, effects on thermokarst lakes, changes in biomass burning regimes). A more detailed discussion on some of these indirect effects on CH_4 emissions can be found in Chapter 5 ("Permafrost") and Chapter 6 ("Lakes").

Table 2-6. Projected Changes in Wetland CH_4 Emissions (Tg CH_4/Year)

Ecosystem	Time Frame	Environmental Change	Flux Change	Reference
Global		2X CO_2	Increase of 78% from 156 to 277	Shindell et al., 2004; majority of increase from tropics
Global	2100	Model simulation of IPCC IS92a emissions scenario	Doubling, an increase from ~300 to 500–600; flux increase similar to projected anthropogenic flux increase	Gedney et al., 2004; change due largely to temperature response
Northern, < 50°N	2100	Climate change from Integrated Global Systems Model (IGSM)	More than double from current 41 to 58	Zhuang et al., 2006; permafrost thaw and CO_2 fertilization increase fluxes
Northern, < 40°N	2030	GHGs[a]	Increase ~13% from 1960 estimate (35 to 40)	Gauci et al., 2004; uses Walter process model and tests a combination of environmental changes; S pollution decreases 1960 flux and reduces GHG effect
		GHGs + SO_4 deposition[b]	Increase 13% from 1960 estimate (31 to 35)	
		GHGs + SO_4 dep + SO_4 aerosols	Unchanged at 35	
	2080	GHGs	Increase 30% from 1960 estimate (35 to 45.5)	Gauci et al., 2004; S suppression becomes less important, fluxes similar to GHG alone
		GHGs + SO_4 deposition	Increase 39% from 1960 estimate (31 to 43)	
		GHGs + SO_4 dep + SO_4 aerosols	Increase 23% from 1960 estimate (35 to 43)	
Global	2030	GHGs	Increase ~10% from 1960 estimate (165 to 181)	Gauci et al., 2004; flux reduced 21–25 Tg by S pollution.
		GHGs + SO_4 deposition	Increase ~3% from 1960 estimate (155 to 160)	
		GHGs + SO_4 dep + SO_4 aerosols	Decrease ~1% from 1960 estimate (157 to 156)	
	2080	GHGs	Increase ~17% from 1960 estimate (165 to 193)	Gauci et al., 2004; increases under S suppression scenario are smaller; S pollution reduced by anticipated cleaner technologies
		GHGs+ SO_4 deposition	Increase ~19% from 1960 estimate (155 to 185)	
		GHGs+SO_4 dep+SO_4 aerosols	Increase ~13% from 1960 estimate (157 to 178)	

[a] Greenhouse gases.
[b] Simulates acid rain.

A rising sea level is also likely to affect emissions. Coastal inundation will flood terrestrial systems and may transform some of them to CH_4 sources. In addition, some current freshwater wetlands may transition to more saline systems as they are flooded, which is likely to decrease emissions. Coastal inundation and/or an increase in storm frequency is also likely to increase shoreline erosion, resulting in wetland loss (Nicholls, 2004). Shoreline retreat, the natural response to sea level rise, is made difficult due to human land use in coastal zones. The rate of sea level rise is an important variable in determining the fate of coastal fresh and saline wetlands. If it is approximately equal to the rate of soil or peat accretion in these systems, they are likely to remain relatively stable (Moorhead and Brinson, 1995; McFadden et al., 2007). Carbon stored in the peats of coastal wetlands after inundation has a largely unknown future, but has the potential to be a significant C source to the atmosphere (Henman and Poulter, 2008).

Anthropogenic activities in addition to those that release greenhouse gases also impact emissions from wetlands. Gauci et al. (2004) model the effects of the sulfur in acid deposition on wetlands. They calculate that sulfur deposited by acid rain has already (year 2000) suppressed fluxes over their pre-industrial level by roughly 15 Tg CH_4/yr. The projected time course of the effects of S deposition are complex, in part due to regional changes in economic growth and anticipated cleaner technologies, but sulfur pollution appears to be a potentially important factor in understanding future emissions (Table 2-6).

Manipulative field experiments are observations made in natural systems in which something (usually a controlling variable such as water level, nutrient inputs, or temperature) has been altered in order to assess ecosystem response.

In addition to modeling extrapolation, there have been manipulative field experiments as well as work comparing naturally existing environmental gradients that can be used as analogs for the anticipated changes under altered climate scenarios. As for modeling climate scenarios, the majority of this work has focused on northern systems. A major unknown is the effect of the loss of permafrost on tundra vegetation, surface water distribution, soil respiration, and organic matter accumulation (Jorgenson et al., 2006; Walter et al., 2007; Riodan et al., 2006). Turetsky et al. (2002) suggest that, in the short term at least, permafrost melting is associated with a 30-fold increase in CH_4 flux. Strom and Christensen (2007) found that the change in plant species caused by permafrost degradation and hydrologic changes created changes in plant productivity, photosynthetic rate, and CH_4 flux. These changes may ultimately mean that CH_4 from melting permafrost will act as an increasing source of radiative forcing in the future. Wickland et al. (2006) found that the formation of thermokarst wetlands by permafrost melting caused a 13-fold increase in a site's annual CH_4 flux, an increase similar to that reported by other studies (Turetsky et al., 2002; Bubier et al., 1995; Christensen et al., 2004; Johansson et al., 2006). Changes in emissions due to the formation of thermokarst lakes are discussed in Chapter 6 ("Lakes").

Thermokarst wetlands are wetlands formed in depressions by meltwater from thawing permafrost. These depressions are often produced by ground subsidence associated with permafrost melt and may also form small lakes (see Chapter 3 for more detail on flux from thermokarst lakes). Continued melting of the permafrost can lead to the drainage and eventual disappearance of thermokarst wetlands and lakes.

Changes in precipitation are clearly crucial, since small changes in water saturation may result in large flux changes (von Fischer and Hedin, 2007). Strack and Waddington (2007) demonstrate, however, that the response of a wetland to water table drawdown is complex and will vary with the existing microtopography. In their work, relatively high areas showed an increase in net global warming potential (CO_2 and CH_4) over controls while the global warming potential of topographic lows decreased. Roulet et al. (1992) compare the effects of temperature and precipitation changes associated with a $2 \times CO_2$ climate change scenario (if CO_2 concentrations were to double) on emissions from a northern fen. Their model found that increased peat temperatures could raise flux by 5 to 40 percent, but that the projected drop in water table decreased flux by 74 to 81 percent, suggesting that northern peatlands may be more sensitive to changes in moisture than temperature. A decrease in wetland water level would impact other radiatively important gases such as CO_2 and N_2O in addition to CH_4. Laine et al. (1996) have attempted to integrate the response of all three gases to a water table drop by comparing drained and undrained peatlands of varying productivity. They suggest that a general drying may decrease the impact of northern peatlands by about 0.1 W/m^2 due to a decrease in CH_4 flux, small changes in peat C storage, and an increase in tree-stand biomass.

An important, but difficult factor to include in future emission scenarios is the difference between short-term and long-term change. Part of the difficulty is that changing systems never reach a steady state, but in addition, biological systems respond to change with both short-term and long-term adaptations. Experimental manipulations seldom observe long-term responses since they typically do not last for more than a year or two. For this reason, some studies have used natural spatial gradients, for example in nutrient deposition, water table drainage, or disturbance, as analogs to changes over time since these can potentially include long-term environmental responses. Summarizing the apparently contradictory literature on peatland responses to lowered water levels, Laiho (2006) suggests that differences may be due to observation time scales. Short-term changes in an environmental control such as water level represent a disturbance to a system that is in relative equilibrium with previous conditions, while long-term changes result in adaptations to a new regime. He proposes that although disturbed systems will always lose C in the short term, the long-term response can be highly variable. These adaptations to a new hydrologic regime will depend on variables such as the peatland type, climate, and the amount of change from previous conditions. Frolking et al. (2006) also emphasize the difference between short- and long-term responses to an environmental perturbation and the necessity of taking a holistic approach when evaluating the impacts of climate change. They suggest that the net effect of peatland gas fluxes is a balance between the rapid, strong warming due to CH_4 flux and the slow cooling due to CO_2 uptake. In the short term, the CH_4 response will dominate radiative impacts, but after several decades, changes in CO_2 emissions will take over. Short-term and long-term effects are thus quite different.

CH_4 emissions from wetlands have been impacted by humans in the past and will continue to be impacted into the future as a consequence of climate change and land use change. Current knowledge suggests that emissions in the Northern Hemisphere will likely be significantly altered by anticipated changes in temperature and water regime, two of the key variables that control flux. In the tropics, it is likely that land use changes will have the greatest impact on emissions as these regions undergo developmental and population growth. The potential exists for large emission changes from both regions, both positive and negative.

2.5 Areas for Further Research

Continued improvements in large-scale process models should yield an increased understanding of the smaller-scale variability in flux. One way to approach this problem is to test models against long-term measurements to assess natural variability. These long-term datasets are few in number, which limits model development and verification. Existing long-term measurement programs should therefore be continued and new measurement sites added, particularly in the tropics.

Global emissions estimates have consistently pointed to tropical wetlands as major CH_4 sources, but work at these latitudes remains sparse and incomplete. Although satellite measurements have begun to fill gaps in the atmospheric observational network, increased surface sampling will help resolve current inverse modeling difficulties with low latitude sources.

Since seasonal variability in these systems is driven largely by changes in water level, improvements in our ability to model or accurately measure hydrologic change are crucial to being able to apply process models. The inclusion of ephemeral wetlands at all latitudes remains difficult.

Ephemeral means “short-lived.” An ephemeral wetland, pond, or spring exists for only a brief period, usually following precipitation or snowmelt. An ephemeral wetland is different from a seasonal wetland, which may exist for a longer period (still less than a year).

The empirically based NPP:CH_4 flux relationship, which has served as a fundamental core of many process models, has proven useful, but does not appear to be universally applicable. Testing of the relationship should continue and more habitat-specific relationships should be developed.

Incorporating small-scale heterogeneity into large-scale modeling remains difficult. Improvements in the ability to assign uncertainties will aid in distinguishing short-term variability from true long-term trends and will make assessment of the response of emissions to climate changes more powerful.

Combining a spatially explicit flux process model with an atmospheric transport model would produce seasonal and interannual simulations of atmospheric distributions. Comparing these to satellite-derived distributions and/or surface sampling network distributions should prove informative.

Because emission to the atmosphere is a function of the competing processes of CH_4 production and consumption, both processes and their responses to environmental controls must be understood across the landscape. Episodic emissions, which may release a sizeable fraction of annual flux, remain difficult to both measure and include in models. Failure to adequately incorporate these fluxes, however, can yield inaccurate and misleading results.

Fluxes of N_2O from wetlands remain largely unknown, particularly from tropical regions. Although measurements indicate they are relatively low, at least in the wetlands sampled to date, the seasonal changes in water level that characterize many tropical wetlands suggest that there may be brief periods of emissions. Experimental work examining emissions over wetting and drying cycles suggests that N_2O fluxes may be enhanced by these moisture changes. Understanding of the global extent and importance of the uptake of atmospheric N_2O in wetland soils should be improved.

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Chapter 3. Upland Soils and Riparian Areas

This chapter focuses on upland soils and riparian areas and their contribution to global greenhouse gas emissions. The original 1993 report (U.S. EPA, 1993) focused solely on the trace gas CH_4, and only considered the potential source strength of the wetland soils category in contributing to global CH_4 emissions. The report did not discuss upland and riparian soils as significant sources or sinks of CH_4 and other trace gases such as N_2O.

In the years since the publication of this 1993 report, the role of upland soils as a sink for global atmospheric CH_4 has become better understood. This sink strength has been quantified and modeled under various scenarios, and upland soils have been shown to provide a significant sink for atmospheric CH_4.

Upland soils are well-aerated soils with lower moisture content than wetland soils. They are found throughout the world, and include soils which support forests, grasslands, and agricultural lands.

Riparian areas are vegetated ecosystems along a waterbody through which energy, materials, and water pass. As they form the interface between terrestrial and aquatic soils, they often contain characteristics of both dry and water-saturated soils.

In addition, there have been profound advances in the understanding of the role of N_2O as a greenhouse gas and of the biogeochemical processes that regulate N_2O emissions from both upland and riparian soils. These breakthroughs have led to refined top-down and bottom-up estimates of global N_2O budgets, and increased understanding of the effects of anthropogenic influences, such as agricultural practices, on emissions from upland and riparian soils.

In the AR4, the IPCC reported that dry upland soils serve as one of the primary global CH_4 sinks by biologically oxidizing CH_4. They estimate that this source accounts for 30 Tg CH_4 removed per year from the atmosphere. The same upland soils have also been shown to release 6.6 Tg N/yr as N_2O through the microbiological processes of nitrification and denitrification (Denman et al., 2007). Although the IPCC report did not consider riparian zone soils separately, several other recent studies have described their potential as CH_4 sinks and N_2O sources.

This chapter reviews the current scientific understanding of upland and riparian soils as sources and sinks for N_2O and CH_4. It describes recent findings on biogeochemical processes that regulate emissions of these greenhouse gases in soils. It also reviews the factors that influence gas fluxes in these soils and their ultimate role as sources and sinks of greenhouse gases, with particular attention to spatial variations. Estimates of current global emissions from upland and riparian soils are provided and compared, and projections of future emissions scenarios and sensitivity to climate disruptions are summarized.

3.1 Description of Emission Source

Upland soils can be distinguished from wetland soils based upon their lower moisture content, which significantly alters the biogeochemical processes that take place in these soils. Upland soils are well-aerated, not water-saturated, and generally oxic (Conrad, 1996). The dry conditions favor microbial processes that make dry upland soils a sink for CH_4 and a source of N_2O (these processes are described in Sections 3.1.1 and 3.1.2). Upland soils include forests and grasslands under natural vegetation and arable lands. Chapter 10 of this report covers the contribution of vegetation growing on these soils to global CH_4 budgets; this chapter focuses only on the contribution of the soils themselves.

Riparian zone soils are often permanently wet and rich in organic matter. Riparian soil moisture content is distributed spatially, with gradients from the hill slope down toward the stream (Hefting et al., 2006). These saturated conditions and microbially available C contribute to higher rates of production of N_2O

than in dry upland soils. The degree of soil moisture also determines whether riparian zone soils will serve as net sources or net sinks of CH_4 (Hope et al., 2004).

3.1.1 Soils as Nitrous Oxide Sources

Soil N_2O production in upland and riparian soils with natural vegetation cover is influenced by various microbiological, chemical, and physical properties and processes in the soil. N_2O emissions from soils are produced predominantly by the microbial processes of nitrification and denitrification. Nitrification is the main source of N_2O under aerobic conditions, while denitrification dominates under anoxic conditions. Both processes can occur simultaneously in soils, and the production of N_2O depends on the balance between these two microbial processes (Butterbach-Bahl et al., 2004; Conrad, 1996).

Globally, about 65 percent of all N_2O emissions arise from nitrification and denitrification processes in soil (Smith and Conen, 2004).

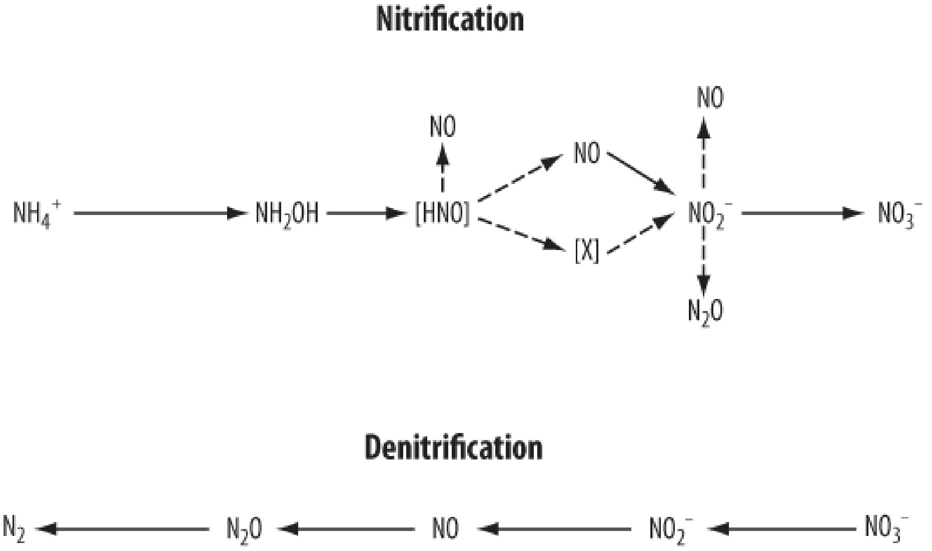

Figure 3-1. Pathway of nitrification and denitrification in soils. Dashed lines and square brackets indicate incompletely known processes and intermediates. Adapted from Firestone and Davidson, 1989.

In addition to these microbiological processes, chemical processes in neutral and acidic soil pH can contribute a small fraction of soil N_2O (Bremner, 1997). Also, the physical composition of the soil can influence emissions, as increasing soil clay content increases emissions of N_2O (Chatskikh et al., 2005).

Therefore, microbial community composition, physical parameters, and chemical environment of soils all influence the rates of N_2O production and emission. Worldwide, upland soils exhibit a mix of these various characteristics. Beside agricultural soils, tropical rainforest soils have been found to be the main source of atmospheric N_2O (Werner et al., 2007b). Nitrogen availability is high in these clay-rich, weathered tropical soils, and the high temperature, high moisture, and aggregation of clays create conditions where N_2O can be produced both by nitrification and denitrification (Neill et al., 2005).

3.1.2 Soils as Methane Sinks

Soils can act as either net sources or net sinks of CH_4, depending primarily upon soil moisture content. CH_4 is produced in waterlogged, wetland soils, but in well-aerated upland soils, CH_4 is oxidized (and therefore consumed). Upland soils may contain anoxic microsites (small volumes of soil) where CH_4 is produced, but dry upland soils are overall net sinks of CH_4 (Castaldi et al., 2006; Del Grosso et al., 2000; Hein et al., 1997; Jang et al., 2006; Wuebbles and Hayhoe, 2002). Dry soil oxidation of CH_4 makes up about 5 percent of the global CH_4 sink (Wuebbles and Hayhoe, 2002).

One of the most important global biological sinks for CH_4 is forest soils, where methanotrophic bacteria oxidize atmospheric CH_4 to CO_2 in the presence of O_2. In most soils, atmospheric CH_4 consumption seems to be located in the subsoil, usually between the A and B soil horizons (Conrad, 1996). The concentration of CH_4 in soil microsites drives this CH_4 oxidation, along with soil water content and other physical properties (Del Grosso et al., 2000).

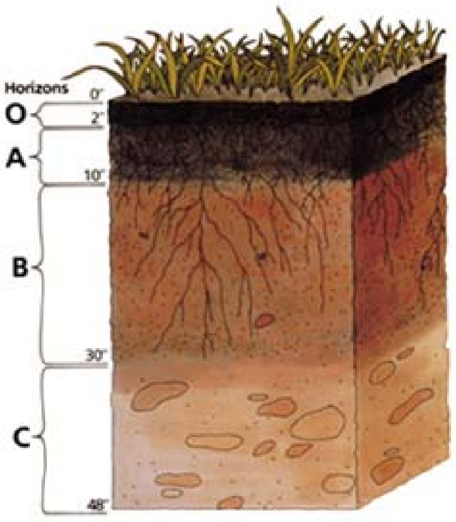

Figure 3-2. Typical soil profile. (Source: U.S. Department of Agriculture.)

The CH_4 consumption potential of upland and riparian soils has been characterized in a variety of ecosystems and land use categories (Groffman et al., 2006; Hope et al., 2004; Kaye et al., 2005; Werner et al., 2007b). Most CH_4 consumption has been found to occur in the well-drained soils of temperate and tropical areas (Ridgwell et al., 1999).

3.2 Factors That Influence Emissions

The factors that determine both the magnitude of emissions of N_2O from upland and riparian soils and the sink strength for CH_4 are numerous and interrelated. As the carbon and nitrogen cycles in soils are linked, changes in N and C availability strongly influence the rate of emission or sequestration.

Both upland and riparian soils have been significantly impacted by human activity. Many of the arable lands where dry upland soils occur have been cleared for agricultural use, which is responsible for an estimated 80 percent of anthropogenic emission of N_2O through soil emission, biomass burning, and animal production (Kroeze, 1999). During the 20th century, an expansion of agricultural land coupled with intensification of use of N fertilizer inputs caused a net increase of global N_2O emissions from 11 Tg N/yr in 1850 to 18 Tg N/yr in 1994 (Kroeze, 1999). Land use change, as forests and grasslands are converted to agriculture, has also decreased the global soil CH_4 sink (King, 1997). Arable land has a much smaller CH_4 uptake rate than untreated soils, particularly when treated

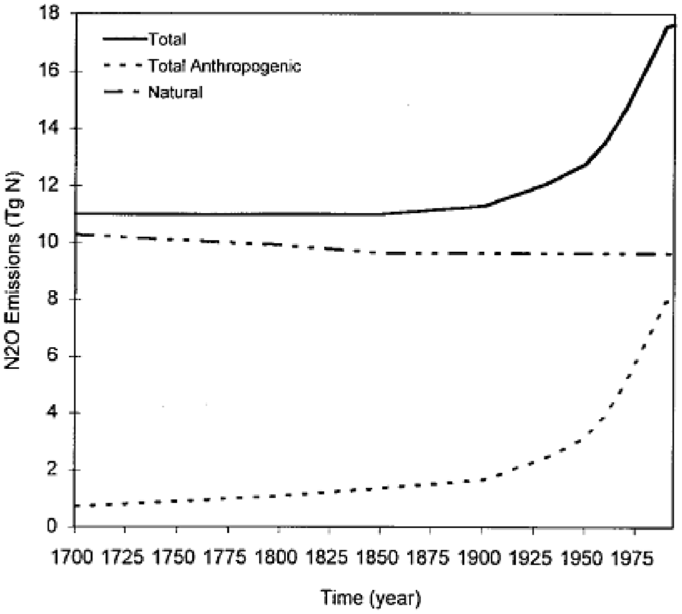

Figure 3-3. Global emissions of N_2O (1700–1994) used in the base scenario calculations. (Source: Kroeze, 1999.)

with certain fertilizers (Wuebbles and Hayhoe, 2002).

Riparian zones, located at the interface of terrestrial and aquatic environments, have been significantly impacted by agricultural activities as well. Riparian buffer zones serve as sites for nitrate removal from agricultural runoff, and are often loaded with high levels of N. Recent studies have suggested that prolonged exposure to N from agricultural runoff leads to higher N_2O emissions compared to emission rates from non-exposed forest soils (Dhondt et al., 2004; Hefting et al., 2003, 2006; Ullah and Zinati, 2006). The increased N levels in riparian soils may also suppress CH_4 oxidation processes in these soils.

Clearly, the human-induced changes in N_2O emissions and CH_4 sink potential of upland and riparian soils are significant. As this chapter focuses on the natural processes occurring in these soils, however, anthropogenic effects on these trace gases are not considered.

3.2.1 Factors That Influence Emissions of Nitrous Oxide

One method of identifying factors that influence N_2O emissions has been the development of process-based models such as DNDC (Li et al., 1992a,b, 1994) and DAYCENT (Parton et al., 1996), which simulate trace gas fluxes from soils. In addition, summaries of emission measurement data from field studies, using statistical techniques, have led to the development of emission factors such as those used by the IPCC (Bouwman, 1996).

Field measurements of N_2O emissions from soils under natural vegetation cover have been undertaken worldwide, in a variety of ecosystems and land uses. In a recent paper that reviewed 207 studies of emissions measurements from soils under natural vegetation, it was found that soil organic C content, vegetation type, soil pH, bulk density, and drainage were the major factors influencing N_2O emissions (Stehfest and Bouwman, 2006).

As soil organic content increases, emissions of N_2O increase as well due to increased availability of C for denitrifying bacteria (Kanerva et al., 2007; Stehfest and Bouwman, 2006). Vegetation type also influences emissions, as N_2O emissions decrease with increasing plant species diversity, and increase in the presence of legumes (Niklaus et al., 2006).

Chemical and physical characteristics of soil also influence emissions of N_2O. As soil pH increases, N_2O emissions decrease (Stehfest and Bouwman, 2006). As soil bulk density decreases, so do N_2O emissions (Stehfest and Bouwman, 2006). Soil moisture also plays a role in N_2O emissions: as Khalil and Baggs (2005) reported, N_2O emissions were the highest from the wettest soils (at 75 percent water-filled pore spaces). In the same study, it was found that 90 percent of the N_2O was produced through denitrification—proof that these water-filled soil microsites were primarily anaerobic.

The various microbiological, chemical, and physical properties of soil that influence N_2O emissions are distributed throughout upland and riparian soils worldwide. However, some general trends for particular biomes (ecological communities in particular climates) appear. Specifically, emissions of N_2O from rainforests are significantly higher than from grasslands, savannah, and tropical dry forest and.emissions from grasslands are significantly lower than those from deciduous forests and rainforests (Stehfest and Bouwman, 2006). High nitrogen availability, coupled with high moisture content, makes tropical soils especially likely to emit N_2O (Bouwman et al., 2002; Hirsch et al., 2006; Keller et al., 2005).

3.2.2 Factors That Influence Methane Sink Strength

Soil CH_4 sink strength depends on oxidation by methanotrophic microbes in the soil, and therefore is influenced by environmental factors that control this oxidation rate. The primary factor is soil diffusivity, which controls the amount of CH_4 transferred into the soil and, therefore, its availability to methanotrophs. Soil diffusivity is influenced primarily by soil moisture content (King, 1997). Soil moisture strongly controls the uptake of atmospheric CH_4 by limiting the diffusion of CH_4 into the soil, resulting in a negative correlation between soil moisture and CH_4 uptake rates under most non-drought conditions (Borken et al., 2006). Seasonal changes in soil moisture have also been shown to affect the exchange of CH_4 and, therefore, the soil sink/source strength (McLain, 2006).

CH_4 oxidation factors reflect the amount of CH_4 converted by the microbes. In a study by Jang et al. (2006) that reviewed 28 studies of CH_4 oxidation factors, the main variables shown to control CH_4 oxidation rate were soil water content and inorganic N presence or absence. The inhibitory effects of nitrate on CH_4 oxidation in forest soils were reported to range from 10 to 86 percent (Jang et al., 2006).

The influence of temperature on oxidation rate is unclear. One global model suggests that the colder winter temperatures in the Northern Hemisphere inhibit microbial activity, therefore slowing CH_4 uptake and affecting global budgets (Potter et al., 1996). Site-based measurements suggest that temperature does affect CH_4 oxidation rates, with the highest rates shown in warm, dry soils (Price et al., 2003). However, several models indicate that CH_4 oxidation in soil is insensitive to temperature increase (Jang et al., 2006; Ridgwell et al., 1999; Zhuang et al., 2004).

CH_4 oxidation also varies spatially, with CH_4 oxidation rates shown to be higher in upland soils located adjacent to CH_4 sources such as subalpine wetlands (Wickland et al., 1999). Soil:atmosphere fluxes of CH_4 are also strongly influenced by exposure to an urban land use matrix and atmosphere (Groffman et al., 2006). Also, CH_4 oxidation rates tend to be lower in coniferous forests than in deciduous forests (Jang et al., 2006).

3.3 Current Global Emissions

Estimating global emissions budgets of trace gases such as N_2O and CH_4 has thus far relied on three principal techniques: (1) extrapolation from field measurements, (2) process-based modeling (bottom-up approach), and (3) inverse modeling (top-down approach). Each of these methods contains uncertainties, as they depend upon the complex set of interrelated factors detailed above. However, the increasing numbers of emissions measurements in field studies coupled with refinements of existing models have led to updated global emissions estimates for both N_2O and CH_4.

3.3.1 Current Global Emissions of Nitrous Oxide From Soils

The various microbiological, chemical, and physical parameters that determine N_2O emissions create complex interactions that make extrapolating global emissions budgets difficult and uncertain. Also, the vast majority of studies to date have focused on N_2O emissions from agricultural, not natural, soil sources. However, some global budgets of N_2O emissions from natural soils have been established, based on both top-down and bottom-up estimates (Bouwman et al., 2002; Butterbach-Bahl et al., 2004; Del Grosso et al., 2005; Galloway et al., 2004; Hirsch et al., 2006; Kroeze, 1999; Stehfest and Bouwman, 2006; Werner et al., 2007a). **The AR4 provides a global emissions total for soils under natural vegetation (including upland and riparian soils) of 6.6 Tg N/yr (with an uncertainty range of 3.3 to 9.0 Tg N/yr)** (Denman et al., 2007). This global budget was based on data for the 1990s, provided by key studies from Bouwman et al. (2002).

Since the publication of the AR4, the number of N_2O emissions measurements has been increasing steadily, allowing for improvements in emission models and budgets. In particular, Stehfest and Bouwman (2006) revised previous global N_2O emissions estimates based on 207 field measurements of soils under natural vegetation conditions. This study provides the first comprehensive statistical analysis of published measurement data from N_2O emissions measurements of soils under natural conditions. Table 3-1 summarizes the emissions estimates by ecosystem provided by this statistical approach. However, this statistical model relies upon incomplete coverage of global vegetation zones and a high uncertainty in the developed statistical models. Models such as this are useful for site-specific estimates, but cannot be used to create a global N_2O budget (Stehfest and Bouwman, 2006).

Table 3-1. N_2O Emissions From Soils Under Natural Vegetation

Vegetation Classes	Area *(Mha)*	Emissions Estimates *(Tg N_2O - N/Yr)*
Temperate forest	230	0.147
Open tropical forest	1,598	0.333
Closed tropical forest	854	1.170
Grassland/steppe	2,765	0.403

Source: Stehfest and Bouwman, 2006.

Werner et al. (2007a) recently used the biogeochemical model ForestDNDC-tropica to estimate the global source strength of tropical rainforest soils between 1991 and 2000, at about 1.34 Tg N/yr (0.88 to 2.37 Tg N/yr). According to this study, detailed biogeochemical models provide useful methods for global N_2O emissions estimates; however, there are insufficient field measurements and soil and vegetation data for this model to be applied to other ecosystems (Werner et al., 2007a). Table 3-2 shows the tropical rainforest emissions data from Werner et al. (2007a), separated by the contribution of different continents. Kesik et al. (2005) also used the Forest-DNDC model to estimate N_2O emissions from European forest soils from 1990 to 2000 to be between 77.6 and 86.8 kt N/yr (0.07 to 0.086 Tg N/yr).

Table 3-2. Global N_2O Emissions From Tropical Rainforest Soils

Continents	Area *(10^6 km^2)*	N_2O Source Strength *(Tg N/Yr)*
South America	6.026	0.671 ± 0.154
Africa	3.055	0.344 ± 0.084
Asia	1.432	0.258 ± 0.063
Central America	0.310	0.051 ± 0.011
Oceania/Australia	0.104	0.011 ± 0.003
Total	**10.926**	**1.335 ± 0.315**

Source: Werner et al., 2007a.

While recent advances have been made in collecting and analyzing emissions measurements (Stehfest and Bouwman, 2006) and the source strength of tropical soils has been characterized (Werner et al., 2007a), there still exist a lack of field measurements and significant model uncertainties. Therefore, the estimate provided by Bouwman et al. (and used by the IPCC) of 6.6 Tg N/yr (3.3 to 9.0 Tg N/yr) stands as the most comprehensive estimate of global N_2O emissions from soils under natural vegetation cover. Tropical rainforest soils, with emissions of 1.34 Tg N/yr, clearly play a significant role in the global N_2O emissions scenarios. Figure 3-4 below illustrates the global distribution of N_2O emissions from natural sources, and highlights the significance of tropical rainforests to the global N_2O budget.

3.3.2 Current Global Sink Estimates for Methane

CH_4 budget estimates developed using process-level (bottom-up) measurement techniques contain significant uncertainties due to the aggregation of local measurements, taken on short time scales and at large spatial variability (Mikaloff Fletcher et al., 2004). Inverse modeling is a top-down approach that uses observations of atmospheric mixing ratios, a model of atmospheric transport, and the spatial distributions of sources or sinks to estimate magnitudes and match observations in bottom-up estimates (Mikaloff Fletcher et al., 2004). While inverse modeling also contains uncertainties, the AR4 used a top-down method to estimate the global sink strength of CH_4, with an uncertainty of $\pm$ 5 percent constrained mainly by uncertainty in sink estimates and the choice of CH_4 lifetime used in the mass balance calculation (Solomon et al., 2007).

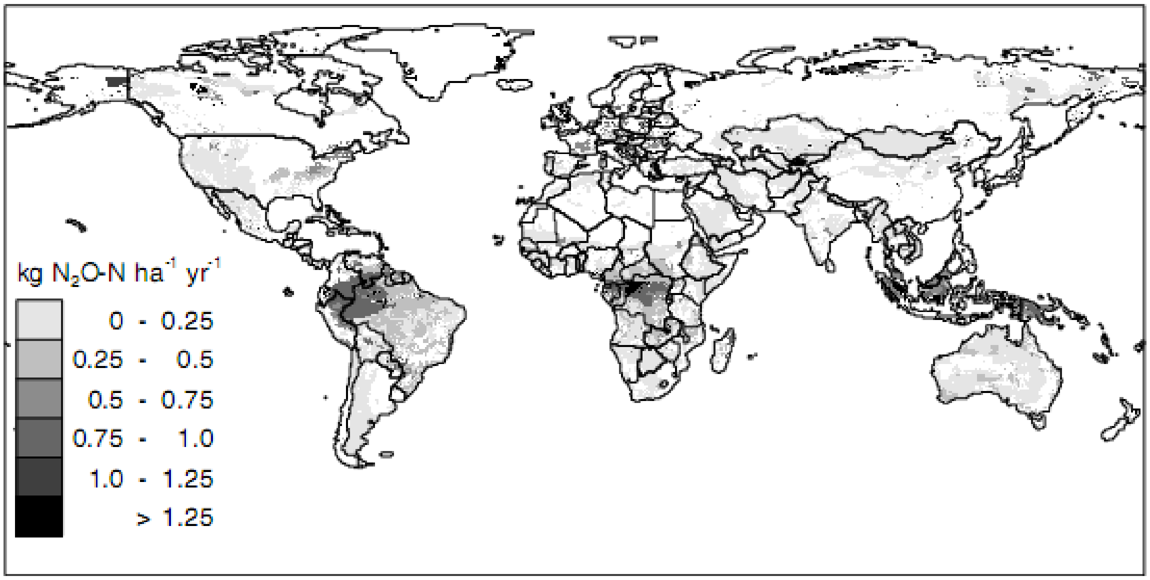

Figure 3-4. Simulated annual N_2O emission rates for natural ecosystems for 1998 land cover. Agricultural area, regrowth forest, arid climate, and polar climate are excluded. (Source: Stehfest and Bouwman, 2006.)

The IPCC reported an overall CH_4 sink strength of soils of 30 Tg CH_4/yr (Solomon et al., 2007), a value that closely reflects estimates made in other top-down studies (Table 3-3).

Table 3-3. Estimates of Global Methane Sink

Study	Data Collection Period	Global Sink Estimate *(Tg CH_4/Yr)*
Potter et al., 1996	1982–1994	17–23
Hein et al., 1997	1983–1989	26
Wang et al., 2004	1988–1997	34
Mikaloff Fletcher et al., 2004	1998–2000	30
Solomon et al., 2007	2000–2004	30

One process-level estimate by Ridgwell et al. (1999) calculated the global CH_4 sink to be 37.8 Tg CH_4/yr. In this study, annual CH_4 sink rates were calculated for aggregated Holdridge life zones, a set of characteristic life zone classes as predicted by climate (Table 3-4). While this process-level estimate did not take into account seasonal moisture fluxes that influence oxidation, the estimate did reveal the importance of dry tropical forest ecosystems as sites of CH_4 uptake, representing 28 percent of the global soil CH_4 sink.

Table 3-4. Methane Consumption by Soils (From Ridgwell et al., 1999)

Aggregated Holdridge Life Zone *(From Leemans, 1992)*	Area *(10^6 km^2)*	Annual Sink *(Tg CH_4/Yr)*
Tundra	10.5	1.05
Cold parklands	2.8	0.59
Forest tundra	8.9	1.45
Boreal forest	15.2	2.99
Cool desert	4.0	1.11
Steppe	7.4	2.36
Temperate forest	10.0	2.98
Hot desert	20.9	3.83
Chapparal	5.6	2.42
Warm temperate forest	3.2	1.24
Tropical semiarid	9.5	4.42
Tropical dry forest	**14.9**	**7.5**
Tropical seasonal forest	**15.1**	**6.64**
Tropical rain forest	8.5	2.92

In light of the similar estimates achieved by various inverse modeling scenarios, the global budget provided by the IPCC of 30 Tg CH_4/yr represents the best estimate of the CH_4 sink strength provided by soils. As indicated by Werner et al., the dry, relatively undisturbed soils of dry and seasonal tropical forest regions provide a significant sink for CH_4.

3.4 Future Scenarios of Nitrous Oxide and Methane Fluxes

Future emissions of N_2O and CH_4 oxidation by soils will depend on the changing human activities on these soils, as well as on climate patterns that are shifting as a result of global climate change. The clearing of land for agricultural use has been shown to lead to increased N_2O emissions and a decreased capacity for CH_4 oxidation. Predictive models of global climate show changed patterns of temperature and precipitation worldwide. As soil moisture is a key determinant of the microbial processes that consume or produce N_2O and CH_4, these shifting climate patterns will likely determine the fluxes of these greenhouse gases into the future.

3.4.1 Future Emissions of Nitrous Oxide From Soils

The AR4, while not specifically predicting future N_2O emissions scenarios, highlights a few studies that have speculated about future emissions from upland and riparian soils. These studies do not make global predictions of N_2O emissions, but rather use site-specific parameters that underscore the importance of N supply, temperature, and soil moisture as regulators of N_2O emissions (Solomon et al., 2007).

Agriculture remains the single biggest source of anthropogenic N_2O (Bouwman et al., 2002). In a model analysis of major U.S. cropping systems, Del Grosso et al. (2005) found that modern agricultural N_2O emission was more than 2 times that of pre-1940 management and about 6 times that of native vegetation. In the future, intensification of modern agricultural techniques that use N fertilizers or N-fixing crops could lead to a further increase in N_2O flux (Neill et al., 2005).

Land use changes that involve clearing of forests for agricultural use can also increase N_2O flux from soils. Logging in the Amazon has been shown to increase N_2O and NO emissions by 30 to 350 percent (Keller et al., 2005). If similar perturbations in land management in tropical rainforests continue, then regional emissions of N_2O (as well as CH_4) from the Brazilian Amazon could be increased by 5 to 10 percent (Keller et al., 2005). As tropical soils are already the largest natural source of N_2O to the atmosphere, any land use changes such as logging or modern agriculture would further increase their contribution to global N_2O emissions.

Future climate changes that affect soil moisture will also affect N_2O emissions: as Khalil and Baggs (2005) pointed out, N_2O emissions are highest from the wettest soils. Riparian soils, with their higher soil moisture content and potentially high N deposition from adjacent agricultural areas, appear to have the potential to create hotspots for N_2O production (Neill et al., 2005). Kesik et al. (2006) used the Forest-DNDC process model to simulate changes in N_2O emissions from EU forests for a climate change scenario for 2030 through 2039. They predicted a 6 percent decrease in N_2O emissions relative to the 1990–2000 period, primarily due to an increase in denitrification with an increase in NO production relative to N_2O.

3.4.2 Future Emissions of Methane From Soils

The AR4 did not predict the future global CH_4 sink strength of upland and riparian soils; however, it did state that future changes to Earth's climate will influence future CH_4 oxidation in these soils.

Temperature and precipitation shifts that accompany global climate change could substantially affect global CH_4 stocks, while a doubling of atmospheric CO_2 would likely change the sink strength only marginally (in the range of -1 to +3 Tg CH_4/yr) (Ridgwell et al., 1999). As in the case of N_2O, anthropogenic land use changes will also significantly affect the degree to which the CH_4 sink potential of upland soils is affected.

Several model studies indicate that CH_4 oxidation in dry, upland soils is relatively insensitive to temperature increase (Ridgwell et al., 1999; Zhuang et al., 2004). However, any temperature changes that alter the amount and pattern of precipitation may significantly affect the CH_4 oxidation capacity of soils (Solomon et al., 2007). As CH_4 oxidation is a function of soil moisture content, if rising temperatures create drier conditions, CH_4 oxidation rates may increase and provide some negative feedback on the accumulation of CH_4 in the atmosphere (Del Grosso et al., 2000). In one model based on temperate soils in New England, results suggest that the extension of snow periods may decrease the annual rate of CH_4 oxidation while summer droughts may increase soil CH_4 oxidation rates of temperate forest soils (Borken et al., 2006).

In addition to the temperature and precipitation effects of climate change, human-induced disturbances to the CH_4 oxidation capacity of soils may also significantly affect the global CH_4 sink. As forests and grasslands are converted to agriculture, the soil CH_4 sink decreases, and if land use changes continue, the decrease is likely to continue into the future. Agricultural land has a much smaller CH_4 uptake rate than untreated soils, especially when treated with N fertilizers (Jang et al., 2006; Suwanwaree and Robertson, 2005). Any intensification of agriculture in the dry tropical forest regions will have especially important effects, due to those regions' significant share of the global CH_4 sink (Ridgwell et al., 1999). Even when converted back to its previous state, agricultural land has a lower oxidation rate than before clearing. This points to an apparent irreversibility of human impacts on these soils, and has implications for future land management strategies as a growing population exerts pressure to use more upland and riparian soils for agriculture (Wuebbles and Hayhoe, 2002).

3.5 Areas for Further Research

The complex interactions of soil microbial, chemical, and physical properties that regulate N_2O and CH_4 fluxes are still being detailed. This complexity is compounded by the rapid climate changes that accompany global warming. The variability among estimates makes it difficult to monitor and model trace gas emissions. In order to improve emissions scenarios of the trace gases N_2O and CH_4, researchers have called for both increasing numbers of field measurements and refined global emissions models.

While field measurements of N_2O have increased steadily in the past several years, incomplete coverage of global vegetation zones remains. Stehfest and Bouwman (2006) point out that far more measurement data are needed, especially for the dry tropical forest, savanna, tundra, and temperate ecosystems not affected by N deposition. These measurements should be carried out over prolonged periods, to improve understanding of the complexity of interactions (Kanerva et al., 2007; Stehfest and Bouwman, 2006). The lack of detailed field measurements was also cited by Werner et al. (2007a) as a crucial step in narrowing the uncertainty range of the biogeochemical models used to generate global inventories of N_2O emissions.

While advances have been made in constraining estimates of CH_4 sources and sinks, estimates of global emissions are still constrained by uncertainties (Solomon et al., 2007). Aggregation of spatially distinct source estimates to achieve global estimates introduces a source of error (Mikaloff Fletcher et al., 2004), as does reliance on incomplete and short-term field measurements (Wang et al., 2004). One improvement recommended by Zhuang et al. (2004) involves combining terrestrial CH_4 flux data with atmospheric CH_4 transport models to more accurately simulate seasonal and interannual fluxes. Also, as seasonally dry ecosystems have emerged as a significant sink of CH_4, more study in these ecosystems is needed (Potter et al., 1996).

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Chapter 4. Oceans, Estuaries, and Rivers

Oceans cover roughly 71 percent of the Earth's surface and have a surface area of approximately 361 million km^2. They are critical to controlling the planet's temperature and serve as both a source and a sink for a number of atmospheric trace gases. This chapter covers emissions from flowing waters. This includes open and coastal oceans, estuaries, and rivers. It does not include emissions from lakes, which are discussed in Chapter 6. Lakes and ponds differ from oceanic, estuarine, and riverine systems in many ways, but a key difference is the effect of active and continuous water movement on biological, chemical, and physical characteristics.

Earth's interconnected waters form a gradient from freshwater rivers, to estuaries where fresh and salt waters mix, through the relatively shallow coastal ocean on the continental shelves, to the deepwater, open ocean. These environments increase in water depth and salinity as distance from shore increases. Nearshore waters are generally shallow and can be well mixed throughout the water column. Sediments and shallow waters are often linked, and these nearshore waters are often heavily impacted by the adjacent land. In deeper water, the water column is often stratified by sharp changes in temperature called thermoclines. These serve to separate shallow and deep waters, which may be only loosely linked. Direct land impacts decrease with distance from the coast. In this chapter, emissions from all of these environments will be assessed, although the primary focus will be on the full-salinity coastal and open ocean. The oceans are believed to be one of the major natural sources of N_2O to the atmosphere. In the most recent IPCC assessment (the AR4: Denman et al., 2007), natural emissions from oceans were estimated at 3.8 (1.8 to 5.8) Tg N/yr. Oceans, estuaries, and rivers are thought to be a relatively minor natural source of CH_4 and are not explicitly estimated in the 2007 IPCC report or in the earlier version of this report (U.S. EPA, 1993).

4.1 Description of Emission Source

N_2O in aquatic environments is produced by microbial communities using the processes of nitrification and denitrification, through a series of complex and interacting pathways. N_2O is produced in both the water column and in sediments. CH_4 is also produced in both sediments and the water column, although the relative importance of the sediments is much greater. The environments of open ocean, coastal ocean or continental shelf, estuaries, and rivers differ in the quantity and source of their organic inputs, nutrient inputs, water depth (and therefore the amount of interaction between sediments and the water column), mixing dynamics, and salinity. Because of these differences, their emissions of trace gases can be very different.

Fluxes from the deep open ocean come from the water column, not the sediments. Deep ocean sediments, because of their great depth and low organic matter inputs, are thought to have little impact on N_2O and CH_4 budgets. The continental shelves occupy a much smaller area than the open ocean, but their emissions per area are greater. Estuaries and rivers typically have higher organic inputs and nutrient levels than the oceans. Because they are relatively shallow, mixing is active and commonly extends throughout the entire water column. This mixing can transport gases produced in the sediments into near-surface water where they can be released to the atmosphere.

The most recent IPCC assessment of greenhouse gas sources estimates that oceans, coastal zones, estuaries, and rivers release roughly 5.5 Tg N/yr. Oceans (3.8 Tg N/yr) are categorized as a natural source, while the other aquatic environments (releasing 1.7 Tg N/yr) are classified as anthropogenically controlled (Denman et al., 2007). The oceans and upland soils under natural vegetation are the major natural sources of N_2O to the atmosphere. At 3.8 Tg N/yr, oceans are thought to contribute roughly 21 percent of global emissions. The AR4 does not explicitly estimate the flux of CH_4 from oceanic, estuarine, and riverine environments. However, it cites literature estimates that range from 4 to 15 Tg

CH_4/yr and does not treat the various environments separately. If the aquatic source of CH_4 is on the order of 4 to 15 Tg CH_4/yr, it would contribute roughly 1 to 3 percent of the global source of CH_4.

4.2 Factors That Influence Emissions

This chapter discusses aquatic N_2O and CH_4 emissions separately, because of differences in the importance of their relative contributions as well as in the factors that control fluxes. It also treats the environments of open ocean, coastal ocean (continental shelf), estuaries, and rivers separately.

4.2.1 Nitrous Oxide

Nitrification and denitrification are often closely coupled in aquatic systems, where denitrification may be limited by the rate of production of nitrate (NO_3) through nitrification (Capone, 1991; Suntharalingam and Sarmiento, 2000). N_2O production and consumption at low oxygen levels is complex. Concentrations may be low in anoxic waters due to denitrifiers using the gas for respiration, but may be higher in suboxic waters or on the periphery of anoxic areas, suggesting production in these environments. In a summary analysis integrating 136 published reports of denitrification rates, Piña-Ochoa and Alvarez-Cobelas (2006) found that annual rates of denitrification were highest in lakes, followed by rivers, coastal ecosystems, and estuaries. Rates were highly correlated with NO_3 levels, which explained 70 percent of the observed variability, and were inversely correlated with O_2 levels.

Oxic means "containing oxygen." **Anoxic** means "without oxygen." **Suboxic** means "oxygen deficient" and may describe the transition zone between the two extremes.

Reactive N refers to forms of N that can be used by bacteria. It includes inorganic reduced forms (ammonia {NH_3] and ammonium [NH_4]), inorganic oxidized forms (nitrite [NO_2], nitrate [NO_3], nitric acid [HNO_3], nitric oxide [NO], and nitrous oxide [N_2O]), and organic forms (urea, amines, and proteins). Nitrogen gas (N_2) is the most common form of N but is chemically inert and cannot be used by bacteria.

Nitrogen is a critical nutrient for plant growth, and productivity in many environments is controlled by its availability. Adding usable N increases crop yields, and man's use of fertilizers has resulted in changes in the N cycle on a global scale. It is estimated that anthropogenic sources of reactive N increased by an order of magnitude from the late 19th century to the early 1990s, and that human sources now make up 40 percent of the global total (Galloway et al., 2004). Much of the N added to land surfaces and cycled through human food and energy production is carried away from its original site of introduction. This may occur, for example, through volatilization and runoff. Green et al. (2004) calculate that the total global N flux from river basins has doubled since the pre-industrial period as a result of losses from the land. Understanding the fate of N added to the land has been an active area of research for many years, for economic as well as environmental reasons. The anthropogenic changes in the N cycle have implications for aquatic emissions of N_2O, since rates of nitrification and denitrification depend on reactive N. The anthropogenic influence on emissions decreases with distance offshore and impacts the approaches used to estimate fluxes.

Gases dissolved in water bodies will come into balance with their concentration in the air above. The balance (or equilibrium) concentration depends on temperature, salinity, and the how soluble the gas is in water. If a dissolved concentration is higher than the equilibrium concentration, it is termed "**supersaturated.**" Gas will be lost to the air, and thus the water will be a source of the gas. If it is lower than the equilibrium concentration, it is "**undersaturated.**" It will absorb gas from the air, and thus will act as a sink to the atmosphere.

Early studies of oceanic N_2O found widespread supersaturations of the gas, which varied seasonally. This suggested that oceans could be an important atmospheric source (Nevison et al., 1995). N_2O production in the surface layer is thought to be small because oxygen inhibits denitrifiers and light inhibits nitrifiers, so subsurface production and then transport to the surface is believed to occur. In the open ocean, high apparent oxygen utilization (AOU, a measure of aerobic decomposition) in the 100 meters below the near-surface mixed layer was found to be highly correlated with both N_2O production and elevated surface concentrations. This is consistent with N_2O production by nitrifiers. Sampling suggests that high dissolved levels are seen in biologically productive upwelling regions along the eastern margins of ocean basins where low oxygen areas are also seen. Concentrations closer to atmospheric equilibrium or even small undersaturation are seen in the oceanic gyres (Nevison et al., 2003; Suntharalingam and Sarmiento, 2000). Making up less than 1 percent of the ocean's volume, low-oxygen areas are located primarily in the northeast tropical Pacific, the northern Arabian Sea, and off the coast of Peru. Based on model calculations, Suntharalingam et al. (2000) suggest that these regions could make up roughly 25 percent of the total open ocean source of N_2O.

AOU (**a**pparent **o**xygen **u**tilization) is the difference between a measured dissolved O_2 concentration and that expected when at atmospheric equilibrium saturation. It is therefore a measure of the sum of the biological activity that has occurred since last surface exposure.

Concentrations of N_2O are also high relative to atmospheric equilibrium in coastal and estuarine waters and in general have been found to be inversely correlated with salinity. This suggests a land impact and then losses with mixing (Bange et al., 1996). Measurements indicate that N exported by rivers to estuarine systems is much less than the N put into rivers, meaning that it is transformed within the river system. Most of this N is lost by denitrification or burial. A range of denitrification rates in rivers have been measured. Lowest rates are generally in unpolluted systems and highest rates are where pollution inputs are significant (Seitzinger et al., 2006). The fraction of N removed by denitrification may be affected by river geometry (length and depth), flow rate and water residence time, oxygen content, sediment organic content, and season/temperature (Seitzinger and Kroeze, 1998). In oxygenated water, ammonium is quickly used by nitrifying bacteria. Nitrification rates have been found to be influenced by ammonium concentrations, temperature, oxygen, suspended particulate material, and light (Seitzinger and Kroeze, 1998).

An oceanic **gyre** is a relatively stationary region of the open ocean with a circular current created by the Coriolis effect. Gyres are permanent large-scale water circulation features whose circulation tends to isolate them from the rest of the ocean.

4.2.2 Methane

Sampling conducted in the 1960s and 1970s found that surface aquatic waters in general were commonly supersaturated in CH_4 with respect to atmospheric equilibrium, indicating that they were likely small sources to the atmosphere. Since surface waters are highly aerobic, it was thought unlikely that these levels were generated in place. Possible sources of oceanic CH_4 include horizontal transport, diffusion from sediments, in situ production, and, in the coastal ocean, submarine groundwater discharge. Recently, Karl et al. (2008) have also proposed a possible aerobic metabolic pathway that produces CH_4 from an organic, phosphorous-containing compound. In the open ocean, depth profiles frequently reveal a subsurface maximum, from which the gas is mixed to the surface and released (Holmes et al., 2000). Oremland (1979) hypothesized that this CH_4 was produced in the anaerobic guts of zooplankton and fish. Current thought is that the subsurface maxima occur at the pycnocline, and that CH_4 is produced from the suspended organic particles that accumulate there (Holmes et al., 2000). Budget calculations suggest that flux across the air-water interface is also from production within anaerobic micro-environments within

A **pycnocline** is a water layer with a large change in density caused by temperature or salinity. When caused by temperature, it is usually called a **thermocline**. Mixing is impeded across such a layer.

particles in the near-surface. This production was found to be independent of diurnal cycles, indicating that it is not related to photosynthesis, grazing, and the vertical migrations of zooplankton (Holmes et al., 2000). Mixing and loss across the air-water interface is calculated to be the major sink of CH_4 in seawater. A model that allowed particles to settle and decompose according to simple mixing/diffusion equations was able to reproduce oceanic CH_4 profiles (Nihous and Masutani, 2006). This suggests that these processes did a good job describing the system and that these particles were the primary CH_4 source.

Upwelling areas, with higher rates of organic material falling to depth and lower O_2 levels, are sites of enhanced CH_4 production and flux (Sansone et al., 2001; Rehder et al., 2002). Rapid transport to the air-water interface also decreases time in the oxygenated water column and therefore reduces oxidation.

In shallower environments closer to continents, sedimentary methanogenesis is thought to contribute to water column concentrations. Continental shelf waters may also receive inputs from hydrocarbon seeps and from hydrate reservoirs. These sources are discussed in Chapters 7 and 8. The relative importance of submarine groundwater discharge varies significantly, but in some areas it has been found to account for 83 to 99 percent of the total CH_4 input to the water column (Bugna et al., 1996). Although its global significance is largely unknown and the driving factors poorly understood, groundwater discharge into coastal waters may rival riverine inputs in many systems and serves as a transport mechanism delivering nutrients and other dissolved compounds such as CH_4 offshore (Kim and Hwang, 2002; Slomp and Van Cappellen, 2004). Bange et al. (1994) and Rehder and Suess (2001) suggest that continental shelves may contribute the majority of oceanic CH_4 sources because they receive high-CH_4 waters from the continents and are areas of active mixing.

Upwelling refers to a pattern of coastal and open water oceanic circulation. It is created by persistent winds blowing across the ocean surface. As winds move surface waters, they are replaced by deeper waters that are richer in nutrients and can support increased phytoplankton growth. Phytoplankton in turn support higher populations of fish and other consumers, making these areas some of the most productive fisheries in the world. Upwelling occurs along some coasts as well as along the equator. Regions of coastal upwelling include coastal Peru and Chile, the Arabian Sea, western South Africa, eastern New Zealand, and the coast of California.

The distribution of CH_4 in some estuaries appears to be controlled by inputs from rivers and simple mixing between river waters and lower-CH_4 seawater (de Angelis and Lilley, 1987). Mixing behavior is more complex in other estuaries, with production, oxidation, and de-gassing occurring (de Angelis and Scranton, 1993; Abril and Iverson, 2002; Sansone et al., 1999). Middelburg et al. (2002) found that CH_4 was only partially correlated with salinity in well-mixed, long-residence-time European estuaries. In these systems, CH_4 initially decreased as salinity rose, then increased to a maximum at medium to high salinities before decreasing again offshore. In river-dominated systems with relatively short residence times, there was little correlation between CH_4 and salinity.

4.3 Current Global Emissions

This section discusses N_2O, then CH_4 emissions. For N_2O, emissions from rivers and estuaries, the continental shelves, upwelling regions, and the open oceans will be estimated separately. Emissions from all of the environments are summarized in Section 4.3.1.4.

4.3.1 Current Ocean, Estuarine, and Riverine Nitrous Oxide Fluxes

Global estimates of N_2O fluxes have generally been made through two approaches: (1) gas transfer calculations that combine measurements of near-surface concentrations and wind speed through gas transfer coefficients and (2) calculations based on organic matter decomposition, using the “yield” of N_2O as a fraction of nitrification and denitrification or nitrate. Anthropogenic sources of N dominate natural sources in nearshore environments, so efforts to estimate emissions from these areas have used the well-developed literature on anthropogenic N export to rivers to calculate cycling through nitrification and denitrification and therefore N_2O production. Both of these approaches are considered “bottom up” and use a combination of inventories, measurements, and emission coefficients to calculate fluxes. Recently, the expanding database on atmospheric N_2O mixing ratios and the development of inverse modeling techniques has permitted the use of this “top-down” approach to constrain the distribution and magnitude of fluxes. None of the estimates of emissions from aquatic environments are based on actual flux measurements using chambers or eddy correlation techniques.

4.3.1.1 River and Estuarine Nitrous Oxide Fluxes

Although rivers and estuaries are not large areas globally, they are active sites for aquatic productivity and biogeochemical cycling. Flux estimates are relatively high in comparison to those from the open ocean, which led to the suggestion that oceanic fluxes were underestimates because they did not include coastal, estuarine, or riverine emissions (Bange et al., 1996; Bange, 2006a). Although shallow water emissions are relatively high (Table 4-1) as a result of the impact of humans on the N cycle, only a modest fraction of this N_2O arises from natural N sources (Seitzinger et al., 2000). For this reason, although these river and estuarine fluxes were newly added to global sources in the AR4 (Denman et al., 2007), they were classified as anthropogenic, rather than natural sources.

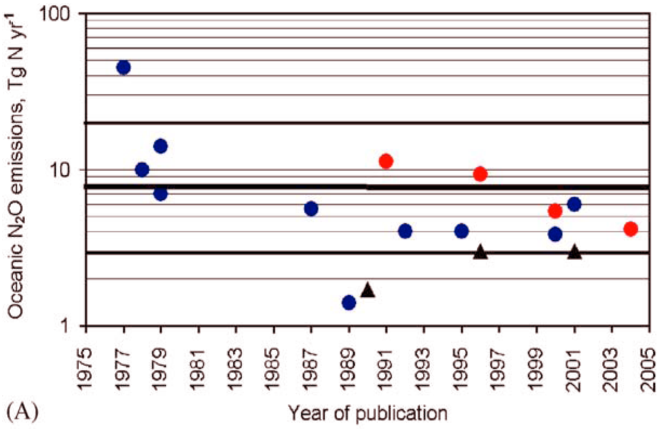

Figure 4-1. Global N_2O ocean emission estimates. Red points include coastal fluxes; black triangles are IPCC estimates. Horizontal lines mark the 2001 IPCC mean and standard deviation. From Bange, 2006b.

The first estimates of these river and estuarine fluxes were based on surface dissolved concentrations and gas-transfer calculations (Bange et al., 1996). More recent estimates are based on estimating N inputs and calculating the fraction released as N_2O (Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Kroeze et al., 2005). The basic assumption for these calculations is that N_2O production is related to rates of nitrification and denitrification, which are in turn related to inputs of N. Published estimates of aquatic N inputs have been based both on inventories (Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Seitzinger et al., 2000) as well as models (Boyer et al., 2006; Dumont et al., 2005; Schaefer and Alber, 2007). However, the actual production of N_2O from nitrification and denitrification has been an assumed constant fraction of the N_2 produced, 0.3 percent N_2O:N_2 for denitrification in rivers and estuaries with low N loadings (0 to 10 kg N/ha/yr) and 3 percent for those with high N inputs (> 10 kg N/ha/yr) (Seitzinger and Kroeze, 1998). The same constants were used for N_2O yield from nitrification, largely because there were few data available. Seitzinger et al. (2000) and Seitzinger (1988) indicate that laboratory and field studies have estimated the ratio of N_2O to N_2 generally between 0.1 and 0.5 percent, with values ranging up to 6 percent in highly polluted sediments, although the database is quite small.

Clearly this is a critical but poorly known value in calculating emissions and depends upon a suite of biogeochemical variables (Schlesinger et al., 2006). The importance of this ratio may be demonstrated by comparing global estimates made by Capone (1991), who assumed different yield values—0.3 percent for nitrification under aerobic conditions, 1 percent for nitrification linked to denitrification in low-oxygen waters and sediments, and 5 percent for denitrification. Although estimates of N aquatic reservoirs are also derived differently, Capone's nearshore/estuarine N_2O flux of 0.74 Tg N/yr is appreciably higher than that made by the Seitzinger/Kroeze research group (0.22 Tg N/yr, see Table 4-1).

Although natural aquatic N inputs were known to vary geographically, Seitzinger and Kroeze (1998) calculate natural N contributions by assuming a globally constant natural N input rate. They use a model to calculate anthropogenic sources (human sewage, fertilizer, and atmospheric deposition). The model does not explicitly include either agricultural or non-agricultural soil N fixation inputs to watersheds, although these were known to be large. They calculate that natural river and estuarine DIN (dissolved inorganic nitrogen, often the most abundant and available N form) makes up about 25 percent of total inputs. Recent calculations by Boyer et al. (2006) suggest a significantly different breakdown. This more sophisticated model also finds important regional differences in natural N sources. Boyer et al. (2006) estimate natural N exports to rivers based on calculations of biological N fixation in forests and other natural vegetation with minor inputs from N fixation by lightning. They find that natural sources dominate riverine N inputs in Africa, Latin America, and Oceania. Anthropogenic sources dominate in Europe and the former Soviet Union, North America, and Asia. These calculations indicate roughly equal N export from natural and anthropogenic sources rather than the 25:75 percent breakdown of Seitzinger and Kroeze. Overall, anthropogenic sources are concentrated in the Northern Hemisphere, but as land use changes and food and energy production patterns continue to change, this geographic distribution will be altered. Asian sources, with high inputs and a growing population and economic base, were found to drive the overall global N budget.

Dumont et al. (2005) also describe a more sophisticated and spatially explicit model based on the work of Seitzinger and Kroeze (1998). Although modeling DIN rather than total N, they also find that natural biological N fixation is the dominant N source over large areas. Globally, the model calculates that natural N sources contribute 36 percent of total exports to rivers; the authors hypothesize that this fraction may be somewhat lower than that for total N because natural systems export N primarily in forms other than DIN.

These more sophisticated models suggest that the IPCC AR4 classification of all riverine and estuarine N_2O as wholly anthropogenic may be an oversimplification. Given a conservative assumption that 41 percent of the N exported has natural origins (an average of the Boyer and Dumont models) rather than 25 percent, by ratio riverine N_2O from natural sources would be 8 percent of the total rather than 5 percent and estuarine N_2O would be 15 rather than 9 percent. Natural N_2O fluxes are then calculated to be on the order of 0.09 (rivers) to 0.24 (estuaries) Tg N/yr, for a total of 0.33 Tg N/yr (Table 4-1). This estimate is about 19 percent of the AR4 estimate from rivers, estuaries, and coastal environments, assumed to have wholly anthropogenic sources (1.7 Tg N/yr, Table 4-1). It is on the same order, however, as N_2O sources such as fossil fuel combustion and industrial processes, biomass burning, human excreta, and anthropogenic atmospheric deposition (Denman et al., 2007).

Table 4-1. River and Estuarine Nitrous Oxide Emissions (Tg N/Year)

Habitat	Flux (Range) 1990s	Source	Comment
Rivers	1.05 (0.19–1.87)	Seitzinger and Kroeze, 1998; Seitzinger et al., 2000	Only 5% (0.05 Tg N/yr) considered natural; range based on use of low and high emission factors
Rivers	0.05	Galloway et al., 2004	Natural only; cites Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Seitzinger et al., 2000, as basis
Rivers	1.26	Kroeze et al., 2005	Cited as basis for AR4; based on N export model; mix of natural and anthropogenic
Rivers	**0.09** **(0.08–0.10)**		**8% of range of total estimates, midpoint (Boyer et al., 2006; Dumont et al., 2005)**
Nearshore/estuaries	0.74	Capone, 1991	Estimated from N_2O released during nitrification and denitrification
Nearshore/estuaries	3.0 (2.34–3.63)	Bange et al., 1996	Midpoint of range; mix of natural and anthropogenic
Estuaries	0.22 (0.07–0.69)	Seitzinger and Kroeze, 1998; Seitzinger et al., 2000	Only 9% (0.02 Tg N/yr) considered natural; range based on use of low and high emission factors
Estuaries	0.02	Galloway et al., 2004	Natural only; cites Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Seitzinger et al., 2000, as basis
Estuaries	0.25	Kroeze et al., 2005	Cited as basis for AR4; based on N export model; mix of natural and anthropogenic
Estuaries	**0.24** **(0.03–0.45)**		**15% of range of total estimates, midpoint (Boyer et al., 2006; Dumont et al., 2005)**
Rivers, estuaries, and coast	1.7 (0.5–2.9)	Denman et al., 2007 (AR4)	Considered all anthropogenic; new source added since the IPCC Third Assessment Report; cites Kroeze et al., 2005; Nevison et al., 2004 (upwelling)
Rivers and estuaries	**0.33** **(0.11–0.55)**		

4.3.1.2 Coastal Ocean Nitrous Oxide Fluxes

The coastal ocean bordering the continents can be broken into two systems of importance for N_2O fluxes: the continental shelves and upwelling regions. Making up roughly 7 percent of the ocean's area, the continental shelves are commonly defined as the relatively flat regions, less than 150 to 200 meters deep, adjacent to continents. All are sites of greater primary productivity, biological activity, and sedimentation than the deeper open ocean. Upwelling areas, where nutrient-rich deep water is brought to the ocean surface, are usually located along the eastern margins of ocean basins. These regions support enhanced primary productivity, which in turn supports greater populations of fish and other consumers. Regions of upwelling include coastal Peru, Chile, the Arabian Sea, western South Africa, eastern New Zealand, and the California coast.

Continental Shelves

The continental shelves receive riverine and estuarine drainage and are therefore impacted by anthropogenic activities. Most of the N input to rivers and estuaries, however, is not exported to coastal waters. Although the amount exported from rivers to estuaries varies, it is commonly estimated at about 25 percent globally and can vary from roughly 8 to 40 percent (Boyer et al., 2006; Schaefer and Alber, 2007). Export from estuaries is dependent on a number of variables such as estuarine water residence time, extent of intertidal area, and sediment O_2 consumption. Seitzinger and Kroeze (1998) estimate that perhaps 50 percent of external DIN inputs to estuaries are removed by denitrification. These approximations would suggest that perhaps 10 to 50 percent of the N input to rivers and estuaries may reach coastal waters. The continental shelves also receive N via atmospheric deposition and from the adjacent continental slope waters.

Because terrestrial N exports are not the major driver of N_2O production on the continental shelves, emissions estimates for these areas have been made using different methodologies than those for rivers and estuaries. Seitzinger and Giblin (1996) report a model correlating rates of shelf denitrification with phytoplankton primary productivity through rates of sediment O_2 uptake. Predicted rates varied with latitude, with higher rates at lower latitudes. Grouping latitudes into three classes, Seitzinger and Kroeze (1998) use this relationship to estimate average global denitrification rates and then apply the constant $N_2O{:}N_2$ fraction for river and estuarine lower N loading to calculate emissions. Rates of nitrification are estimated differently, by assuming an average shelf depth and constant nitrification rates from 25 to 50 meters deep and below 50 meters. The emission of N_2O, therefore, is calculated as a simple function of the area of sediment and water surface multiplied through constant rates. Natural N sources to the continental shelf are estimated by assuming that rivers and estuaries supply 40 to 50 percent of total N inputs (50 percent of which are anthropogenic in origin). The balance is assumed to be from the open ocean and considered natural in origin (Seitzinger and Kroeze, 1998). Natural sources would therefore make up 75 percent of the total. Note that Seitzinger and Kroeze conservatively assume that only 50 percent of river and estuarine N inputs to continental shelves were of anthropogenic origin, rather than 75 percent as their model had suggested (see discussion above). This conservative figure would be in better agreement with later modeling results. Other estimates of continental shelf N_2O flux are based on surface dissolved concentrations and gas-transfer calculations (Bange et al., 1996; Rhee et al., 2009) and nitrification/denitrification yields and oceanic reservoir estimates (Capone, 1991). Although some of these flux estimates tend to be higher than those of Seitzinger and Kroeze (Table 4-2), all are highly uncertain. The Capone (1991) estimate includes both coastal and upwelling systems. The most recent estimate is that of Rhee et al. (2009), based on samples from the Atlantic basin. They find appreciably lower levels of N_2O in coastal surface waters than Bange and co-workers, with calculated fluxes similar to those of Seitzinger and Kroeze. If the fraction of natural N sources is assumed to be 75 percent as in Seitzinger and Kroeze (1998) and in agreement with the more recent Boyer and Dumont model results, using all four estimates for the continental shelf results in a range of estimates of 0.37 to 3.52 Tg N/yr, differing by about an order of magnitude. The midpoint of this range is a flux of 1.5 Tg N/yr (Table 4-2).

Upwelling Regions

Sampling of oceanic dissolved N_2O concentrations has found unusually high levels of supersaturation in the vicinity of upwelling areas. Since N_2O is largely produced in subsurface waters due to light inhibition, upwelling provides a rapid way to the surface, where it degasses. Areas of upwelling are also regions of enhanced primary productivity, which results in higher fluxes of organic material sinking into mid-waters. In turn, this organic input depletes O_2 levels and creates conditions favorable for denitrifiers as well as nitrifiers.

Table 4-2. Coastal Ocean Nitrous Oxide Fluxes (Tg N/Year)

Habitat	Flux (Range)	Source	Comment
Coast/upwelling	4.7	Capone, 1991	Estimated from N_2O released during nitrification and denitrification
Coastal ocean and marginal seas	2.22 (1.74–2.71)	Bange et al., 1996	Midpoint of range; mix of natural and anthropogenic
Continental shelves	0.64 (0.64–6.43)	Seitzinger and Kroeze, 1998; Seitzinger et al., 2000	Only 75% (0.48 Tg N/yr) considered natural; range based on use of low and high emission factors
Continental shelves	0.4	Galloway et al., 2004	Natural only; cites Seitzinger and Kroeze, 1998; Kroeze and Seitzinger, 1998; Seitzinger et al., 2000, as basis
Coastal ocean	0.37 (0.23–0.51)	Rhee et al., 2009	Natural (75% of original figures of 0.31–0.68 TgN/yr)
Continental shelves	**1.5 (0.37–3.52)**		**75% of range of total estimates (Seitzinger et al., 2000; Boyer et al., 2006; Dumont et al., 2005)**
Upwelling	0.26 (0.2–0.32)	Bange et al., 1996	Midpoint of range
Upwelling	1.0	Suntharalingam et al., 2000	Model for low-O_2 zones; given as model best fit (25% of fixed ocean flux of 3.6 Tg N/yr)
Upwelling	0.2 (0.06–0.34)	Nevison et al., 2004	Range given as ∀ 70%; classified as anthropogenic in AR4
Upwelling	0.003 (0.002–0.003)	Rhee et al., 2009	Uses smaller area for extrapolation
Upwelling	**0.37 (0.0003–1.0)**		**Average of reported fluxes**
Coastal ocean (continental shelf and upwelling)	**1.87 (0.37–4.52)**		

Although the areas where strong upwelling occurs are relatively well known, the intensity of the process depends upon wind speed, velocity, and duration and can therefore be quite episodic. This also complicates both sampling and modeling efforts, since air-sea flux calculations commonly employ long-term means of wind speeds.

Regional estimates suggest that areas of upwelling contribute significantly to the global oceanic source. Law and Owens (1990) calculate that upwelling in the northwest Indian Ocean, an area covering only 0.43 percent of the global ocean, could contribute 5 to 18 percent of the total oceanic flux. Measurements in the Arabian Sea over several years suggest that conservative estimates of annual flux range from 0.35 to 0.48 Tg N/yr, on the order of 13 to 17 percent of oceanic flux (Lal and Patra, 1998). Sampling over only a 2-month period in the Somali Basin, De Wilde and Helder (1997) calculate that even over this brief time, emissions were 0.4 to 0.8 percent of the oceanic total from an area < 0.011 percent of the world ocean surface. Upstill-Goddard et al. (1999) calculate a 6-month N_2O flux of 0.26 to 0.48 Tg N during the southwest monsoon and inter-monsoon transition in the northwestern Indian Ocean based on in situ wind speeds and surface N_2O levels. Their measurements suggest that seasonal changes in wind speed are the dominant control on air-sea exchange. Bange et al. (2001) summarize N_2O measurements from the Arabian Sea from 1977 to 1997; emissions ranged from 0.21 to 0.44 Tg N/yr and were dominated by fluxes during monsoonal periods. In addition, atmospheric N_2O sampling at the coast of California has captured enhanced N_2O levels for periods lasting for several days that can be traced to upwelling (Lueker et al., 2003). This suggests that emissions resulting from upwelling have a significant regional impact. In the past, denitrification in upwelling regions may have been a major driver of atmospheric N_2O variability (Agnihotri et al., 2006).

Global estimates of the upwelling N_2O flux have been made using several approaches. Bange et al. (1996) calculate a mean surface saturation level from tabulated literature reports and derive a flux based on average wind speeds and gas-transfer coefficients. They estimate that upwelling areas, covering 0.2 percent of the world ocean, contribute 3 percent of the global aquatic N_2O total flux (Table 4-2). Suntharalingam et al. (2000) use a modeling approach that treats N_2O as a tracer in an ocean general circulation model. Model results are then compared to observed profiles of water column dissolved N_2O distributions. The authors find that although the modeled low-O_2 regions occur primarily in known upwelling areas (to the north and south of the equator in the eastern tropical Pacific and in the northwest Arabian Sea), these environmental conditions were not limited to narrow coastal bands and were found to include deep-water O_2 minima zones existing over hundreds of km^2. Model results suggest that low-O_2 regions could supply a significant fraction of the global oceanic source. Model simulations in which 25 and 50 percent of the oceanic flux was attributed to these regions had the best fit to observed distributions. If the global oceanic source is on the order of 4 Tg N/yr (Nevison et al., 1995; Table 4-3), this suggests that the flux from low-O_2 regions would be 1 to 2 Tg N/yr.

Nevison et al. (2004) extend an upwelling atmospheric flux model developed by Lueker et al. (2003) to estimate the fluxes required to account for enhanced atmospheric N_2O levels. The model is driven by wind and sea surface temperature data (which therefore predict the occurrence of upwelling) and by relationships between temperature and subsurface N_2O levels. Verifying the model is difficult due to spatial and temporal mismatches between modeled surface N_2O levels and observations of annual means, but the two appear to be consistent. However, in regions of large subsurface O_2 deficits (Peru, Mexico, the Arabian Sea), the model is thought to significantly underestimate the amount of N_2O brought to the surface—by a factor of 3 or more. Because of this, Nevison et al. (1995) suggest that traditional gas-transfer flux calculations are likely to underestimate coastal upwelling sources by a factor of 3 to 8 from poorly sampled regions such as the western coasts of South America and Africa.

Comparison between regional and global upwelling fluxes reveals an apparent disagreement, although uncertainties are large. Much of the disagreement may be due to the relatively sparse global database on N_2O from these small areas and to mismatches in spatial and temporal resolutions, since the upwelling phenomenon is episodic. Global upwelling estimates are on the order of 0.5 Tg N/yr (Table 4-2). However, regional/site-specific estimates from small areas and for periods of less than 1 year, as discussed above, are similar in size and range from 0.21 to 0.48 Tg N. If we simply sum regional and short-term estimates and conservatively assume that emissions are zero when there are no measurements, upwelling from the Arabian Sea, Somali Basin, and northwestern Indian Ocean alone would release 0.5 to 1.0 Tg N/yr.

4.3.1.3 Open Ocean Nitrous Oxide Fluxes

Since the vast proportion of anthropogenic N input to aquatic systems is consumed and recycled in rivers and estuaries, Galloway et al. (2004) suggest that the terrestrial and open ocean N budgets are essentially disconnected. Although there is some anthropogenic impact on the amounts of atmospheric N deposition, contributions decrease away from continental regions and all oceanic N_2O emissions are considered natural in origin. Estimates of open ocean N_2O fluxes have been made using several different techniques, which are discussed in more detail below. Initial calculations used measurements of dissolved concentrations in surface waters and estimates of gas-transfer based on wind speeds. Estimates have also been made using observations of the correlation between dissolved N_2O and other gases. Recently, inverse modeling techniques have applied to making relatively coarse scale emissions estimates such as Northern vs. Southern Hemisphere and land vs. ocean fluxes.

The majority of aquatic N_2O flux estimates have been made for the open ocean. Surface sampling during the 1970s and 1980s demonstrated that much of the surface of the world ocean was supersaturated with respect to atmospheric levels of N_2O, indicating that it was a likely net global source. Nevison et al. (1995) tabulate more than 60,000 N_2O measurements and use gas-transfer calculations to estimate a global flux of 4 Tg N/yr, with a range of 1.2 to 6.8 Tg N/yr. This large range was thought to be largely due to uncertainties in gas-transfer coefficients and to seasonally biased data collection. Incomplete geographic and temporal sampling coverage contributes additional uncertainty. Other early global estimates, made by Capone (1991) and Najjar et al. (1994) using estimates of N_2O yield from nitrification and denitrification, are in rough agreement (4 to 5.8 Tg N/yr; Table 4-4).

Oligotrophic means "nutrient-poor" and therefore usually having low productivity. **Euphotic** means "having light"; **aphotic** means "having no light."

Based on observations of water column profiles, N_2O is thought to be produced at intermediate depths in the ocean. Nitrification is believed to be the dominant source process because N_2O and O_2 are commonly inversely correlated and N_2O and NO_3 are positively correlated. Based on isotopic measurements of N_2O in the oligotrophic subtropical North Pacific, Dore et al. (1998) find that nitrification in the lower euphotic and upper aphotic zones (100 to 300 meters) could supply 70 to 90 percent of the oceanic N_2O source.

Nevison et al. (1995) and Global Emissions Inventory Activity (GEIA) inventories based on this work (Bouwman et al., 1995; see Table 4-3) estimated that most oceanic emissions (45 percent) are located in the Southern Ocean (30 to 90°S), where high winds combine with high levels of supersaturation. Some areas in subtropical gyres and in the North Atlantic may change seasonally from weak sinks (winter) to weak sources (summer).

GEIA (the **G**lobal **E**missions **I**nventory **A**ctivity) is part of the International Geosphere-Biosphere Program (IGBP), an international research organization that studies global change and earth system science. The IGBP is funded by roughly 40 countries, among which the United States is the single largest contributor. GEIA develops gas and aerosol emissions inventories of both natural and anthropogenic sources and contributes to global assessments such as the IPCC.

The strong correlation between the degree of N_2O saturation relative to atmospheric equilibrium and AOU provides an additional way to estimate N_2O flux by estimating N_2O production relative to O_2 consumption. Suntharalingam and Sarmiento (2000) use this relationship in combination with a global ocean biogeochemical model. They derive an open ocean source (excluding N_2O from low-O_2 regions such as upwelling) that is similar to those based on gas-transfer estimates (Table 4-4). However, there are difficulties in using this relationship to estimate fluxes. There is variability in the oceanic N_2O saturation/AOU relationship that may be the result of differences in the N_2O/NO_3 yield due to the sensitivity of nitrifiers to O_2 (Nevison et al., 2003). These authors find that the correlation of N_2O supersaturation and AOU is a poor predictor of the N_2O yield/mole O_2 consumed because the relationship is strongly affected by mixing. By calculating N_2O production relative to O_2 consumption as a function of O_2 and depth, Nevison et al. (2003) estimate the oceanic N_2O production at 5.8 Tg N/yr. They suggest this figure could be decreased by perhaps 1 to 3 Tg N/yr by denitrifier consumption in low-O_2 environments. Approximately 70 percent of production was calculated to occur in the tropics, between 30°N and 30°S, in contrast to earlier estimates of flux dominance by southern latitudes (Table 4-3).

The apparent disagreement in the relative importance of southern latitude oceans was examined in more detail by Nevison et al. (2005). They used the 10-year atmospheric N_2O record at Cape Grim, Tasmania, to estimate the seasonal atmospheric cycle and calculate the transfer of N_2O from the subsurface to the atmosphere. The calculations make use of observations from the coast of California during periods of upwelling (Leuker et al., 2003). At these times, the subsurface correlation between N_2O saturation and AOU (N_2O/AOU) is mirrored by an inverse relationship between atmospheric N_2O and O_2/N_2. Comparison between atmospheric N_2O observations and those predicted by an ocean biogeochemical model coupled with an atmospheric transport model suggests that the Southern Ocean N_2O flux is roughly 0.9 Tg N/yr, although the large corrections applied to the atmospheric N_2O data create significant uncertainty (Table 4-3).

Nevison et al. (2005) find that oceanic N_2O saturation should not be treated as an annual constant, as was done earlier in Nevison et al. (1995), since it exhibits strong seasonality. This seasonality is a result of thermal effects during the summer and a larger mixing effect during the winter as the depth of the surface mixed layer deepens and deeper N_2O-enriched waters are mixed in. Since the majority of surface N_2O measurements have been made during the summer, this implies that annual mean fluxes may be overestimates. It may also help explain some of the apparent discrepancy in Southern Ocean emissions.

Table 4-3. Open Ocean Nitrous Oxide Fluxes (Post-1990) Broken Down by Latitude Band (Tg N/Year)

Latitude	Flux (∀ Std. Dev. or Range) 1990s	Source	Comment
Northern	1.2 ∀1.0	Bouwman et al., 1995	Based on Nevison (1994), subtracting 0.2 Tg N/yr for scaling conversion; used for GEIA inventory
Tropical	0.9 ∀ 3.3		
Southern	1.7 ∀ 2.0		
Northern	0.9	Nevison et al., 2003	N_2O production rate; may be 1–3 Tg N/yr less due to N_2O consumption by denitrifiers; based on)N_2O/AOU relationship
Tropical	4.1		
Southern	0.9		
Southern	0.9	Nevison et al., 2005	Modeled using atmospheric N_2O seasonal cycle and production as a function of O_2 consumption (Jin and Gruber, 2003)
Northern	1.8 (1.7–2.1)	Hirsch et al., 2006	Inverse model; mean and range of model scenarios; uses GEIA estimate of 3.8 Tg N/yr as a priori; likely includes upwelling and continental shelves; latitude grouping broken at 15° rather than 30°
Tropical	3.5 (2.6–4.1)		
Southern	0.4 (0–0.8)		

Northern = 90°N–30°N; tropical = 30°N–30°S; southern = 30°S–90°S.

Recently, Hirsch et al. (2006) have applied inverse modeling techniques to atmospheric N_2O measurements in an attempt to infer fluxes and estimate their uncertainties between 1998 and 2001. Due to its relatively long atmospheric lifetime, applying large-scale inverse techniques to N_2O presents some challenges because its atmospheric concentration is nearly constant. Seasonal cycles, for example, are on the order of 0.1 percent of the mean concentration (Jiang et al., 2007) and until recently they have been difficult to isolate from necessary sink corrections. Using the GEIA inventory (Bouwman et al., 1995) as initial fluxes, Hirsch et al. (2006) test whether these emissions are consistent with atmospheric concentration distributions. Results suggest that flux from the Southern Ocean is lower than the initial estimate of 1.7 Tg N/yr; this is consistent with other recent reports. They also find that tropical emissions are substantially higher than GEIA estimates. However, because sampling is sparse in the tropical region (15^{o}N to 15^{o}S), it is difficult to separate and determine land and ocean fluxes. The ratio of Northern Hemisphere to Southern Hemisphere modeled fluxes ranged from 1.9 to 5.2. These values are significantly higher than the initial GEIA inventory ratio of 1.5 and highlight the importance of emissions from the Northern Hemisphere. Overall, Hirsch et al. (2006) calculate that oceans contribute 26 to 36 percent of total flux. This is consistent with GEIA estimates (29 percent), but generally higher. Hirsch et al. (2006) also compare land and ocean emissions. Globally, the mean ratio of land to ocean N_2O emissions was calculated at 2.04, less than the initial GEIA inventory ratio of 2.47 and implying a greater relative contribution from oceans. However, because tropical land and ocean fluxes are difficult to distinguish, this figure is somewhat uncertain. Ratios of land to ocean fluxes increased from northern latitudes (an average of 1.6) through tropical (1.9) to southern (3.7), reflecting the large estimated decrease in Southern Ocean fluxes. Globally, oceans were estimated to release an average of 5.7 Tg N/yr with estimates ranging from 4.5 to 6.5 Tg N/yr.

An important consideration, however, is what is included in the Hirsch et al. classification of "ocean." Since the authors are working at large geographic scales, discriminating only between "land" and "ocean," the ocean class includes all oceanic environments (open ocean, continental shelves, upwelling areas). Because rivers and estuaries are relatively small-scale features, they are likely included into the land category. If we remove the flux estimates for continental shelf and upwelling regions derived in Table 4-2 from the Hirsch et al. ocean flux estimate, it is reduced to a figure similar to earlier estimates (Table 4-4).

Seasonal and interannual variability in atmospheric N_2O also yields insight into sources and sinks. Only recently has the accumulation of high-quality data made it feasible to examine variability on these shorter time scales. Nevison et al. (2007) compare observations of N_2O and a suite of chlorofluorocarbons (used as tracers) with atmospheric transport model simulations. They generate monthly mean oceanic N_2O fluxes from a model described by Jin and Gruber (2003), which combines a number of 3-D coupled biogeochemical models with an N_2O component based on Suntharalingam et al. (2000). These calculations estimate an oceanic flux of 3 Tg N/yr but find that uncertainties in stratospheric mixing tend to overwhelm source variability on shorter time scales.

Jiang et al. (2007) also examine the seasonal cycle of atmospheric N_2O and derive information on sources and sinks from its latitudinal distribution. They find that the peak to trough amplitude of the seasonal cycle increases systematically from 0.29 ppb at the South Pole to 1.15 ppb at Alert, Nunavut, Canada. The month of the seasonal minimum concentration also changes systematically, from April at the South Pole to September at Alert. The Northern Hemisphere seasonal cycle appears to be driven largely by stratospheric influences, which control the loss of N_2O. In the Southern Hemisphere, surface sources such as the oceans appear to have greater impact. Over the 3-year period from 2000 to 2002, the mean N_2O concentration in the Northern Hemisphere was 0.73 ppb greater than that in the Southern Hemisphere. This difference requires that sources in the Northern Hemisphere be 4.7 Tg N/yr higher, significantly greater than the inter-hemispheric difference of 2.657 Tg N/yr derived from the GEIA inventory. This value, however, is lower than the inter-hemispheric source difference estimated by Hirsch et al. (2006), which ranged from 5.5 to 11.9 Tg N/yr and averaged 8.8 Tg N/yr. A greater inter-hemispheric difference may in part be due to the increase in Northern Hemisphere anthropogenic emissions since 1995 as well as the downward revision in Southern Ocean fluxes.

Table 4-4. Open Ocean Nitrous Oxide Fluxes (Post-1990) (Tg N/Year)

Flux (Range)	**Source**	**Comment**
1.3	Prinn et al., 1990	Early inverse modeling; adopts 4 Tg N/yr a priori by subtraction (the few previous estimates varied widely); atmospheric lifetime used too long
5.8	Capone, 1991	Estimated from N_2O released during nitrification and denitrification
2 (1.4–2.6)	Houghton et al., 1992	The first IPCC estimate
4	Najjar, 1994	Estimated from N_2O released during nitrification
3.8 (2.8–5.7)	Nevison, 1994	Dissertation; based on compiling cruise data
4 (1.2–6.8)	Nevison et al., 1995	Based on surface measurements, upwelling not treated separately
3 (1–5)	Houghton et al., 1995	The IPCC Second Assessment Report estimate
3.6	Bouwman et al., 1995	Based on Nevison (1994), subtracts 0.2 Tg N/yr for scaling conversion; used for GEIA inventory
1.8 (1.34–2.18)	Bange et al., 1996	Midpoint of range
3.5	Seitzinger et al., 2000	Based on Nevison (1994) with continental shelf subgrids subtracted; 100% considered natural
3.85 (2.7–8.0)	Suntharalingam and Sarmiento, 2000	Model of organic matter remineralization and)N_2O/AOU relationship
3.0/3.6 (0.9–5.7)	Ehhalt et al., 2001	The IPCC Third Assessment Report estimate
5.8 (3.8–7.8)	Nevison et al., 2003	N_2O production rate; may be 1–3 Tg N/yr less due to N_2O consumption by denitrifiers; based on)N_2O/AOU relationship
3.5	Galloway et al., 2004	Continental shelf estimate subtracted from Nevison et al. (1995)
3.7	Nevison et al., 2005	Modeled using atmospheric N_2O seasonal cycle and production as a function of O_2 consumption (Jin and Gruber, 2003)
5.7 (4.5–6.5)	Hirsch et al., 2006	Inverse model; mean and range of model scenarios; uses GEIA estimate of 3.8 Tg N/yr as initial fluxes; likely includes upwelling and continental shelves—with these subtracted (1.9 Tg N/yr; Table 4-2), would = 3.8 Tg N/yr, range = 3–5 Tg N/yr
3	Nevison et al., 2007	Based on Jin and Gruber (2003) model
3.8 (1.8–5.8)	Denman et al., 2007	Cites Nevison et al. (2003; 2004—upwelling) as sources, combining uncertainties in production and exchange; this is the estimate from AR4
1.2 (0.9–1.7)	Rhee et al., 2009	
3.2 **(1–4)**	**Open ocean only, best guess**	Average of Seitzinger et al. (2000), Suntharalingam and Sarmiento (2000), Nevison et al. (2005), Rhee et al. (2009), and Hirsch et al. (2006) with continental shelf (1.5 Tg N/yr; Table 4-2) and upwelling (0.37; Table 4-2) removed

In summary, mean open ocean N_2O flux estimates have remained in the range of 3 to 6 Tg N/yr despite the variety of approaches used to calculate their magnitude (Table 4-4). A 3 Tg N/yr range, however, is significant, making up about 16 percent of the global total of 18.8 Tg N/yr (see Table ES-1). Inclusion of the uncertainties for individual estimates increases this range further. The most significant revision of oceanic flux estimates in recent years has been the reduction of the relative importance of the Southern Ocean (Table 4-3). Once thought to make up nearly half of the oceanic source, it is now thought to contribute 7 to 15 percent. Assuming open ocean flux is roughly 3.2 Tg N/yr (Table 4-4), open oceans contribute on the order of 17 percent of the total.

4.3.1.4 Summary: Rivers, Estuaries, Continental Shelves, Upwelling, and Open Ocean

An important improvement in our capability to estimate oceanic and other emissions is the accumulating database of high-quality atmospheric N_2O measurements. This database makes it possible to use inverse modeling techniques (Hirsch et al., 2006) and examine sources at higher spatial and temporal resolutions, a strategy that has yielded important insights for other trace gases. Because many important N_2O sources, including those from aquatic environments, are biogenic in nature, seasonality is a critical consideration. As the spatial scales of estimates are reduced, discrimination between different biogeochemical environments (open ocean, regions of upwelling, continental shelves) is enhanced and the inclusion of episodic emissions is made possible. These improvements should allow significant progress in refining emissions, which in turn will aid in predicting changes in emissions as the effects of climate change are felt.

Mean fluxes from Tables 4-1 through 4-4 are summarized below. The total flux of 5.4 Tg N/yr is higher than that calculated in the AR4 report (an average of 3.8 Tg N/yr with a range of 1.8 to 5.8 Tg N/yr; Denman et al., 2007), but includes natural emissions from rivers and estuaries that are classified as entirely anthropogenic there. The relatively shallow oceanic environments of the continental shelves and upwelling regions are treated explicitly here. Upwelling may be included in the AR4 anthropogenic class, although it is natural in origin. Continental shelves, here calculated as releasing 1.5 Tg N/yr and contributing 28 percent of flux, are highly uncertain. The few reported emissions vary by roughly an order of magnitude (Table 4-2). If the low estimate of 0.46 Tg N/yr based on the work of Seitzinger and Kroeze (1998) and Seitzinger et al. (2000) is used, rather than the mean of reported fluxes, total emissions are reduced to 4.88 Tg N/yr. If the global atmospheric source of N_2O is 18.8 Tg N/yr (see Table ES-1), then ocean, estuarine, and riverine sources would contribute on the order of 29 percent.

Table 4-5. Summary of Natural Ocean, Estuarine, and Riverine Nitrous Oxide Flux Estimates

Environment	Avg. Flux *(Tg N/Yr)*	Range	Comment
Rivers	0.09	0.08–0.10	Average taken as midpoint of range; 1% of total
Estuaries	0.24	0.03–0.45	Average taken as midpoint of range; 4% of total
Continental shelves	1.5	0.37–3.52	28% of total
Upwelling areas	0.37	0.0003–1.0	7% of total
Open ocean	3.2	1–4	59% of total
Total	**5.4**	**1.5–9.1**	Range from summing minima and maxima

4.3.2 Current Ocean, Estuarine, and Riverine Methane Fluxes

The flux of CH_4 from oceans, estuaries, and rivers has been calculated to make a relatively small contribution to total emissions. Initial estimates were made by Ehhalt (1974), based on only a few dissolved concentrations and gas-transfer calculations. Ehhalt and Schmidt (1978) suggest that the oceans release 1.3 to 16.6 Tg CH_4/yr, based on limited sampling and gas-transfer calculations. Although they indicate that upwelling regions may transfer deep water enriched in CH_4 to the surface and therefore be areas of enhanced emissions, there were no data available to make estimates. Because the oceans have been considered to be a minor source, they have not been the focus of extensive research and these early estimates have been carried forward (Cicerone and Oremland, 1988; Fung et al., 1991). Oceanic fluxes are frequently not included in inverse modeling studies because emissions are relatively low and are distributed over large areas. Atmospheric samples, upon which inverse techniques are based, tend not to be sensitive to them therefore (Chen and Prinn, 2006). Mikaloff Fletcher et al. (2004), for example, simply define oceanic CH_4 flux at 5 Tg CH_4/yr.

A small database reported by Lambert and Schmidt (1993) yielded estimates similar to those used earlier, with coastal (continental shelf) emissions roughly twice that of the open ocean despite making up about 7 percent of ocean surface area (Table 4-6). Bange et al. (1994) report CH_4 saturation levels in the Baltic and North Seas and summarize literature reports to derive the first ecosystem-specific flux estimates. They derive a somewhat higher annual oceanic flux of 11 to 18 Tg CH_4/yr, but acknowledge that there are significant uncertainties in the estimate. The majority of measurements upon which it is based are from summer months, which is likely to bias the estimate high. In addition, northern water bodies are ice-covered for much of the year, which impedes gas exchange. All early estimates neglect possible seasonality and assume emissions are constant year-round. Differences in assumed wind speeds, gas transfer model, and coefficients also add considerable uncertainty to estimates. Despite caveats, Bange et al. (1994) calculate that the majority (75 percent) of emissions occur in the shallow water habitats of estuaries and continental shelves, even though they have relatively small surface areas. Although the range of continental shelf emissions is relatively large (see Table 4-6), it is similar to that of Lambert and Schmidt (1993).

Bates et al. (1996) report a multi-year database of open ocean CH_4 concentrations from the Pacific Ocean. Surface waters in the equatorial tropical Pacific were supersaturated with respect to atmospheric equilibrium, while those outside of the tropics were often under-saturated during fall and winter. Their measurements provide the first estimates of seasonality and the large-scale distribution of emissions. Open water CH_4 fluxes based on this dataset are roughly an order of magnitude lower than those calculated by Bange et al. (1994) and Lambert and Schmidt (1993). Although both the Kelley and Jeffrey (2002) and Rhee et al. (2009) estimates are calculated based on a single cruise, they also report low open ocean emissions, consistent with those of Bates et al. (1996). Seasonal sampling in the tropical South Atlantic gyre suggests intermediate levels and demonstrates the importance of seasonal variability, with higher emissions in the fall than the spring (Robinson et al., 2006). In contrast, sampling near Hawaii over the course of a year found little variation in fluxes (Holmes et al., 2000).

Regional open ocean sampling has yielded CH_4 fluxes that range from 1.2 to 3.2 μmol/m^2/d (e.g., Scranton and Brewer, 1977; Ward, 1992; Tilbrook and Karl, 1995; Holmes et al., 2000; Oudot et al., 2002). If we assume emissions are relatively constant year-round and that the open ocean surface area is roughly 340×10^6 km^2 (Bates et al., 1996), these regional estimates would extrapolate to global emissions of 2 to 6 Tg CH_4/yr.

There are very few global estimates for CH_4 from upwelling regions, although Bange et al. (1998) and Upstill-Goddard et al. (1999) have noted their importance in the Arabian Sea and Sansone et al. (2001) have done the same for the eastern tropical North Pacific. Working in the Atlantic, Rhee et al. (2009) calculate very low fluxes, 0.001 Tg CH_4/yr. Owens et al. (1991) found that high CH_4 production in the Arabian Sea was associated the increased phytoplankton biomass supported by monsoon-driven upwelling. They calculate that fluxes were up to 5 times that of the average ocean flux and that the Arabian Sea (making up < 1 percent of the global ocean surface area) could account for 1.3 to 133 percent of the estimated open ocean flux.

Although there are a limited number of estimates of CH_4 flux from estuaries, they fall within the same, relatively narrow range of roughly 1 to 3 Tg CH_4/yr (Table 4-6). It is important to note, however, that these estimates are derived from limited sampling, much of which is from the North and Baltic Seas. There are no samples from tropical systems. While CH_4 distributions in a number of rivers have been studied and budgets have been attempted, few estimates of the global contributions from these systems have been calculated, aside from that of Upstill-Goddard et al. (2000). Working in the North Sea basin, they report that CH_4 was highly, but non-linearly correlated with salinity. They calculate that over 90 percent of the riverine, low-salinity CH_4 input to estuaries was lost there, the vast majority through air-water exchange. Recently, Saarnio et al. (2009) have attempted to calculate the flux of CH_4 from European lakes and rivers. Their river estimate of 0.14 Tg CH_4/yr is relatively high compared to the Upstill-Goddard et al. global estimate of 0.25 Tg CH_4/yr. This may be due to the inclusion of emissions from small streams draining peatlands and wetlands in addition to those from rivers. We calculate the flux of CH_4 from oceans, estuaries, and rivers by averaging recent habitat-specific estimates and summing (Table 4-6). Emissions total 9.1 Tg CH_4/yr, with the majority released from the continental shelves (5.5 Tg CH_4/yr; 60 percent of total). Fluxes from the open ocean and from estuaries and rivers are similar at 1.8 and 1.85 Tg CH_4/yr, respectively. Emissions compiled in Table 4-6 suggest that additional research since the early 1980s has served to confirm initial estimates of oceanic, estuarine, and riverine CH_4 fluxes of 10 to 15 Tg CH_4/yr. This report's estimate of roughly 9 Tg CH_4/yr falls within this range, given the uncertainties involved in these estimations. If the global annual flux of CH_4 to the atmosphere is roughly 566 Tg CH_4/yr (see Table ES-1), oceans, estuaries, and rivers would contribute 2 percent.

There are, however, significant uncertainties in these estimates. Sampling is poor in tropical and southern latitudes and is seldom performed over an annual or multi-year scale. Virtually all estimates are calculated from sporadic samples assumed to be representative of the entire year. This is a simplification, since CH_4 saturation levels and wind speeds vary seasonally. Calculated open ocean emissions vary by an order of magnitude, due perhaps to methodological problems and/or unrepresentative sampling. Current estimates do not include emissions from upwelling areas. It would not be expected that such emissions would greatly change total fluxes; they would be unlikely to increase fluxes by more than a few Tg. Perhaps unsurprisingly, emissions appear to be dominated by coastal and shelf systems, where organic sources are greater and contact with anaerobic sediments is greater.

Table 4-6. Ocean, Estuarine, and Riverine Methane Fluxes

Flux *(Tg CH_4/Yr)*	Environment	Reference	Comment
4–6.7	Open ocean	Ehhalt, 1974	
1.3–16.6	Open ocean	Ehhalt and Schmidt, 1978	
10 (5–20)	Open ocean	Cicerone and Oremland, 1988	Cites Ehhalt (1974)
10	Oceans	Fung et al., 1991	Cites Ehhalt (1974)
3.6	Open ocean	Lambert and Schmidt, 1993	Total of 93 measurements
3.6 (2.8–4.4)	Open ocean	Bange et al., 1994	Flux calculated as midpoint of range
10	Open ocean	Houghton et al., 1995	The IPCC Second Assessment Report; used by Lelieveld et al. (1998)
0.4	Open ocean	Bates et al., 1996	
15 (± 10)	Open ocean	Houweling et al., 2000	Cites Lambert and Schmidt (1993)
10–15	Open ocean	Ehhalt et al., 2001	The IPCC Third Assessment Report; cites Lelieveld et al. (1998); Fung et

Flux ***(Tg CH_4/Yr)***	**Environment**	**Reference**	**Comment**
			al. (1991); Houweling et al. (2000)
0.8 ± 0.6	Open ocean	Kelley and Jeffrey, 2002	Single cruise, 41°S–27°N
4 (0.2–2)	Open ocean	Wuebbles and Hayhoe, 2002	Cites Bates et al. (1996); Holmes et al. (2000)
0.44 (0.41–0.46)	Open ocean	Rhee et al., 2009	Single Atlantic cruise, 50°S–50°N
0.7–14	Shelf	Ehhalt, 1974	
6.1	Coastal ocean	Lambert and Schmidt, 1993	
9.7 (7.3–12.1)	Shelf	Bange et al., 1994	Flux calculated as midpoint of range
0.58 (0.41–0.77)	Coastal ocean	Rhee et al., 2009	
0.0009 (0.0009–0.001)	Upwelling	Rhee et al., 2009	
1.06 (0.8–1.32)	Estuaries	Bange et al., 1994	Flux calculated as midpoint of range
2.1 (1.1–3)	Estuaries	Middelburg et al., 2002	Flux calculated as midpoint of range
0.1–0.4	Rivers	Upstill-Goddard et al., 2000	
Summary			
1.8 (0.4–3.6)	**Open ocean**	Avg. of Rhee et al. (2009), Kelley and Jeffrey (2002), Bates et al. (1996), Bange et al. (1994), and Lambert and Schmidt (1993)	20% of total
5.5 (0.58–9.7)	**Shelf**	Average of Rhee et al. (2009), Bange et al. (1994), and Lambert and Schmidt (1993)	60% of total
1.85 (1.06–2.1 estuaries) (0.25 rivers)	**Estuaries and rivers**	Average of Bange et al. (1994) and Middelburg et al. (2002) + range midpoint of Upstill-Goddard et al. (2000)	20% of total
9.1 (2.3–15.6)	**Total**		Range calculated from summing minima and maxima

4.4 Future Oceanic, Estuarine, and Riverine Nitrous Oxide and Methane Emission Scenarios

In general, natural oceanic, estuarine, and river emissions of N_2O and CH_4 are expected to remain largely unchanged. Even though atmospheric levels of both gases have increased sharply in the last several hundred years, this is primarily due to increases in anthropogenic sources. The impact of human activities is centered on the continents, so aquatic ecosystems closer to continents are affected more than the open ocean. Galloway et al. (2004), for example, suggest that open ocean N cycles are largely unconnected to those in terrestrial systems. In extrapolating N_2O emissions for 2050, Kroeze and Seitzinger (1998) have estimated that natural sources will remain constant and that their relative contribution will decrease as anthropogenic sources continue to rise.

The sensitivity of denitrification and nitrification to O_2 levels suggests that in some systems, coastal eutrophication may enhance denitrification rates, leading to flux increases (Naqvi et al., 2000). Increases in hypoxia and the extent of anaerobic sediments may also increase CH_4 emissions, although there are no estimates available. These increases, however, would be considered largely anthropogenic in origin. Since submarine groundwater discharge appears to be an important source of nutrients and other dissolved materials to some coastal systems, this may provide a mechanism by which anthropogenic impacts are conveyed offshore.

Because N_2O and CH_4 production in upwelling areas is a function of the enhanced primary production there, it is possible that changes in production due to increases in CO_2 may also change their flux (Altabel et al., 2002). For example, ocean iron fertilization, proposed to enhance productivity and mitigate increasing atmospheric CO_2, may also increase N_2O emissions. This feedback would therefore offset possible radiative benefits (Jin and Gruber, 2003).

Overall, it is not expected that possible changes in oceanic emissions of N_2O and CH_4 will greatly affect climate policy. Emissions of CH_4 are a relatively small fraction of total emissions; significant changes would require large environmental alterations. While ocean N_2O emissions do make a significant contribution to global emissions, the majority of emissions are from the open ocean and are less susceptible to anthropogenic impacts. Based on the current understanding of emissions, major controls are fundamental physical oceanic properties (wind parameters, mixing) that would not be easily changed.

4.5 Areas for Further Research

Because there are almost no estimates of the global upwelling source of CH_4, focused sampling and the compilation of available literature on CH_4 saturation ratios to derive a first-order estimate would likely be a useful way to decrease this uncertainty. Sampling and modeling the episodic nature of these emissions is challenging.

Current estimates of N_2O fluxes from the continental shelves vary by an order of magnitude, so refining emissions from this region should be a priority.

Because the ratio of N_2O/N_2 is a critical but poorly constrained variable in estimating the production of N_2O from N exported to rivers and estuaries, improving our understanding of its magnitude and controls would help refine both natural and anthropogenic emissions from these environments.

Data in general from tropical and southern latitude environments are sparse for both gases. Since tropical systems in particular are suggested as globally important (Hirsch et al., 2006), this region should receive increased attention and research. Most current flux estimates do not include seasonal or episodic inputs, which also greatly increases uncertainties. Because the enlarging atmospheric database has higher temporal resolution (hourly to weekly), the full exploitation of this valuable resource requires a better understanding of the variability in fluxes. Currently, there is considerable temporal mismatch between emissions and atmospheric samples for inverse modeling.

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Chapter 5. Permafrost

Permafrost is soil, sediment, or rock that is continuously frozen (temperature below 0°C) for at least two consecutive years. It forms when ground is sufficiently cold during winter to remain frozen during the following summer. It occurs both on land and in sediments of the shelf regions of the Arctic Ocean. On land, there is a thin surface layer—called the active layer—that thaws each summer, typically reaching a maximum thickness of about 0.5 to 1.0 meters in late summer. Ground below the active layer can be perennially frozen to depths of less than 10 meters to more than several hundred meters. Permafrost occurs primarily at high latitudes, but also at high elevations. The area of permafrost, and its potential as a source of CH_4 and N_2O emissions to the atmosphere, are much greater at high latitudes than at high altitudes (except the Tibetan Plateau), so most field measurements have occurred at high latitudes.

Permafrost regions are classified, based on the prevalence of frozen ground, as continuous (over 90 percent of exposed ground underlain by permafrost), discontinuous (50 to 90 percent), sporadic (10 to 50 percent), or isolated (below 10 percent). Permafrost currently underlies about 23 million km^2 of exposed land surface (i.e., land not under ice sheets) in the Northern Hemisphere (Zhang et al., 1999). Of this, about 11 million km^2 is classified as continuous, and about 4 million km^2 each as discontinuous, sporadic, and isolated (Zhang et al., 1999). Note that, for example, 4 million km^2 of land with isolated permafrost has less than 10 percent of its area, or less than 400,000 km^2,of actual permafrost.

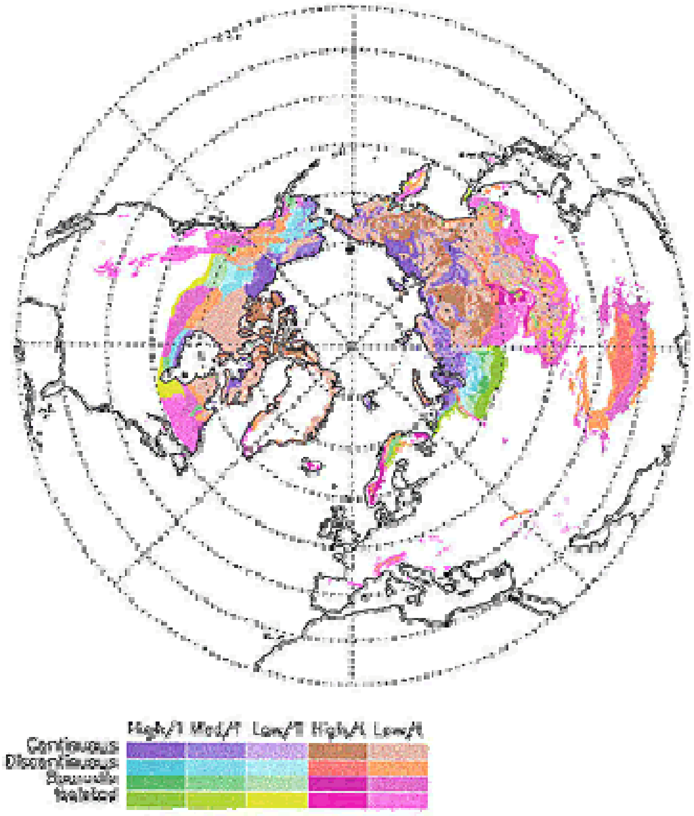

Figure 5-1. Distribution of permafrost and ground ice in the Northern Hemisphere, based on the EASE-Grid version of the International Permafrost Association (IPA) map. “High,” “Med,” and “Low” refer to ice content, and “T” and “t” refer to thick and thin overburden, respectively. Image courtesy of the IPA, supplied by Tingjun Zhang, National Snow and Ice Data Center, University of Colorado, Boulder.

5.1 Description of Emission Source

CH_4 or N_2O can be frozen within permafrost, and thus permafrost represents a stock or reservoir of CH_4 and N_2O that can be released upon thawing. This chapter focuses on that potential source, but also briefly addresses the role of permafrost in other natural source categories covered in other chapters (Chapter 6, "Lakes"; Chapter 2, "Wetlands"; Chapter 4, "Oceans"). Gas hydrates or clathrates, which can co-occur with permafrost but which also are common in non-permafrost regions, are discussed as a CH_4 and N_2O source in Chapter 7, "Gas Hydrates," and the presence of thermogenic (non-microbial) CH_4 in deeper permafrost strata has been noted (Collett and Dallimore, 1999; Yakushev and Chuvilin, 2000); geologic sources of CH_4 are discussed in Chapter 8.

There have been no direct field measurements of CH_4 or N_2O emissions from permafrost, because gas losses are negligible while the permafrost remains frozen (Rivkina et al., 2004, 2007). However, when permafrost melts, gas bound within the frozen soil is released, and can then diffuse to the surface and be emitted to the atmosphere. Since permafrost, when thawing from above, is overlain by a seasonally thawed active layer, field measurements of surface emissions can include CH_4 and N_2O generated in the active layer and/or CH_4 and N_2O released from the thawing permafrost; little effort has been made to discriminate between these two possibilities. Permafrost can also thaw at its base, due to geothermal heat flux from deeper in the earth (temperatures increase with depth into the earth), but gas released by this thawing is likely to remain trapped under the overlying frozen ground. Studies of permafrost as a direct greenhouse gas source have included (1) measurements of greenhouse gas concentrations in frozen samples of permafrost collected from below the active layer; (2) incubations of these samples at a range of temperatures, above and below freezing, to measure potential greenhouse gas production; and (3) modeling studies of permafrost thaw (over centuries) to estimate the amount of gas that might be released during future climate change.

Permafrost was included among the natural sources of CH_4 reviewed in the earlier version of this report (U.S. EPA, 1993) when some early measurements of CH_4 concentration in permafrost were just being reported. The U.S. EPA (1993) reported the magnitude of emissions to be highly uncertain and probably relatively small. However, permafrost has not been listed as a separate, specific source of CH_4 or N_2O in the IPCC assessments of 1990, 2001, or 2007 (Watson et al., 1990; Prather et al., 2001; Lemke et al., 2007), but CH_4 emissions are discussed in the U.S. Climate Change Science Program Synthesis and Assessment Product 3.4 on abrupt climate change (Brook et al., 2008). As discussed elsewhere (e.g., Section 6.1), there can be overlap between the source categories this report is organized around, and operationally these overlapping or co-occurring sources may be difficult to distinguish in the field (e.g., if permafrost and gas hydrates are co-located).

5.2 Factors That Influence Emissions

Gas diffusion rates in frozen permafrost are very slow (Rivkina et al., 1998), so the release of greenhouse gases directly from permafrost occurs when permafrost melts. This can happen as a result of climatic warming, surface disturbance that changes the land surface energy balance (e.g., fire), exposure of permafrost due to thermokarst or coastline erosion, and new construction (e.g., roads and buildings) that changes the surface energy balance, although most construction now is designed to preserve the underlying permafrost in order to increase the future integrity of the structures. Thermokarst erosion occurs when ice-rich permafrost melts, and the land surface slumps or collapses. The rate of melting (or formation) of permafrost can be highly variable, as it is a function of several factors: the land surface energy balance, the depth of the permafrost in the ground, and the thermal properties (i.e., heat conductivity and heat capacity) of the permafrost and overlying ground.

The quantity of CH_4 or N_2O released from permafrost also depends directly on several factors. First, it depends on the total extent of permafrost, which is a primarily a function of climate (Zhang et al., 1999).

Second, it depends on the concentration of CH_4 or N_2O in the permafrost. Finally, it depends on the rate at which the permafrost is melting, which (as noted above) itself can depend on several factors.

An important consideration that has received little study is the transport of greenhouse gases from the melting permafrost, through the overlying melted soil or sediment, to the atmosphere, and potential transformations of these gases before reaching the atmosphere (e.g., oxidation of CH_4 to CO_2 by methanotrophic (or "methane-eating") bacteria, or reduction of N_2O to N_2 by denitrifying bacteria in the unfrozen soil column above the permafrost). The amount of gas reaching the atmosphere (net emission) could be significantly less than the amount released from the thawing permafrost (Kvenvolden et al., 1993). For example, in non-permafrost systems that emit CH_4, such as wetlands and rice paddies, a substantial fraction of the CH_4 produced in the flooded soil is oxidized in overlying oxic soils and fresh water (i.e., soils and fresh water containing enough dissolved oxygen to support aerobic organisms) before reaching the atmosphere (Reeburgh, 2004).

The high-latitude permafrost region has been warming over the past several decades, but this warming has not been spatially or temporally uniform (ACIA, 2004). Permafrost has been observed to be degrading (thawing) over the past several decades in several regions (e.g., Christensen et al., 2004; Camill et al., 2001), but at this time there is no large-scale quantification of the rate of melt. These changes in permafrost distribution and prevalence, and in active layer depth, will impact regional hydrology, vegetation distributions, ecosystem productivity, and soil organic matter decomposition rates. These landscape effects of melting permafrost in turn will impact net greenhouse gas emission rates from wetlands, soils, and lakes in permafrost landscapes. These indirect emissions are not considered in this chapter.

5.3 Current Global Emissions

In permafrost regions, the ground surface thaws each summer (this is called the active layer), so the actual permafrost is below the ground surface. Direct CH_4 or N_2O emissions from *in situ* permafrost are not measured, and estimates of emissions are based on measured concentrations of CH_4 in permafrost, and estimates of contemporary permafrost degradation rates.

5.3.1 Methane

Similar ranges in permafrost CH_4 concentrations have been measured near Prudhoe, Alaska (0.4–8.7 mg CH_4/kg: Rasmussen et al., 1993), near Fairbanks, Alaska (<0.001–22 mg CH_4/kg: Kvenvolden et al., 1993), and in northeastern Siberia (0–6 mg CH_4/kg: Rivkina et al., 2004). Brouchkov and Fukuda (2002) also measured permafrost CH_4 in northeastern Siberia, but their reported values (2–6,000 ppmv in bubbles in permafrost) cannot be converted into mg per kg. Moraes and Khalil (1993) and Kvenvolden et al. (1993) used a model of heat transfer into permafrost soils to estimate climate change impacts on CH_4 emission from permafrost (discussed in more detail in Section 5.4, "Future Emission Scenarios"). These studies did not report or discuss contemporary emissions, but the initial emission rates of their future scenarios provide an estimate of current emissions. Both studies estimated that contemporary CH_4 release from permafrost is about 0 to 1 Tg CH_4/yr. These simulations did not include CH_4 oxidation during transport from the melting permafrost to the surface, and so these are likely to be an overestimate or an estimate of the maximum net emission to the atmosphere.

5.3.2 Nitrous Oxide

Global emissions of N_2O from permafrost are negligible. Very few studies have measured N_2O concentrations in permafrost. Rasmussen et al. (1993) collected shallow-core permafrost samples from Alaska's North Slope, near Prudhoe Bay, and measured N_2O concentrations of µg/kg, or parts per billion by weight, about 1,000 times smaller than for CH_4 (mg/kg, or parts per million by weight). Using this factor of 1,000 and the CH_4 emission rate estimated from the same study (Moraes and Khalil, 1993), the current N_2O flux would be about 1 Gg N_2O/yr, or about 0.005 percent of the total annual global N_2O flux from all sources. The very low concentrations reported by Rasmussen et al. (1993) are consistent with biogeochemical measurements made on permafrost samples from northern Siberia by Rivkina et al. (1998). They observed that viable microbes (including denitrifiers, bacteria that generate N_2O) were present in permafrost samples collected from 1 meter to about 35 meters below the surface, and that sample Eh (or oxidation-reduction potential) was +40 to -250 mV. Eh values in this range indicate highly reduced conditions, in which most nitrogen has been reduced by denitrifiers to N_2, and typical N_2O concentrations are very low. Low N_2O concentrations in permafrost are also consistent with negligible N_2O production measured in incubations of soil samples collected from the active layer and shallow permafrost in northern Siberia by Rodionow et al. (2006).

5.3.3 Indirect Impacts of Permafrost on Methane Emissions

Permafrost has a number of indirect effects on CH_4 emissions. These are not included in this chapter's quantification of direct emissions from permafrost.

Some scientists consider permafrost to be the nominal source of greenhouse gases emitted when organic matter frozen into permafrost decomposes after thawing (e.g., Zimov et al., 1997). A number of studies have established that the old soil organic matter frozen into permafrost readily decomposes if thawed, and that microbial populations that can decompose the organic matter are present and viable in the permafrost (Rivkina et al., 1998, 2004, 2007; Zimov et al., 1997, 2006). It has been demonstrated in laboratory incubations that microbial metabolism and CH_4 production can occur, albeit at very low rates, with soil samples held at temperatures as low as -16°C (Brouchkov and Fukuda, 2002; Rivkina et al., 2004). It is likely, however, that most of the CH_4 contained in permafrost was produced before the soils froze (e.g., in the Pleistocene), that the CH_4 froze into the permafrost as the permafrost developed, and that the CH_4 has remained stably bound in the permafrost for thousands of years (Rivkina et al., 2007).

Permafrost in the ground acts as an impervious boundary to water infiltration, and thus can generate wetter soils and the conditions necessary for denitrification (which can generate N_2O) and CH_4 production. Melting permafrost leads to changes in land surface hydrology, which, together with the warming that caused the melting, affects emission rates (e.g., Christensen et al., 2004; Van Huissteden et al., 2005; Tarnocai et al., 2007). The effect of hydrology on N_2O and CH_4 emissions is discussed in more general terms in Chapter 2, "Wetlands," and Chapter 3, "Soils"), which also include quantitative summaries of emissions.

Ice-rich permafrost has large ice wedges (tens of centimeters to several meters in scale) within the frozen soil and rock. As these ice wedges melt, the water can drain away, leaving voids; these can collapse, causing ground surface subsidence and the formation of small lakes and ponds called thermokarst lakes. Measurements in northeastern Siberia have shown that these thermokarst lakes can be significant sources of CH_4 to the atmosphere (Zimov et al., 1997; Walter et al., 2006, 2007); this source is discussed and quantified in Chapter 6, "Lakes." Coastal erosion of permafrost can also lead to the release of CH_4 into coastal waters; Shakhova et al. (2005) measured very high CH_4 concentrations (supersaturation) in Arctic Ocean coastal waters (East Siberian and Laptev Seas on the Siberian coast). Shakhova et al. (2005) suggest four possible mechanisms for these high CH_4 concentrations: (1) coastal erosion and the subsequent release of CH_4 trapped in permafrost ice; (2) release of CH_4 trapped in sub-sea permafrost; (3) release of CH_4 trapped in shallow gas hydrates; and (4) biogenic CH_4 generated from decomposition of eroded carbon in sub-sea sediments. They did not measure CH_4 fluxes.

Melting of permafrost will likely be accompanied by hydrate destabilization in regions where permafrost and hydrates co-occur (e.g., Harvey and Huang, 1995). Emissions to the atmosphere from this situation are likely to be dominated by hydrate sources, which make up a substantially larger pool; this source is discussed and quantified in Chapter 7, "Gas Hydrates."

5.4 Future Emission Scenarios

Like the contemporary emission estimates discussed above, estimates of future emissions of CH_4 or N_2O from permafrost are based on estimates of climate-change-induced melting of permafrost, and the concentrations of CH_4 or N_2O in that permafrost.

5.4.1 Methane

Moraes and Khalil (1993) and Kvenvolden et al. (1993) estimated future CH_4 emissions from permafrost melting for the next several hundred years. Their estimates were based on several factors: (1) air temperature increases of 5° and 8.5°C in 2100, (2) permafrost CH_4 concentrations measured in Alaska (Rasmussen et al., 1993; Kvenvolden et al., 1993), and (3) one-dimensional modeling of soil heat transfer (Moraes and Khalil, 1993). Both studies concluded that emissions would rise slowly from current low values (about 0 to 1 Tg CH_4/yr) to rates of 5 to 30 Tg CH_4/yr over the next 30 to 60 years, and then decline back to low values within another 50 to 100 years. Neither of these analyses included any CH_4 oxidation during the transport of CH_4 from the melting permafrost through the overlying thawed soil to the atmosphere. As permafrost melts, the active layer eventually thickens to at least tens of meters in most regions, and the potential for CH_4 oxidation before reaching the atmosphere is high. In addition, neither model included any changes in soil thermal dynamics due to changing vegetation cover (e.g., see Christensen et al., 2004) and/or hydrological regimes (e.g., see Smith et al., 2005); these changes can either enhance or diminish the rate of thawing.

More recently, estimates of global permafrost melting were made with a land-surface model coupled to a general circulation model (CLM3 in the CCSM3; Lawrence and Slater, 2005). In these simulations, permafrost area declined by 60 to 90 percent by 2100, depending on the greenhouse gas emission scenario used to drive the model. Under the assumption that CH_4 emissions are proportional to rate of permafrost decline, the permafrost decline simulated by Lawrence and Slater (2005) would generate similar results to the earlier studies of Moraes and Khalil (1993) and Kvenvolden et al. (1993), again noting that changes in vegetation and hydrology were not taken into account in the simulations reported by Lawrence and Slater.

Permafrost melting may also indirectly have significant impacts on landscape-scale CH_4 emissions to the atmosphere, through related changes in vegetation and hydrology (e.g., see Christensen et al., 2004).

Future emissions from permafrost melting will be directly related to the rate and magnitude of climatic warming at high latitudes. Direct net CH_4 emissions from permafrost melting are not likely to be very high, though they would be a small positive feedback on the climate system. Given other, more important issues related to high-latitude warming (including potential indirect effects of permafrost melting), direct net CH_4 emissions from permafrost are not a key issue in climate policy development (Brook et al., 2008).

5.4.2 Nitrous Oxide

Given the small stock of N_2O frozen into permafrost in northern Alaska (Rasmussen et al., 1993) and the negligible N_2O production measured in incubations of permafrost and active layer soils in northern Siberia (Rodionow et al., 2006), it is unlikely that future emissions of N_2O from permafrost will be significant over at least the next several decades to hundred years. It is important to note, however, that this conclusion is based on a very limited number of field studies.

5.5 Areas for Further Research

Recent modeling of permafrost melting (e.g., Lawrence and Slater, 2005) has a more realistic treatment of the soil physical processes involved, and much more detail about their variability across permafrost landscapes, than the heat transfer modeling of Moraes and Khalil (1993) that drove the initial estimates of CH_4 release. However, even the recent models lack detailed treatment of vegetation and landscape hydrology changes that will occur with high-latitude warming, and that can have both significant direct and indirect impact on CH_4 emissions. A second significant uncertainty is the estimation of the fraction of CH_4 released from melting permafrost that will be oxidized (to CO_2) before reaching the atmosphere. The only global estimates of direct CH_4 emissions from melting permafrost did not account for any oxidation. In some cases, however, particularly for deeper permafrost, most of the CH_4 is likely to be oxidized before reaching the atmosphere.

Fully addressing these issues will require sophisticated models that include several features not common in current models: (1) lateral movement of surface water, soil water, and shallow groundwater (as opposed to just vertical percolation); (2) dynamic vegetation algorithms to simulate changes in plant community composition; and (3) detailed soil physics, including gas transport, to simulate CH_4 oxidation. This type of model will also be better able to estimate indirect impacts of permafrost melting on CH_4 emissions. At this time, it is not known whether direct or indirect effects will have a stronger impact on net CH_4 emissions.

Several field studies indicate that N_2O emissions from melting permafrost, both directly and indirectly, are likely to be very low. However, very few field studies have been conducted, and so it is difficult to even estimate the uncertainty of this conclusion.

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Chapter 6. Lakes

Lakes and ponds are naturally formed permanent water bodies contained on a body of land. (This report only addresses freshwater lakes.) Recently, Downing et al. (2006) estimated that there are about 300 million natural lakes and ponds globally, with a total area of about 4.2 million km^2, or about 3 percent of the global land surface area. Ninety percent of these lakes are smaller than 1 hectare (0.01 km^2), and 43 percent of the total lake area is from lakes smaller than 1 km^2 (Downing et al., 2006). Downing et al. (2006) estimated that impoundments with large, engineered dams cover about 0.25 million km^2 and that small farm impoundments occupy an additional 0.1 million km^2, but some earlier estimates of impoundment/reservoir area are substantially higher (e.g., St. Louis et al., 2000).

In the 1990 IPCC assessment, tabulated sources of CH_4 include both natural wetlands and fresh waters (Watson et al., 1990), with freshwater source strength estimated at 5 Tg CH_4/yr (estimated range of 1–25 Tg CH_4/yr). This freshwater source could include natural lakes, impoundments/reservoirs, and rivers, but no specifics were discussed. Cicerone and Oremland (1988) noted that this range came from a very early estimate by Ehhalt (1974) and was very uncertain. In the 2001 and 2007 IPCC assessments, the only comparable CH_4 source is natural wetlands (Prather et al., 2001; Denman et al., 2007). Lakes are not tabulated as a source of N_2O in the IPCC assessments of 1990, 2001, or 2007, although the 2007 assessment includes rivers/estuaries/coastal zones (Watson et al., 1990; Prather et al., 2001; Denman et al., 2007).

6.1 Description of Emission Source

This quantification of freshwater lakes as a source of CH_4 and N_2O to the atmosphere includes both lakes and ponds, but excludes impoundments/reservoirs. Gas emissions from impoundments/reservoirs, water bodies formed by dams and other engineering works, are considered to be anthropogenic. (Although not discussed further here, reservoirs can be a significant source of greenhouse gases; see, for example, St. Louis et al., 2000.)

There is the potential for overlap between natural lakes and wetlands as methane and N_2O sources for several reasons. Some (but not all) wetland area inventories include shallow lakes as wetlands (Matthews, 2000), but lake area estimates (e.g., Downing et al., 2006) also include shallow lakes. The littoral (or shoreline) zone of many lakes has emergent vegetation, and could be considered wetland in some inventories. Juutinen et al. (2003) define the littoral zone as the area between the highest shoreline and the outer limit of floating-leaved vegetation; this can include temporarily flooded grass and sedge-dominated zones, continuously inundated reed-dominated zones, and slightly deeper zones dominated by floating vegetation. Many wetlands contain numerous small ponds (e.g., Hamilton et al., 1994; Repo et al., 2007), and in scaling up wetland area these ponds are likely to be included, but they may also be included in lake and pond inventories such as that of Downing et al. (2006). Beaver ponds are small, temporary, natural impoundments that can be sources of CH_4 (e.g., Naiman et al., 1991; Bubier et al., 1993; Roulet et al., 1997) and that can be interspersed among wetland or rivers, and difficult to map separately from them. Finally, in a tropical regional assessment of CH_4 emissions for the floodplains of the central Amazon Basin, Melack et al. (2004) used remote sensing to quantify the area of different landscape classes. They noted that there is much seasonal inundation of the major and minor river floodplains. Their “wetland habitat” classes include open water (lakes and channels), flooded forests, and aquatic macrophytes (floating emergent herbaceous plants during inundated periods). Some fraction of this could be classified as lake, some as river, and some as wetland.

6.2 Factors That Influence Emissions

6.2.1 Methane

In lakes, CH_4 is produced by methanogenic or methane-producing bacteria in anoxic (oxygen-free) sediments (Cicerone and Oremland, 1988; Conrad, 1989; Kiene, 1991). CH_4 production rates depend on temperature, organic matter availability, and isolation from oxygen; these factors are influenced by climate, lake size and depth, and productivity of microscopic and macroscopic plants and animals. The death of these plants and organisms generates organic matter that serves as a substrate (or 'food') for methane production in the sediments. Roulet et al. (1997) made high-frequency, near-continuous CH_4 flux measurements from a beaver pond in Central Canada. They found that daytime CH_4 flux was highly correlated with sediment temperature and inversely correlated with dissolved oxygen concentration, and that nighttime flux was most correlated with wind speed. Oxidation in overlying oxic sediments and/or lake water can consume a large fraction of the CH_4 generated in the sediments, and reduce the net flux to the atmosphere (e.g., Reeburgh, 2003; Kiene, 1991; Galchenko et al., 1989).

There are four pathways for CH_4 emissions from lakes (e.g., see Bastviken et al., 2004; Whalen, 2005): bubbling, diffusion, plant-mediated transport, and seasonal overturning (see text box). In their synthesis study, Bastviken et al. (2004) refer to the seasonal overturning flux as a storage flux (i.e., CH_4 is stored in deeper lake water during a season, then emitted episodically upon overturning). Seasonal lake overturning can occur in both spring and autumn. In spring, overturning occurs following ice-out (e.g., see Rudd and Hamilton, 1978; Striegl and Michmerhuizen, 1998). Autumn overturn occurs in northern lakes when thermal stratification established during the summer breaks down. During summer months when incoming solar radiation is high, the surface water is warmed. This makes it less dense than the colder deeper waters, and it floats above the denser deep water (this is thermal stratification). As the surface waters cool in the autumn, the thermal stratification breaks down, and the deeper water, which can have relatively high dissolved CH_4 concentrations, mixes to the surface. This CH_4 is then emitted to the atmosphere (e.g., see Kankaala et al., 2007). Michmerhuizen et al. (1996) estimated that up to 40 percent of the annual CH_4 flux from small lakes could occur during spring turnover.

Four pathways for CH_4 emissions from lakes

- **Bubbling** (or ebullition), in which bubbles contain substantial methane concentrations and transport this methane from a lake's sediments (bubble formation) to the atmosphere (bubble bursting at the water surface).
- **Plant-mediated transport.** Aquatic plants often contain arenchymous tissue (spongy tissue with large pores) in their stems and roots that allows air to move quickly between the leaf surface and the roots. These gas-conducting voids provide a conduit for diffusive flux from the sediment to the atmosphere that bypasses diffusion through the lake water itself.
- **Diffusive emissions** from surface water whose methane concentration is greater than the concentration that would be in equilibrium with the overlying atmosphere.
- **Seasonal lake-overturning,** in which methane builds up in deeper lake water during a season in which the lake water is stratified and not well-mixed, and then is emitted episodically when there is lake water overturning.

Wind speed is an important control on gas exchange between a lake and the atmosphere (Sebacher et al., 1983). Flux rates by all pathways generally increase with increasing wind speed.

Bubbling has been determined to be the dominant pathway for CH_4 flux (more than 90 percent) in a variety of field studies in both the tropics (Keller and Stallard, 1994) and the permafrost zone (Walter et al., 2006). In their review of temperate and boreal lake emissions, Bastviken et al. (2004) estimate bubble fluxes to account for roughly half of the CH_4 flux for lakes with areas ranging from 10^{-4} to 10^{5} km^2. Water depth, and therefore water pressure, are important factors controlling ebullition (Keller and Stallard, 1994).

Walter et al. (2006) measured extremely high CH_4 fluxes from thermokarst lakes in northeastern Siberia, following up on earlier work by Zimov et al. (1997). Thermokarst (or thaw) lakes form in permafrost regions when massive ground-ice wedges melt, causing the ground surface to subside and lakes to form. Further ground melting can eventually lead to drainage and disappearance of thermokarst lakes (Smith et al., 2005). In Siberia, there are huge quantities of soil organic carbon (SOC) frozen into permafrost in which these thermokarst lakes form (about 450 Pg C; Zimov et al., 2006), and this SOC has been shown to be readily decomposable and contributing to the observed CH_4 flux (Walter et al., 2006).

University of Alaska Fairbanks researcher Katey Walter lights a pocket of methane on a thermokarst lake in Siberia in March of 2007. Igniting the gas is a way to demonstrate, in the field, that it contains methane.

Credit: Photo by Sergey Zimov

Many studies have shown that CH_4 fluxes are generally higher from regions with rooted or floating vegetation (e.g., Juutinen et al., 2003; Melack et al., 2004). Kankaala et al. (2005) found that seasonal variation in CH_4 flux from a boreal lake was more correlated with plant growth than variation in sediment temperature for sites with relatively low emission rates, while sites with dense vegetation and high flux rates showed a seasonal flux rate variation more correlated with sediment temperature. Since vegetation is more common in shallower water, the ratio of shoreline length to lake area is an important factor influencing mean lake emissions per unit area (Bergström et al., 2007), and this ratio generally increases as the total lake area decreases.

Stadmark and Leonardson (2005), measuring CH_4 emissions from shallow ponds constructed in southern Sweden for nitrogen retention/removal, found that CH_4 fluxes were strongly dependent on bottom water temperature.

Lake Baikal has been shown to emit methane derived from gas seeps (Schmid et al. 2007). Accordingly, an unknown but likely small fraction of lake fluxes may belong to the “geologic source” category (Chapter 8); attribution of bubble fluxes can be difficult without CH_4 isotopic analyses.

6.2.2 Nitrous Oxide

N_2O is produced by microbial activity in soils, sediments, and water. Under aerobic conditions, N_2O is an intermediate product of nitrification (the oxidation of ammonium to nitrate); under mildly anaerobic conditions N_2O is an intermediate product of denitrification (the reduction of nitrate to dinitrogen, or N_2). In general, high rates of N_2O production are more commonly associated with denitrification than nitrification (Firestone and Davidson, 1989). In lakes, denitrification occurs under several conditions: in aquatic sediments with overlying oxic water, in which nitrate is generated in a thin layer of oxic sediments and diffuses down to a thin band of sediments in which it can be denitrified; in seasonally stratified aquatic systems, in which nitrate produced in situ or from external inputs is available for denitrification when the water stratifies and the bottom layer becomes anoxic; and in permanently stratified (or rarely mixed) aquatic systems with anoxic bottom water, where nitrate diffuses from overlying oxic water (Seitzinger et al., 2006). However, in a study of 15 Swiss lakes of varying size and trophic or nutrient status, Mengis et al. (1997) found that N_2O was produced in three zones: (1) near the surface and attributed to actively growing algae and/or co-existing denitrifiers, (2) in the oxic hypolimnion (or water below the thermocline or thermal boundary in thermally stratified lakes) and attributed to nitrification, and (3) at oxic/anoxic interfaces in the hypolimnion and attributed to both denitrification and nitrification. They also found that denitrification consumes N_2O (i.e., denitrifiers further reduce N_2O to N_2) in the anoxic hypolimnia/sediment.

Huttunen et al. (2003) found that most N_2O flux from a boreal lake came from the littoral (or shoreline vegetated) zone. Fluxes were highest from the eulittoral (or temporarily flooded) zone, and lower from the infralittoral (or permanently flooded) zone. They refer to the temporarily flooded sites as meadow and marsh, and these may be classified as wetlands, while the permanently flooded and vegetated sites are reed and water lily, and are more likely to be considered as lake sites.

Because nitrification and denitrification are highly sensitive to oxygen availability, oxygen concentration is an important factor in the balance between the two processes. Nitrogen levels in available forms such as ammonium and nitrate are also an important control. Piña-Ochoa and Álvarez-Cobelas (2006) summarized literature reports on denitrification rates in aquatic ecosystems. Annual rates of denitrification were found to be higher in lakes than in rivers, coastal ecosystems, and estuaries. Across ecosystems, rates were correlated with nitrate levels and inversely correlated with O_2 levels. Stadmark and Leonardson (2005), measuring N_2O emissions from shallow (<1.5m) ponds constructed in southern Sweden for nitrogen retention/removal, found that N_2O fluxes from the ponds were below their detection limit, but that N_2O production in sediment and water incubations increased with increasing nitrate concentration. Liikanen et al. (2002) found a similar effect in incubations of shallow (4m) and deep (8m) sediments from a eutrophic or nutrient-rich lake in Finland.

6.3 Current Global Emissions

6.3.1 Methane

As noted above, early estimates of 5 Tg CH_4/yr emitted from lakes/freshwater (range 1 to 25 Tg CH_4/yr) were based on very limited data (Cicerone and Oremland, 1988). Khalil and Shearer (2000) included lakes as one of a group of 10 "minor sources that each emit between 10-50 Tg CH_4/yr, but collectively are a significant fraction of the global budget," but provided no additional assessment.

Bastviken et al. (2004) estimated global CH_4 emissions from lakes at 8 to 48 Tg CH_4/yr, with 6 to 25 Tg CH_4/yr from open water and 2 to 23 Tg CH_4/yr of plant-mediated flux. Their estimate is based on CH_4 flux relationship to lake area, based on fluxes from about 20 field studies, and a global lake area database from Kalff (2002). There are two reasons to re-evaluate this estimate. First, the global lake area reported by Kalff (2002) is less than half the lake area of the more recent estimate of Downing et al. (2006), and much of this discrepancy may be due to representation of small lakes and ponds. Other studies have also noted that very small lakes cover substantial areas and must not be overlooked in regional and global lake assessments (Hanson et al., 2007; Walter et al., 2007); small lakes are more likely to have more vegetation, and thus have larger fluxes per unit lake area. Second, the data used to develop an empirical relationship between lake area and CH_4 flux in the analysis of Bastviken et al. (2004) came from temperate and boreal lakes, with no data from arctic or tropical lakes. Bastviken et al. (2004) also note that, since flux for most lakes is dominated by bubbles and since it is difficult to design a measurement program that will capture all of these events, some very large events may be missed, introducing a potential low bias in measured fluxes. Based on the regression equations in Bastiviken et al. (2004), mean lake CH_4 fluxes for bubbles plus diffusion ranged from about 5 mg CH_4/m^2/day for lakes larger than 1,000 km^2 to 40 mg CH_4/m^2/day for lakes smaller than 1 hectare. Episodic storage fluxes (spring and/or fall lake overturning) were estimated at one-third of the total annual flux for small lakes and only a few percent for large lakes, while bubble fluxes were 50 to 60 percent of the total flux across the range of lake sizes.

Data from arctic sites, boreal and sub-boreal beaver ponds, and tropical lakes (Table 6-1) show that flux rates in these lakes are generally higher than the empirical fits to boreal and temperate lake data in Bastviken et al. (2004). Bartlett et al. (1992) measured fluxes from small arctic lakes and ponds, and observed lower fluxes for large lakes and higher fluxes for small lakes, and that their range (Table 6-1) was comparable to other measurements that had been made in Alaska. Walter et al. (2006) reported that CH_4 fluxes from thermokarst (thaw) lakes were highly variable, and predominantly from bubbles, with small hotspots accounting for most of the flux. Walter et al. (2007) extrapolated this and other measurements to an annual flux of 24.2 ± 10.5 Tg CH_4/yr from all lakes north of 45°N.

CH_4 fluxes from beaver ponds in boreal and sub-boreal North America (Table 6-1) were generally higher than the fluxes reported in Bastviken et al. (2004).

In the tropics, most measurements of lake CH_4 fluxes have been made in the neotropics (South and Central America), with very little sampling in tropical Africa or Asia. Again, flux rates (Table 6-1) are generally higher than boreal and temperate zone rates used in the analysis of Bastviken et al. (2004). Bubble fluxes generally accounted for a majority of the total flux (e.g., Keller and Stallard, 1994). Fluxes were typically higher in shallower water (Engle and Melack, 2000; Keller and Stallard, 1994), and if vegetation was present (e.g., Melack et al., 2004) were higher in shallower water, and increased with (or were triggered by) wind speed.

Based on higher flux ranges from thermokarst lakes, other small arctic lakes, beaver ponds, and tropical lakes than the range of values used by Bastviken et al. (2004), the likely underestimation of small lake area in the analysis of Bastviken et al. (2004), and the general pattern across many studies of higher fluxes from smaller lakes, the actual CH_4 emissions from lakes are likely to be at the higher end of the range presented by Bastviken et al. (2004), perhaps 30 ± 20 Tg CH_4/yr.

Table 6-1. Observed Methane Fluxes from Tropical and Arctic Lakes and Boreal and Sub-Boreal Beaver Ponds

Location	CH_4 Flux *(mg CH_4/m/day)*	Reference	Site Type
Alaska	4–77	Bartlett et al., 1992	Arctic lakes
Siberia	70 ± 6	Walter et al., 2006	Arctic thermokarst lakes[b]
Ontario	290	Bubier et al., 1993	Boreal beaver pond
Manitoba	100	Roulet et al., 1997	Boreal beaver pond
Minnesota	50–70	Naiman et al., 1991	Sub-boreal beaver pond
Panama	10–200	Keller and Stallard, 1994	Tropical lake, deeper sections (> 7 m)
Panama	300–2,000	Keller and Stallard, 1994	Tropical lake, shallower sections (< 2 m)

Location	CH_4 Flux *(mg CH_4/m/day)*	Reference	Site Type
Brazil	53–330	Engle and Melack, 2000	Tropical lake, low and falling water
Brazil	2–25	Engle and Melack, 2000	Tropical lake, high and rising water[c]
Brazil	50 ± 8	Melack et al., 2004	Tropical lake, open water
Brazil	120 ± 40	Melack et al., 2004	Tropical lake, with aquatic vegetation, shallow water
Brazil	320 ± 70	Melack et al., 2004	Tropical lake, aquatic vegetation, deeper water
Brazil	140 ± 310	Marani and Alvalá, 2007	Tropical lake and floodplain range[d]

[a] Higher fluxes for small lakes, lower fluxes for large lakes.
[b] Mean value for thermokarst lakes, with most flux from hotspots occupying a small fraction of the lake surface.
[c] Bubble flux not measured, assumed to be 20 percent of total.
[d] Lake fluxes somewhat lower than floodplain fluxes.

6.3.2 Nitrous Oxide

There has been no quantification of freshwater lakes as a global source of N_2O to the atmosphere. In their analysis, Mengis et al. (1997) measured fluxes of 0.01 to 0.84 micromoles/m^2/hour, which, integrated over a 250-day open-water year, is 0.02 to 1.6 kg N_2O-N/ha/yr. Huttenen et al. (2003) report N_2O emissions from boreal lakes of 0.003 to 0.015 kg N_2O-N/ha during spring ice-out, 0.006 to 0.025 kg N/ha during the open water season, and negligible during winter. Applying a mean annual flux of 0.01 to 0.1 kg N_2O-N/ha across 4.2 million km^2 of lakes and ponds (Downing et al., 2006) would generate an annual flux of 0.004 to 0.04 Tg N_2O-N/yr. This represents much less than 1 percent of the global annual N_2O flux from natural sources.

6.4 Future Emission Scenarios

6.4.1 Methane

Climate warming impacts on permafrost and the development of thermokarst (thaw) lakes could significantly affect future CH_4 emissions from high-latitude lakes. Walter et al. (2007) used a space-for-time substitution based on the current and projected lake distributions in permafrost-dominated and permafrost-free terrains north of 45°N, and representative flux rates for these lakes, to generate two estimates of future CH_4 emissions from lakes north of 45°N. One estimate is based on the disappearance of all permafrost in the Northern Hemisphere, with a consequent decrease in lake area of about 60 percent in permafrost regions. The other estimate is based on what they consider to be a more probable transition to a reduced extent of permafrost, with a 10 percent increase in lake area in continuous permafrost regions due to warming and partial melting and a 60 percent decrease in lake area in non-continuous permafrost regions due to melting. Based on mean lake emission rates from their earlier work, Walter et al. (2007) estimated that northern lake emissions (lakes north of 45°N) will eventually decrease by about 12 percent to 22 Tg CH_4/yr in a probable transitional permafrost scenario, and by approximately 53 percent to 12 Tg CH_4/yr in a “permafrost-free” Northern Hemisphere. Before this long-term decline in CH_4 emissions from lakes, due to lake area loss and permafrost thaw, there would be a period of increased CH_4 emissions associated with thermokarst lake development in the zone of continuous permafrost. Walter et al. (2007) estimate that CH_4 emission rates from northern lakes could rise as high as 50 to 100 Tg CH_4/yr during this transitional period lasting hundreds of years, due to thermokarst lake development in current regions of continuous permafrost with abundant soil organic matter. At this time, however, there are few published studies of thermokarst lake CH_4 emissions, and much uncertainty in future projections related to rates of permafrost decay and thermokarsting and the potential role of oxidation to reduce fluxes from warmer lakes.

6.4.2 Nitrous Oxide

There have been no published estimates of future N_2O emissions from lakes. Increased nitrogen loading (e.g., Galloway and Cowling, 2002) and increased temperatures may cause an increase in N_2O fluxes from lakes, but total N_2O flux from lakes is likely to remain a very small fraction of total global N_2O emissions from natural sources.

6.5 Areas for Further Research

Lake fluxes of CH_4 and N_2O are still not well-quantified across the globe. For example, in a recent CH_4 budget assessment for a large catchment in Sweden, Christensen et al. (2007) excluded lakes and rivers (about 15 percent of the total area in their study catchment) due to a lack of data on CH_4 fluxes. All large-scale extrapolations are based on empirical relationships developed from relatively limited field sampling. (This is especially true for N_2O fluxes, of which only a few have been reported, probably because the low flux rates reported to date have discouraged additional field studies.) For CH_4, there are now dozens of studies reporting lake fluxes, but since bubbling is a significant and highly episodic source, there is still substantial range and uncertainty in the seasonal to annual flux rate. In addition, field sampling of lake CH_4 fluxes has not occurred in many parts of the arctic, boreal region, and tropics. Isotopic analysis of methane fluxes may identify deep geological sources (see Chapter 8) that are bubbling through lakes. There has been no process-based modeling of regional or global lake fluxes of CH_4 or N_2O.

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Chapter 7. Gas Hydrates

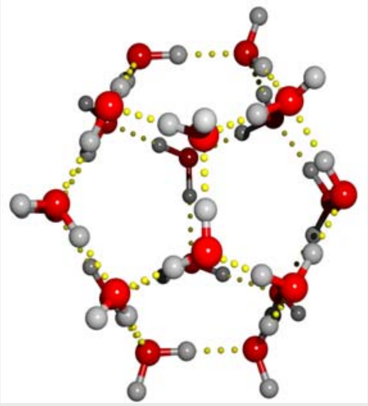
Currently, natural gas hydrates (also called clathrate-hydrates) play two very distinct roles in the global carbon cycle. They act as a dynamic storage capacitor for CH_4 (i.e., a large sink of CH_4, which fluctuates in size as atmospheric concentrations of CH_4 change) (Dickens, 2003), but they also feed CH_4 directly into the ocean water column. Under current conditions, CH_4 emissions from gas hydrates are small, but there is the potential for significant CH_4 release from gas hydrates.

U.S. EPA (1993) examined and summarized CH_4 emissions from gas hydrates as a natural source of CH_4, as did the AR4 (Denman et al., 2007). The AR4 discusses potential CH_4 emissions from hydrates but does not examine them quantitatively. The estimates for future emissions from hydrates reported in U.S. EPA (1993) have been updated significantly and more advanced models have been developed. The emission source discussed in this chapter includes CH_4 currently stored in the form of gas hydrate; CH_4 emitted from gas hydrates is introduced into the ocean water column, where it is dissolved, oxidized, or emitted to the atmosphere. This source differs from the oceanic CH_4 source discussed in Chapter 4: what this report describes as oceanic CH_4 is generated in the water column, but CH_4 from gas hydrates is emitted into the water column.

7.1 Description of Emission Source

Gas hydrates are an ice-like compound formed between water and a gas molecule such as CH_4, under high pressure and at temperatures near the freezing point of water. Pressure and temperature conditions conducive to CH_4 gas hydrate formation are found at ocean depths typically greater than 500 meters and are characterized by the hydrate stability zone (HSZ) shown in Figure 7-2. With increasing temperature, a higher pressure is necessary to stabilize gas hydrates in the solid form. The hydrate stability curve shown in blue in Figure 7-2 is determined from the pressure-temperature data for methane hydrate equilibrium, while the geothermal temperature gradient is an example of a typical temperature-depth curve for an ocean depth of approximately 1.7 km. The water temperature decreases with depth throughout the water column and increases below the seafloor due to the heat flux through the earth’s crust. Due to the low solubility of methane in water and thus the low concentration of methane in the ocean, hydrate deposits are mostly contained in ocean sediments.

Figure 7-1. Small cage of Structure I gas hydrate cage.



Water molecules are illustrated as red (oxygen) and gray (hydrogen) atoms, with hydrogen bonds indicated with yellow dotted lines.

Three major types of crystal structures are formed by gas hydrates: structure I (sI), structure II (sII), and structure H (sH). Structure I is the preferred form for pure CH_4, ethane, and carbon dioxide hydrates. Hydrocarbons including propane and iso-butane and small gases such as argon, krypton, nitrogen, and oxygen form structure II hydrate, as well as certain gas mixtures of CH_4 and ethane.

Gas hydrates have an incredible storage capacity for the gases that they trap. For instance, one cubic meter (1 m^3) of pure methane hydrate, which contains approximately one CH_4 molecule for every six water molecules, can store 170 to 180 standard cubic meters (SCM) of gas (Kvenvolden, 1991; Sloan, 2003). As a result of this storage capacity and their widespread occurrence, gas hydrates have recently gained interest as a potential energy resource. This section, however, examines the worldwide inventory and gas hydrates’ potential as a CH_4 emission source.

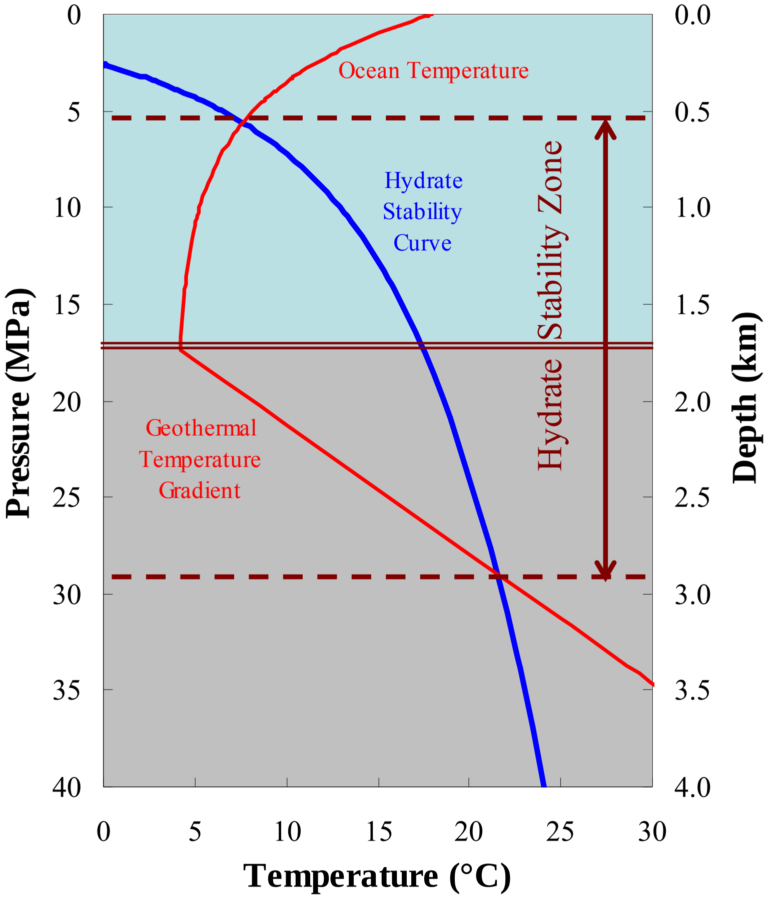


Figure 7-2. Illustration of the water temperature and hydrate stability zone through the water column, with an ocean depth of 1.7 km and a geothermal gradient (i.e., temperature increase with depth below the ocean floor) of 15 degrees Celsius per km.

Methane gas hydrates form if CH_4 is generated within or enters the HSZ (see Figure 7-2). The source of CH_4 generation can be either microbial or thermal in origin. Microbial CH_4 is created by the anaerobic digestion of organic matter by microorganisms in shallow, oceanic, and continental sediments. Thermogenic CH_4 may contain a mixture of other higher hydrocarbons such as ethane and propane, but microbially produced CH_4 is generally pure CH_4. The introduction of the higher hydrocarbon gases will lower the pressures necessary for hydrate formation, thus enlarging the HSZ.

Thermogenesis of CH_4 takes place under high pressure (>20 megapascal [MPa]) and temperature (>80 to 120°C) (MacDonald, 1990). Typically, such conditions exist well below the zone of hydrate stability. When CH_4 is created in this manner, it enters hydrate form only when a migration pathway exists from the lower sediment to the upper sediment layer (Kvenvolden, 1988). Tests of the isotopic composition of the CH_4 extracted from hydrates at several depths and locations worldwide reveal that most of it is microbially generated, not thermally produced (MacDonald, 1990).

Although gas hydrates currently have low CH_4 emission rates, the potential for CH_4 release is great. It is therefore important to detail the amount of CH_4 currently stored as gas hydrate globally. Since the previous EPA report on natural sources of CH_4 (U.S. EPA, 1993), the global methane hydrate inventory estimates have changed substantially. As shown in Table 7-1, the estimates for the amount of CH_4 stored worldwide have varied significantly. Early estimates of the amount of CH_4 in oceanic hydrates ranged from 2.3×10^6 Tg CH_4 (Mclver, 1981) to 5.5×10^9 Tg CH_4 (Dobrynin et al., 1981), and estimates of the amount of CH_4 in continental hydrates ranged from 1×10^5 Tg CH_4 (Meyer, 1981) to 2.4×10^7 Tg CH_4 (Dobrynin et al., 1981). Later, the inventories were thought to have converged to about 1×10^7 Tg of CH_4 in oceanic reserves and 5×10^5 Tg for continental reserves (MacDonald, 1990; Kvenvolden, 1991). However, in recent years the estimates have, for the most part, decreased. Since the amount of continental hydrate is now believed to be only a small fraction of the total hydrate volume, most current estimates focus on the marine hydrate inventory. In the mid-1990s, estimates for oceanic CH_4 in hydrates ranged from 1.8×10^7 Tg (Gornitz and Fung, 1994) to 3.2×10^7 Tg (Harvey and Huang, 1995) while in the current decade estimates include 1×10^7 Tg (Kvenvolden and Lorenson, 2001), 6.7×10^6 Tg in both hydrates and CH_4 bubbles (Buffett and Archer, 2004), 0.7 to 3.4×10^6 Tg (Milkov, 2004), and 7.4×10^7 Tg (Klauda and Sandler, 2005). Harvey and Huang estimated that the CH_4 in continental hydrates totals 1×10^6 Tg, approximately 3 percent of the total CH_4 found in hydrate deposits (Harvey and Huang, 1995). Milkov (2000) estimated that there are 7-700 Tg CH_4 in hydrates associated with mud volcanoes.

Table 7-1. Summary of Methane Inventories in Marine Gas Hydrates

Study	CH_4 Mass/10^6 Tg
(Mclver, 1981)	2.3
(Dobrynin et al., 1981)	5,500
(MacDonald, 1990)	10
(Gornitz and Fung, 1994)	18
(Harvey and Huang, 1995)	32
(Kvenvolden and Lorenson, 2001)	10
(Buffett and Archer, 2004)	6.7
(Milkov, 2004)	2[a]
(Klauda and Sandler, 2005)	74

[a] Midpoint value.

7.2 Factors That Influence Emissions

Gas hydrates, when found within the HSZ, emit CH_4 only though the dissolution of CH_4 into undersaturated water (i.e., water that contains less than the maximum amount of CH_4 at any given temperature). Dissolution rates for CH_4 and carbon dioxide hydrates (i.e., the rate at which they dissolve in ocean water) have been measured experimentally on the seafloor (Rehder et al., 2004). It was concluded that the rate of dissolution of both CH_4 and CO_2 from hydrates into the seawater was limited by the diffusion of the gas away from the hydrate as opposed to any characteristics of the hydrate itself. Dissolution rates of several millimeters per day were found for a sample exposed to the open ocean currents (Rehder et al., 2004). Dissolution rates are influenced by the ocean currents, the exposed hydrate area, and the level of CH_4 saturation in the water at the exposed hydrate interface.

The minimum depth of hydrate stability is proportional to pressure and inversely proportional to temperature (i.e., hydrates are stable if the pressure is sufficiently high and the temperature is sufficiently low). Hydrates do not exist at the ocean's surface because, even under the coldest conditions, the pressure is not sufficient. Conversely, hydrates do not exist at great depths because temperature increases with depth in sediment (according to a geothermal gradient of 0.016 to 0.053°C/meter), and by about 2 kilometers below the sediment surface, temperature is almost always too high for the hydrate structure to be viable. The HSZ can be anywhere from 0 to 2 kilometers thick, and can expand or contract in response to changing temperature and pressure conditions. If it expands (as a result of increased pressure and/or decreased temperature), it can incorporate more CH_4 from the surrounding sediment. If it contracts (as a result of decreased pressure and or increased temperature), large amounts of CH_4 can be liberated from hydrates into the sediment and can migrate into the atmosphere. The global average HSZ is expected to respond to atmospheric temperature changes over time scales on the order of several thousand years. However, initial decreases could occur in as little as 200 years in shallow high-latitude seafloor areas that underlie regions of sea ice loss (Fyke and Weaver, 2006). These areas that would experience sea ice loss would be subject to lowered albedo and increased absorption of incoming radiation at the sea surface. The combination of initially shallow HSZ depths and rapid, large seafloor temperature increases in these regions makes them the first to experience rapid hydrate destabilization (Fyke and Weaver, 2006).

Currently, the major source of CH_4 flux due to methane hydrates is offshore continental hydrates (Kvenvolden, 1991). Offshore continental hydrates are found on the nearshore continental shelf, where melting subsea permafrost has continued since times of lower sea level. Since the last ice age, 18,000 years ago, sea level has risen about 100 to 125 meters, and the temperature of the present shelf has risen about 15°C (Hill et al., 1985; Kvenvolden et al., 1991). Additional increases in shelf temperatures would result in additional areas of hydrates becoming destabilized.

7.3 Current Global Emissions

Since 1993, there has been limited discussion of the current flux of CH_4 from gas hydrate reservoirs. Oceanic and onshore continental reserves are believed to be stable at present, which means that they are not currently emitting CH_4. However, offshore continental shelf reserves are currently unstable, and may emit 2 to 5 Tg of CH_4 annually to the seafloor (Kvenvolden, 1988, 1991; Dickens, 2003), of which a large fraction would likely be oxidized in the ocean water column(MacDonald et al., 2002; Niemann et al., 2006). The Kvenvolden estimates are based on emissions resulting from climate changes within the last 18,000 years, the time since the last glaciation. Since that time, sea level has risen about 100 to 125 meters, inundating large areas of permafrost which contain methane hydrates. Inundation has increased the pressure in this region by about 9 atmospheres or 132 psi, which would be expected to increase the stability of the hydrates. However, over the same period, the temperature at the sediment surface has increased by 15°C, which is more than enough to offset the increase in pressure and destabilize the hydrates (Kvenvolden, 1991). Due to the slow rates of downward thermal diffusion in sediments, this temperature change is still in the process of penetrating downward, melting the permafrost and associated gas hydrates. The emission estimate of 3 to 5 Tg CH_4/yr was determined by assuming that the difference between the calculated and the known amount of CH_4 in sub-sea permafrost hydrates (160,000 - 43,000 = 117,000 Tg) has been uniformly released over the last 18,000 years (Kvenvolden, 1991). These estimates are very sensitive to the estimates of the total amount of CH_4 stored in sub-sea permafrost hydrates. As discussed in Section 7.1, these estimates can vary significantly.

In 2003, Dickens published models of two plausible gas hydrate capacitors that consisted of 13×10^6 Tg of CH_4 in hydrate, 0.67×10^6 Tg of free CH_4 beneath the hydrate reservoirs, and 1.3×10^6 Tg of dissolved CH_4. The two scenarios were a high and low flux of CH_4 into the gas hydrate capacitor from methanogenesis, F_{Meth} = 2.2 and 9.3 Tg/yr. The resulting fluxes of CH_4 to the seafloor are 2.2 and 9.3 Tg/yr from the low and high flux cases, respectively (Dickens, 2003). These likely represent the most accurate estimate of CH_4 flux from hydrate deposits globally and are of the same magnitude of the estimates reported in the previous report on natural sources (U.S. EPA, 1993), as well as the AR4 (Denman et al., 2007); however, Dickens' estimates correspond to emissions to the seafloor, while the EPA report and the AR4 refer to atmospheric emissions.

These estimates assume that the CH_4 being liberated from the gas hydrate form is released into the atmosphere. It is possible, however, that most or all of this gas is not actually emitted to the atmosphere. Instead it is oxidized or absorbed within the sediment or dissolved into the water column. Recent work by Yamamoto et al. (2009) showed while the saturation of methane in the water column does not have to reach 100 percent of its capacity in order for methane to be released to the atmosphere, the current rate of methane release from ocean sediments is insufficient to result in methane being released to the atmosphere.

7.4 Future Emission Scenarios

Due to their proximity to the earth's surface (< 2,000 meters), gas hydrates will likely eventually be affected by climate change. CH_4 emissions from this source are likely to increase if temperature significantly rises. While pressure on hydrates is also expected to change as a result of sea level rise and the melting of polar ice caps, temperature changes are likely to be far more significant than changes in pressure in determining changes in future emissions due to anthropogenic climate change and on the HSZ. The following two sections summarize existing estimates of potential future CH_4 emissions from hydrates.

7.4.1 Continental Hydrates

Kvenvolden (1991) estimates that the most likely additional future source of CH_4 emissions from hydrates is from subsea permafrost. This is a region of CH_4 hydrates that has been submerged since the last glacial maximum, and is currently unstable. The accelerated oceanic temperature rise that would result from an expected atmospheric temperature increase due to climate change over the coming century could penetrate to the subsea permafrost and increase the current rate of emissions from these hydrates by an order of magnitude (from 4–5 Tg CH_4/yr to 40–50 Tg CH_4/yr). This increase would be expected to take place sometime after the 21st century (Kvenvolden, 1991). Similarly, this scenario predicts that onshore gas hydrates will eventually be destabilized by climate change and the permeation of rising temperatures through the permafrost. The rate of emissions from destabilization of onshore hydrates is predicted to be twice that of subsea permafrost hydrates, or about 100 Tg CH_4/yr. However, the time lag before this emission rate is achieved is likely to be greater than the lag for subsea permafrost emissions, with estimates of the time lag for continental hydrates ranging from hundreds to thousands of years.

MacDonald (1990) assumes, based on the analysis of temperature changes in the Arctic by Lachenbruch and Marshall (1986), that Arctic surface temperature will increase by 2°C by 2080 (an extremely conservative estimate). MacDonald predicts that about 0.01 percent of the continental hydrate zone will degas per year, resulting in annual emissions of 50 Tg CH_4/yr.

Based on the assumption that air temperatures in the high latitudes will increase by 10°C as a step change, Bell (1982) predicts that the destabilization of hydrates below the Arctic permafrost region will begin within a few hundred years of the initial temperature rise. Consequently, the permafrost between the -5°C and -15°C isotherms of annual mean air temperature becomes unstable. Bell estimates that half of the continental reserves (2.7×10^6 Tg CH_4) of hydrates will dissociate uniformly over 4,000 years resulting in a flux of about 300 Tg CH_4/yr.

Based on a 19°C air temperature rise within a century in the Arctic Islands resulting from a quadrupling of atmospheric CO_2 concentration, Nisbet (1989) predicts that a large fraction of the hydrates in the Arctic Islands will destabilize. Nisbet assumes that hydrates in this region are stable below 50 to 100 meters of sediment due to the extreme cold temperatures. Because of the large temperature rise and the proximity of hydrates relative to the surface, Nisbet predicts that this region of hydrates will dissociate within approximately the 100 years following the temperature increase, emitting 100 Tg/yr of CH_4 from hydrates. Deeper hydrates would begin degassing in 500 to 1,000 years (Nisbet, 2002). The shallow nature of hydrate deposits in the Arctic Islands and the potential for large temperature increases make these hydrates very vulnerable to warming of the surface (Nisbet, 2002).

Harvey and Huang (1995) built a one-dimensional model with vertical columns on a 1 degree by 1 degree global grid to predict hydrate distribution and potential impact of thermal perturbations on hydrate destabilization. Their base-case clathrate distribution estimates about 24,000 Gt C (3.2×10^7 Tg CH_4) stored as methane clathrate in marine sediments and about 800 Gt C in terrestrial sediments. They predicted that only a small fraction of current stores could be destabilized by future climate change. For the continental hydrates, they examined three global surface warming scenarios (5, 10, and 15°C) and the cumulative release of CH_4 at times ranging from 100 to 5,000 years after the warming. They predict that, after 100 years, no CH_4 will have been released from terrestrial hydrates; after 500 years, 1.1, 7.3, and 14.4 Gt CH_4 will have been released (Harvey and Huang, 1995) for 5, 10, and 15°C warming. If the release is assumed to be uniform over years 100 to 500, the rates of CH_4 emissions are 2.7, 18.3, and 36.0 Tg CH_4/yr. Maximum CH_4 rates of 14.0, 74.5, and 132.1 Tg CH_4/yr are reached between 1,000 and 2,000 years.

A current Department of Energy project (DE-NT0005665) led by the University of Alaska Fairbanks and the U.S. Geological Survey is currently assessing the quantity of methane seepage from methane hydrate deposits under thermokarst lakes on the Alaskan North Slope. Terrestrial permafrost gas hydrates may be a significant source of methane seepage, but remain unquantified on a global scale. These gas hydrate deposits have a much thinner water column for oxidation processes and may be more susceptible to climate forcing than oceanic hydrates. Emission of methane from these terrestrial methane hydrate deposits may present a more direct and potentially more effective method of transfer of methane to the atmosphere.

7.4.2 Oceanic Hydrates

Kvenvolden (1991) predicts that oceanic hydrates will begin to destabilize after thousands of years following a rise in global temperatures, estimating that CH_4 emissions from this reservoir could eventually exceed the emissions from continental hydrates (150 Tg CH_4/yr).

Bell (1982) assumes that the surface water temperature of the Norwegian Sea, which feeds the Arctic Ocean, will rise about 3.5°C over an unspecified timeframe, resulting in a 3.5°C temperature rise along half the length of the 300 meter depth contour in the Arctic Ocean. Given this temperature change, the hydrates extending from the ocean sediment interface to a depth of 40 meters below the sea floor would be destabilized where ocean depths are between 280 and 370 meters. Bell estimates that the CH_4 in this 40 meter zone, which represents about 1 percent of the oceanic methane hydrate reserves, would be entirely and uniformly released over a 100-year span. A global estimate of 160 Tg CH_4/yr results from the assumption that the global oceanic CH_4 reserve of 1.3×10^6 Tg is uniformly distributed in the top 250 meters of ocean sediments, at depths between 200 and 1,000 meters.

Revelle (1983) estimates hydrate emissions under a scenario in which both mean annual air temperature and mean ocean surface temperature rise 3°C globally. The ocean bottom temperature would therefore increase by 1 to 4°C. After approximately 100 years, the top 100 meters of all oceanic hydrates around the world would be destabilized and begin releasing CH_4 into the ocean at a rate of 800 Tg CH_4/yr, with 20 percent absorbed by the water. The net CH_4 released to the atmosphere would be 640 Tg CH_4/yr.

Fyke and Weaver (2006) performed a series of climate sensitivity and potential future climate change experiments using the University of Victoria Earth System Climate Model. They found that the global HSZ responds significantly to elevated atmospheric CO_2 over time scales of thousands of years, with initial decreases of the HSZ occurring after 200 years in shallow high-latitude seafloor areas. The majority of the global HSZ adjustment to warmer seafloor temperatures occurs within the first 5,000 years after the atmospheric CO_2 increase. They estimate that, for average seafloor temperature increases of 1.0, 2.0, and 3.9°C (corresponding to atmospheric CO_2 levels that are allowed to increase exponentially based on the observed 1850–1990 increase, capped at years 2000, 2050, and 2100, and then held constant) that 7, 14, and 27 percent of the global hydrate reservoir is dissociated for their median thermal diffusivity (i.e., rate of temperature propagation) value. About half of this loss occurs in the first 5,000 years resulting in average CH_4 emissions of 67, 138, and 300 Tg CH_4/yr.

Gornitz and Fung (1994) provide estimates of the magnitudes and spatial distribution of potential oceanic methane hydrate reservoirs and examine implications for eventual atmospheric CH_4 release due to climate change. Two models were used: in situ bacterial production and pore fluid expulsion. The potential sensitivity to projected climate change was explored by estimating CH_4 volumes contained within the uppermost 1 meter of the HSZ that lie within 2°C and 2 meters of the equilibrium curve. Uniform release of this CH_4 (according to the bacterial model) would occur over the 100 years following a 2°C increase in ocean bottom temperatures at rates of 6.7 to 45.3 Tg CH_4/yr.

In addition to the continental CH_4 release estimates by Harvey and Huang (1995) discussed in Section 7.4.1, release rates from oceanic hydrates were calculated at ocean bottom temperature increases of 1, 2, 3, 4, 5, and 6°C over a timeframe of 2,000 years. The global hydrate reservoir is assumed to contain 24,000 Gt C (3.2×10^7 Tg CH_4) (Harvey and Huang, 1995). The peak CH_4 fluxes predicted range from 133 to 4,360 Tg CH_4/yr (for 1 to 6°C ocean bottom warming), with this peak occurring at the initial temperature spike.

Recent work by Reagan and Moridis (2008) at the Lawrence Berkeley National Laboratory studied the potential response of oceanic gas hydrate deposits to 1, 2, and 5°C increases in seafloor temperatures using TOUGH+HYDRATE, a multiphase flow and transport model developed for methane hydrates. They studied two cases, one similar to hydrates deposits below the Gulf of Mexico at 570 m depth and one at a depth of 320 m, similar to oceanic methane hydrate deposits on the Arctic continental shelf. Their estimates indicate that fluxes from hydrate deposits exposed to significant temperature increases may exceed the ability of the seafloor environment to consume the released methane via oxidation pathways, similar to observations by Leifer et al. (2006).Their model indicates that a 1 to 5°C rise in ocean temperature could result in 120 to 200 g $CH_4/yr/m^2$. Assuming that the global average methane hydrate saturation in oceanic sediments and a worldwide methane hydrate reservoir containing 10^7 Tg CH_4, this would correspond to a methane flux of about 1,200-2,000 Tg CH_4/yr to the seafloor.

Table 7-2. Ocean Hydrate Scenarios

	Kvenvolden	Revelle	Bell	Fyke	Gornitz	Harvey	Composite
Ocean temperature rise (°C)		1–4	-0.5–3	1–4	1–2	1–6	3
CH_4 reserves (Tg)	1×10^7	1.8×10^7	1.3×10^7	8.7×10^6	8.7×10^6	1.8×10^7	1.0×10^7
Time until destabilization begins (years)	1,000s	100s	100s	200	100	100	
Time to fully destabilize (years)	1,000s		100s	5,000	N/A flux	1,000s	
Avg emissions factor[a] (10^{-6} yr^{-1} $°C^{-1}$)	5.0	150	3.4	8.9	3.1	11.0	6
Annual emissions[b] (Tg/yr)	**> 150**	**800**	**160**	**67–300**	**6.7–45**	**93–2,133**	**186**

[a] Emissions factor at a ΔT_{ocean} of 3°C, either calculated or interpolated.
[b] CH_4 emitted to the ocean.

7.5 Areas for Further Research

Areas for future research in the area of gas hydrates as they relate to atmospheric CH_4 start first and foremost with the quantification of the reserves of CH_4 stored in the form of gas hydrates. Since most of the future emission scenarios depend on the total amount of methane stored as gas hydrates globally, it is very important to have the most accurate estimates possible of the total methane stored as hydrate. Secondly, accurate estimates of the rates of CH_4 absorption into the oceans and the rates of CH_4 oxidation within the water column are absolutely essential. Estimates of future emissions from methane hydrates presented in Table 7-2 only consist of how much CH_4 would reach the oceans from hydrate deposits. In order to close the loop on CH_4 emissions to the atmosphere, absorption and oxidation rates must be known. It is also not clear that the current flux of CH_4 from hydrate deposits has been accurately assessed. Not only are the continental shelf hydrates persisting in an unstable state (Buffett and Zatsepina, 1999), but any hydrates exposed to seawater undersaturated in CH_4 are vulnerable to dissolution (Rehder et al., 2004).

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Chapter 8. Terrestrial and Marine Geologic Sources

Natural seeps of CH_4 and other hydrocarbons from geologic sources deep within the Earth's crust have been known to human civilization for millenia. Perpetual fires, crude oil and gas seeps, and the trance-inducing properties of natural gas emissions from rock fissures have all been objects of fear, wonder, and even worship throughout the centuries (e.g., Kvenvolden and Rogers, 2005; Etiope et al., 2006).

Until recently, however, the contribution of geologic emissions to the global CH_4 budget—arising from a wide range of types of fissures and fractures in the Earth's crust—has been largely ignored. (Geologic seeps are not considered to be a source of nitrous oxide emissions.) Most top-down analyses seeking to resolve the global CH_4 budget through inverse modeling do not include emissions from this source in their *a priori* estimates (Hein et al., 1997; Milakoff et al., 2004; Frankenberg et al., 2005; Bosquet et al., 2006; Chen and Prinn, 2006; Bergamaschi et al., 2007). Bottom-up CH_4 budget estimates summarized in the first, second, and third IPCC reports do not include a terrestrial geologic source (e.g., Ehhalt et al., 2001). The few inverse modeling studies that do include a geologic source (Houweling et al., 1999; Ferretti et al., 2005; Harder et al., 2007) tend to significantly underestimate the magnitude of these emissions relative to bottom-up estimates (Etiope and Klusman 2002; Etiope, 2004, 2005; Etiope et al., 2008b; Kvenvolden and Rogers, 2005) and/or misattribute emissions to single sources such as hydrates or magma-emitting volcanoes.

Over the last decade, systematic measurements of CH_4 emission rates from volcanic geothermal regions and hydrocarbon sedimentary basins around the world—from the mud volcanoes (MVs) and seeps of Italy to those of Azerbaijan—have firmly established both the reality of these emissions and their significance on the global scale (Etiope, 1999; Etiope et al., 1999, 2002, 2004a,b, 2007a, 2008a; Huseynov and Guliyev, 2004; Martinelli and Judd, 2004; Yang et al., 2004). Analyses of the atmospheric abundance ratios of CH_4 also find a higher fossil component than can be accounted for through fossil fuel emissions alone (Lassey et al., 2007a,b; Etiope et al., 2008b), verifying the likelihood of a relatively large geologic source.

Specifically, new interpretation of atmospheric $^{14}CH_4$ measurements (Etiope et al., 2008b) suggests that emissions from all fossil sources make up 30±5 percent of global CH_4 emissions. For a global source estimated at 582±87 Tg CH_4/year, this implies a natural plus anthropogenic fossil source of 175±39 Tg CH_4/year. Anthropogenic emissions associated with fossil fuel extraction and consumption are estimated at 90 to 100 Tg CH_4/year. This range therefore leaves ample room for both additional unidentified anthropogenic fossil sources, as well as geologic CH_4 emissions estimated to be on the order of 30 to 70 Tg CH_4/year (Table 8-2). The best available estimate of present-day emissions of CH_4 from both terrestrial and submarine geologic sources lies in the range of 42 to 64 Tg CH_4/year, suggesting that, after wetlands, geological sources may represent the second largest natural source of methane.

These findings have led to geologic sources being explicitly cited in the CH_4 budget section of the most recent IPCC report (Denman et al., 2007) and assigned a specific emission category by the European Environment Agency (2009). However, much work still remains to be done in resolving the contribution of individual source types to the geologic methane budget.

8.1 Description of Emission Source

Geologic CH_4 is emitted through fissures and fractures in the Earth's crust. Emissions arise from two geologically distinct regions: (1) geothermal regions characterized by emissions from geothermal vents, soil degassing, and magma-producing volcanoes and (2) sedimentary petroliferous or hydrocarbon-containing basins characterized by emissions from both seepage and MVs. Emissions can also be characterized by size: *macroseepage* consists of relatively large, visibly detectable, localized emissions from identified geologic features and events such as MV, magma-producing volcanic eruptions, mid-ocean ridges, and localized vents; *diffuse soil exhalation* occurs over broad areas in geothermal regions, and *microseepage* over broad areas in sedimentary basins (Figure 8-1). Finally, sources can be either submarine (underwater) or terrestrial (land-based), although there is no essential difference in the CH_4 being emitted from these various sources: it is merely a matter of where the fault is geographically located. However, before reaching the atmosphere, the gas is often modified and sometimes even absorbed by the environment through which it passes—in the case of submarine sources, by the overlying sediment layers and ocean water, and in the case of terrestrial sources, by the surface soil layers that can contain both methanogenic or methanotrophic bacteria. We therefore differentiate CH_4 emissions by geological region of origin, by size, and by submarine vs. terrestrial sources (Figure 8-1).

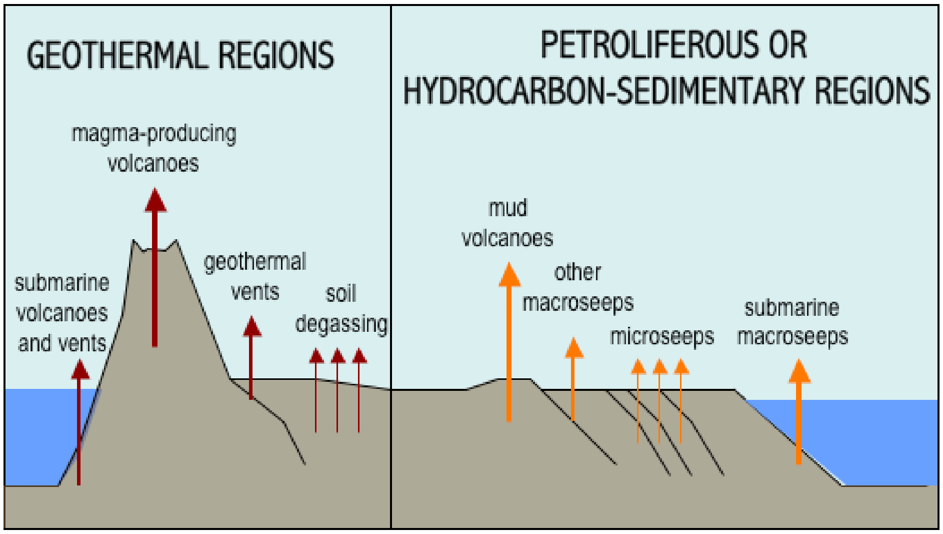

Figure 8-1. Geologic methane sources can be categorized by region (geothermal or petroliferous), source size (macro or micro), and location (terrestrial or marine).

Although primarily associated with areas of geothermal activity or hydrocarbon occurrence, known geologic sources are widespread. Active MV regions with associated vents and microseepage have been identified along the coastlines and continental shelves of nearly every continent (Dimitrov, 2003). CH_4 seepage has been reported from every sea and ocean, and in a broad range of oceanographic settings and geological environments (Judd, 2003).

8.1.1 Mud Volcanoes in Petroliferous Sedimentary Regions

MVs are geologic structures formed as a result of the emission of gas, water, and sediments from the Earth's crust. MVs generally occur in sedimentary areas and are often associated with natural gas and oil deposits. For that reason, much of the gas emitted from MVs is CH_4, with other hydrocarbons and carbon dioxide making up the remainder (Kvenvolden and Rogers, 2005). A global dataset surveying more than 140 terrestrial MVs from 12 countries (Etiope et al., 2009) showed that, on average, CH_4 makes up 90 percent of the gases emitted by MVs.

Unlike high-temperature magmatic or "traditional" volcanoes, MV emissions occur at comparatively low temperatures. Instead of liquid magma, a semi-liquid muddy sediment is formed deep within the Earth's crust. This mud mixture is then forced up through long, narrow openings or fissures to form a MV cone or—in some cases—a "mud pie" (Dimitrov, 2003; Kopf, 2002). Individual MVs can also be very different from one another, with some being less than a meter in diameter while others can cover up to 100 square kilometers. Etiope (2003 and elsewhere) cautions that the term "mud volcano" can actually refer to a single edifice, a group of vents, or an entire cluster.

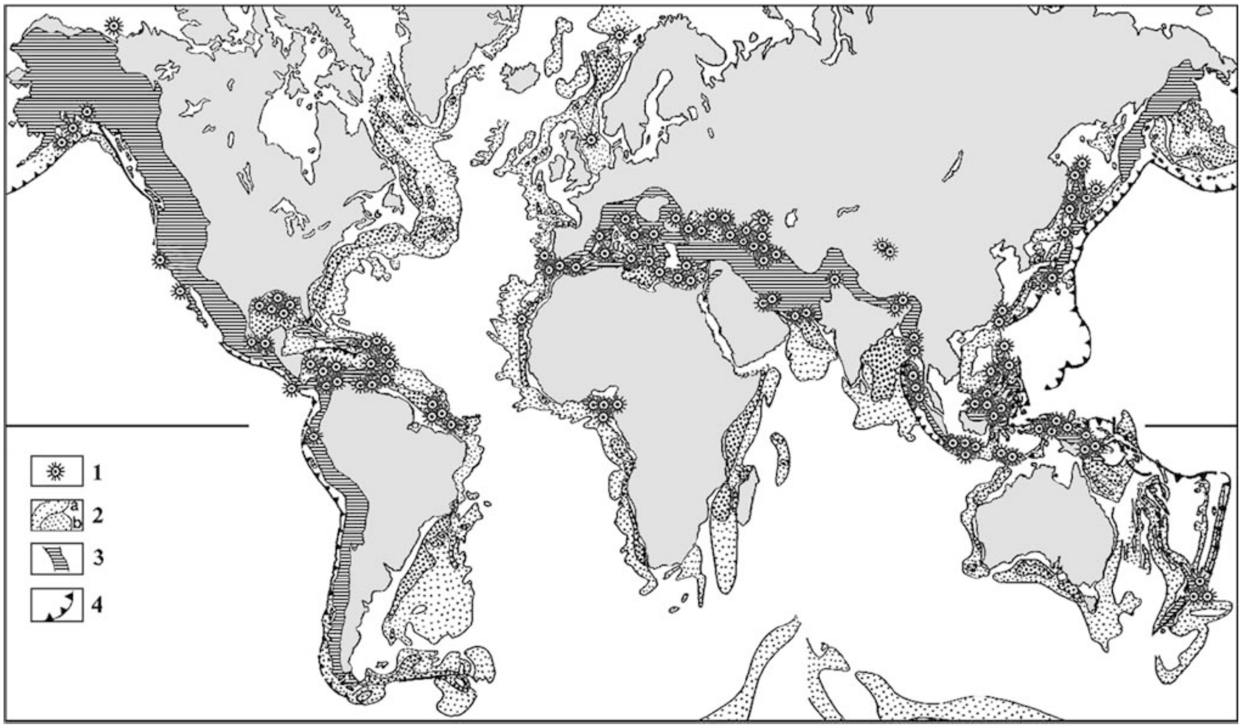

Figure 8-2. Global distribution of mud volcanoes, including single mud volcanoes, separated mud volcano areas, and mud volcano belts, as indicated by symbol 1. Symbols 2, 3, and 4 indicate areas of thinner (a) and thicker (b) sediment, active compressional areas, and subductive zones, respectively.

MV formation can be triggered by a number of pressure-inducing events, including rapid sedimentation, *in situ* gas generation, and structural or tectonic compression (Dimitrov, 2003). Similar to magmatic volcanoes, MVs can also experience both quiescent periods and periods of eruption, with average emission estimates changing accordingly. Significant emissions from MVs can still occur during quiescent periods, during which the volcanoes can grow through gradual outflows of semi-liquid mud. These can often be accompanied by what are known as “eternal flames” when the gases being emitted are ignited. Eruptions occur periodically, with some volcanoes capable of launching mud and ash several kilometers into the troposphere (Dimitrov, 2003).

Approximately 1,100 MVs have been documented onshore and in shallow water on continental shelves (Dimitrov, 2002b). Anywhere from 1,000 to 100,000 MVs may exist below the ocean surface, on continental slopes and abyssal plains (Milkov, 2000). Volcanoes are generally clustered together in belts associated with active plate boundary areas (Figure 8-2; Dimitrov, 2003). Specifically, more than half of the world’s terrestrial MVs are located in the Alpine Himalayas Active Belt, which extends from Italy in the west to Southeast Asia and Indonesia in the east. The largest concentration of terrestrial MVs occurs in Azerbaijan, with over 700 documented examples. Large terrestrial and marine MV belts also occur along the eastern and western sides of the Pacific Basin, and along the Caribbean coasts of Central and South America (Dimitrov, 2003).

8.1.2 Seepage in Petroliferous Sedimentary Regions

Macroseepage in petroliferous or hydrocarbon sedimentary areas refers to emissions of gases from large, visible features other than MVs. Macroseepage can occur via water-seeps or dry-seeps (Etiope et al., 2009). In water-seeps, gaseous emissions are accompanied by bubbling springs, groundwater, or even hydrocarbon wells. The water typically originates deep within the earth’s crust and may have interacted with the gas during its ascent to the surface. In contrast, dry-seeps consist of gaseous emissions only, typically emitted from vents in outcropping rocks, through the soil, or via the beds of rivers or lakes. Gases bubbling from wells or other shallow water bodies filled by groundwater should be considered dry-seeps, as the gas only needs to cross surface water before reaching the atmosphere.

Gaseous emissions from dry seeps can be ignited, and many burn naturally. With continuous emissions, "everlasting" flames from some dry-seeps have been continuously reported for centuries. One example is the Chimaera seep in Turkey, considered by many to be the site of the first Olympic flame. Globally, the number of terrestrial macro-seeps is estimated to exceed 10,000 (Clarke and Cleverly, 1991).

Micro-seeps are fissures in the Earth's crust that produce a slow, continuous flux of visibly undetectable hydrocarbon gases, including CH_4. In contrast to macroseepage, fluxes from these sources are not identified by a visible emitting feature but rather are usually detected using closed-chamber systems, a technique commonly applied to study the exchange of carbon-bearing gases at the soil-atmosphere interface (e.g., Norman et al., 1997). This technique is currently used to detect methane fluxes migrating along faultlines and upward from deep hydrocarbon reservoirs (Etiope, 1999; Klusman et al., 2000).

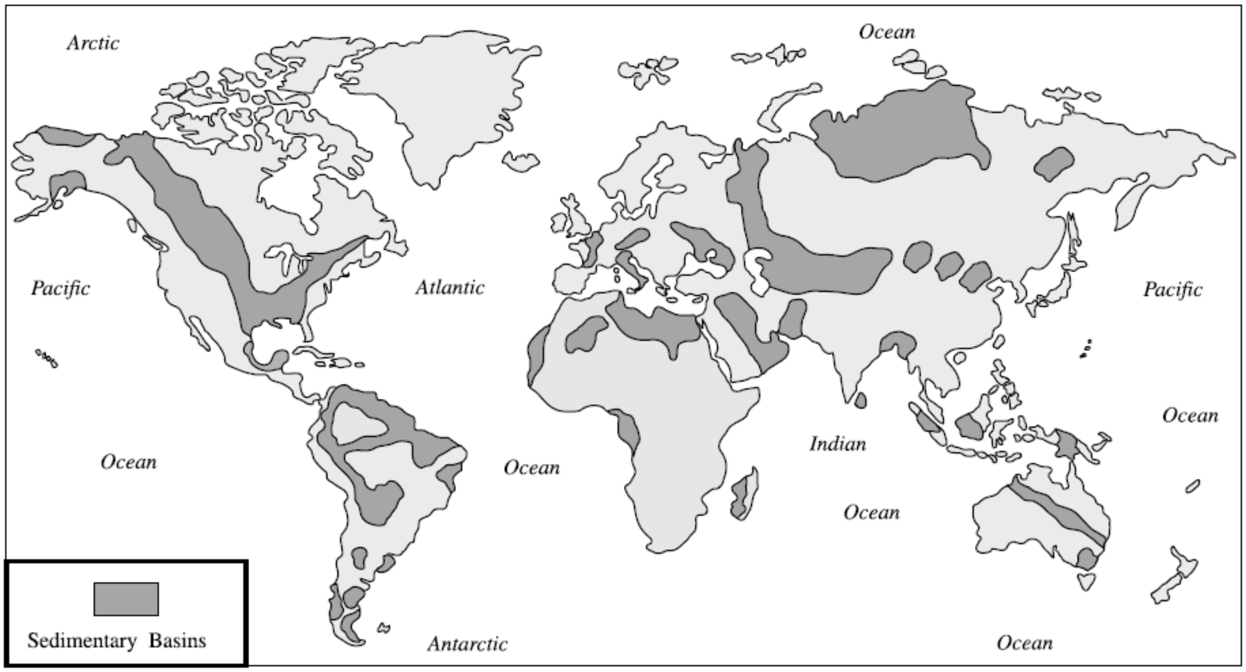

Figure 8-3. Sedimentary basins where terrestrial microseepage may occur (Kvenvolden and Rogers, 2005, after Etiope and Klusman, 2002).

Terrestrial microseepage (the only kind that has been broadly documented so far, since locations of submarine microseepage are very difficult to identify) is basically a diffuse emission of CH_4 from soil, where the CH_4 is originating from underground natural gas reservoirs from depths of about 2 to 5 kilometers (Etiope and Klusman, 2002; Etiope, 2004). Microseepage is generally thought to be driven by the natural buoyancy of gas relative to soil materials, migrating upward in bubble form along faults and fractured rocks (Etiope and Martinelli, 2002). For that reason, microseepage is much more common in faulted regions, as the faults give the gas a means to travel from its underground reservoir to the surface (Etiope, 2005).

Although microseepage emissions often appear to be coming from surface soil itself, in fact the soil lies over fault lines and other openings in the Earth's crust and—as verified by isotopic analysis—is merely allowing gases trapped far beneath the surface to escape to the atmosphere (e.g., see Etiope and Klusman, 2002; Etiope, 2004; Kvenvolden and Rogers, 2005). In dry lands, soil is generally a net CH_4 sink due to methanotrophic bacteria in the soil. In areas where soil is a net producer of CH_4, this is an indicator that microseepage is producing more CH_4 than can be consumed by the soil (Etiope, 2005). For this reason, microseepage generally occurs over sedimentary basins in a dry climate, where thermal decomposition of ancient organic material has created petroleum and gas reservoirs deep below the Earth's surface (Figure 8-3; Kvenvolden and Rogers, 2005; Etiope and Klusman, 2002; Klusman et al., 1998).

Some differentiate between microseepage in sedimentary areas and emissions from geothermal regions (e.g., Kvenvolden and Rogers, 2005). For this reason, microseepage in geothermal zones is generally referred to as "diffuse soil exhalation" or "diffuse degassing" (see Section 8.1.4 below). However, both sources consist of CH_4 escaping through a network of small, often indiscernible cracks in the Earth's crust.

8.1.3 Submarine Seepage

Methane seeping into the marine environment must pass through sea floor sediments and ocean water before entering the atmosphere. This represents a much more significant barrier to CH_4 production than exists for terrestrial geologic sources. Methane passing through seafloor sediments is normally oxidized at the sulfate-methane transition zone; only if CH_4 emissions exceed anaerobic consumption are CH_4 bubbles able to escape into the water column.

Once in the water, CH_4 can still be partially or completely dissolved and oxidized before reaching the surface. The degree of dissolution in seawater depends mainly on the depth of water, water temperature, and the size of the bubbles rising towards the surface. The fraction of bubbles reaching the sea surface is the result of a balance between the rate of bubble dissolution, inflow of air from sea water, and growth due to decreasing hydrostatic pressure as the bubble rises (Patro et al., 2001). The amount of gas entering the atmosphere can be estimated as a function of seafloor depth, bubble size, concentration of dissolved gas around the bubble plume, water temperature, and bulk fluid motions. For seeps at depths shallower than 20 meters, almost all CH_4 emitted reaches the atmosphere. For deep vents on the order of 50 meters, at least 50 percent of CH_4 bubbles with a radius greater than 5 mm survive. Below 100 to 300 meters, CH_4 emissions from submarine seeps are not likely to have a significant impact on the atmosphere (e.g., Schmale et al., 2005).

Submarine features such as pockmarks, gas seeps, and gas-charged sediments are well-documented (see, for example, discussion and references in Etiope and Klusman, 2002; Judd et al., 2002a). Pockmarks are cone-shaped depressions, produced from the "blow-out" of gas and water, that occur within clays, silts, and sands at depths down to thousands of meters. Typical pockmarks range in size from less than 1 meter to 0.5 kilometers in diameter, and depths of more than 20 to 30 meters below the seafloor. Giant pockmarks with diameters of 100 to 200 meters have been reported in Belfast Bay, Maine, and the Barents Sea, Norway. Other areas of pockmarks and seeps have been found on the eastern Canadian continental shelf, the Black Sea, the Adriatic Sea, and even the Arctic Ocean.

8.1.4 Volcanoes, Vents, and Other Geothermal Sources

Regions of geothermal activity can also produce CH_4 during eruptions of high-temperature, magma-producing volcanoes, or through diffuse soil exhalation or degassing from the vents surrounding major volcanoes. In contrast to the processes that produce CH_4 in petroliferous, sedimentary basins, production of CH_4 in geothermal regions is relatively low compared to production of other gases. Typical concentrations of CH_4 in the volcanic gases from fumaroles and crater exhalations is on the order of 0.001 percent or less of total gaseous emissions. Measurements from 27 volcanoes around the world indicate an average CH_4 concentration of about 0.005 percent or 50 parts per million and a median value of 0.0006 percent or 6 parts per million (Etiope et al., 2007b).

Direct estimates of CH_4 emissions from magmatic volcanoes are relatively rare. Significant CH_4 emissions have been measured near volcanoes in the Canary Islands (Hernandez et al., 1998), but other volcanoes, such as Mauna Loa, do not appear to be emitting CH_4 on a regular basis (Ryan et al., 2006). Hence, although magmatic volcanoes are also classified as macro-seeps due to their large physical size, actual emissions from these types of volcanoes appear to be relatively low, contributing little to net global emissions from geologic sources.

The distinction between volcanic and other geothermal emissions is based primarily on the form in which the gases are produced below the surface. Volcanic emissions occur when the gases are released from the craters or flanks of active, or historically active, volcanoes. Volcanic gases, released directly by magma without being dissolved into water before reaching the surface, can be identified by their typically high water vapor content and CO_2 to CH_4 ratio. In contrast, other geothermal emissions are generally the result of boiling or degassing from an aqueous hydrothermal solution below ground. These include gases from extinct volcanoes, paleo-volcanic zones, and CO_2-rich “cold” vents in active tectonic zones, where the gas originates gas from deep thermometamorphic processes and faults.

Macro-seeps through local vents, in terrestrial regions of active geothermal or volcanic activity and undersea regions such as mid-ocean ridges, are widespread globally in both marine and terrestrial environments (Figure 8-4; Wilson et al., 1973, 1974). Compared to volcanoes, the concentration of CH_4 can be higher in gases emitted by degassing or soil exhalation. Even still, it typically reaches little more than a few percent of the total volume of gas produced; thus, chemical analyses are generally required to identify the composition of the gases being emitted (Kvenvolden and Rogers, 2005).

Even when macroseepage locations are relatively close to each other, the mixture of gases being emitted can still vary widely. An example of this is provided by Kvenvolden and Rogers (2005), who compare emissions from Yellowstone National Park (where emissions are dominated by carbon dioxide rather than CH_4) and Grand Teton National Park (where CH_4 is the primary constituent of gas seeps), both located in Wyoming. Higher CH_4 concentrations are generally found over faults that intersect the steam cap or the more extensive liquid-dominated portion of a geothermal reservoir (Etiope et al., 2007b).

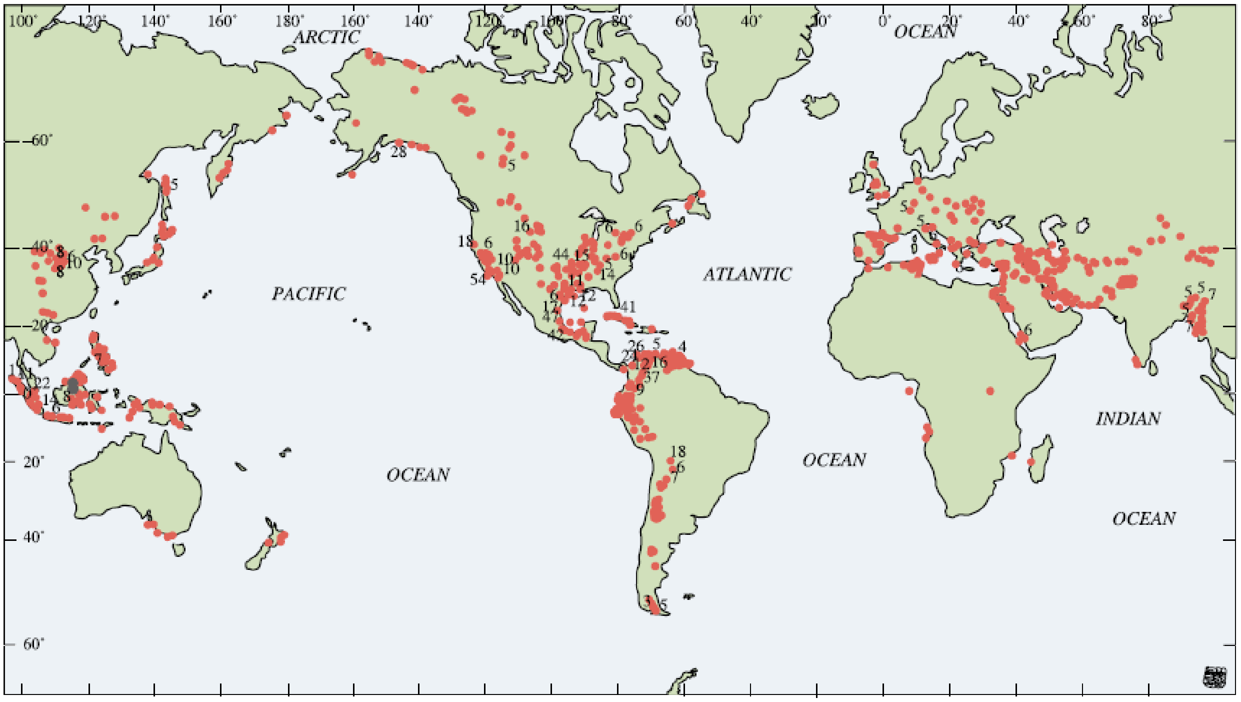

Figure 8-4. Documented onshore and offshore oil seeps, many of which also emit CH_4 (Kvenvolden and Rogers, 2005).

8.1.5 Isotopic Signature

As geologic CH_4 emissions generally originate from underground reservoirs generated by the decay of ancient organic matter, the majority of geologic emissions are estimated to be fossil in origin—i.e., radiocarbon- or ^{14}C-depleted relative to more "modern" sources from wetlands or ruminants that have a relatively high radiocarbon content (Etiope et al., 2007b; Judd et al., 2002a). At the same time, however, CH_4 produced in late Pleistocene and Holocene sediments in estuaries, deltas, and bays or trapped beneath permafrost could also be formally considered geologic even though it does not necessarily display a "fossil" signature. Contributions of this "recent" gas to geologic CH_4 emissions is discussed by Judd (2004) and Judd and Hovland (2007). Others suggest that the composition of geologic CH_4 emissions may be altered by chemical processes during the emission process, including CH_4 generation in shallow sedimentary or soil layers through which the gases pass on their way to the atmosphere (Dimitrov, 2003; Etiope et al., 2007a).

Typically, CH_4 produced by MVs and seeps in petroliferous, sedimentary basins has a carbon isotopic composition ($^{13}\delta C$) ranging from -25 ‰ to -65, with an average of about -46 ‰ and -43 ‰, respectively (Etiope et al., 2009). Microseepage and marine seeps have basically the same signature and range, although a larger microbial component occurs in marine seeps related to shallow sediments. In contrast, geothermal and volcanic methane has a distinctive heavier isotopic ratio, ranging from -10‰ to -20‰. In all cases, the isotopic signature at the surface can be modified by isotopic fractionations due to bacterial oxidation and diffusion. However, higher the gas flux, lower the chance of isotopic fractionation. For this reason, the largest and most intense sources generally maintain an isotopic signature closer to that of the original underground reservoir (Etiope et al., 2009).

8.2 Factors That Influence Emissions

Unlike many other natural CH_4 sources, geologic CH_4 emissions are not directly affected by changes in climate, or most other factors that change over relatively short time scales from decades to centuries.

Over the last century, the only factor that has been proposed to have affected geologic CH_4 emissions is enhanced oil and gas extraction. It has been hypothesized that extraction of oil and gas from subsurface reservoirs can decrease CH_4 emissions from geologic vents due to a reduction in reservoir pressure that had previously been forcing these gases to the surface (Quigley et al., 1999). In support of this hypothesis, Hornafius et al. (1999) compared sonar measurements of bubble plumes near an oil platform in the Santa Barbara Channel from 1973 and 1995 and estimated an 80 percent reduction in seepage over that time. Based on isotopic analyses, Etiope et al. (2008a) estimate that pre-industrial emissions from geologic sources were likely greater than modern emissions because petroleum exploitation has reduced emissions from associated seeps.

Over longer (geologic-scale) time periods, on the order of millennia, the magnitude of CH_4 emissions from geologic sources is likely to have been affected by changes in surface faulting and seepage. Specifically, Etiope et al. hypothesize that geologic emissions are likely to have increased during times of increased seismic activity (Etiope et al., 2008a). These may happen locally over the short term for various reasons, as one region becomes temporarily more active while another becomes less so. Over the longer term and at the global scale, however, these shifts are hypothesized to be connected to changes from glacial to inter-glacial periods as the Earth's crust rebounds, triggering increased seepage rates (Etiope et al., 2008a).

Geologic CH_4 emissions can certainly be altered, however, by the medium through which they pass before being released into the atmosphere. As discussed previously, methanotropic or methanogenic bacteria in soils have been observed to alter both the magnitude and the isotopic signature of CH_4 emissions from terrestrial microseepage and even, in some cases, macroseepage features (Dimitrov, 2003; Etiope, 2005).

In the ocean, CH_4 uptake through the water column affects net emissions to the atmosphere. Under most conditions, most of the CH_4 that seeps into the ocean—particularly from microseepage and smaller macroseepage sources—is consumed by microbial oxidation in sediments and the water column (Judd, 2003). Seep size is a critical factor in the amount of CH_4 emitted to the atmosphere, with a greater fraction of seep CH_4 being emitted to the atmosphere from large seeps (Clark et al., 2003). Using $^{14}C\text{-}CH_4$ source partitioning, a method that examines the radiocarbon content of CH_4 dissolved in the water column and emitted from seeps, Kessler et al. (2006) found that only 1.4 to 4.9 percent of CH_4 from seeps and clathrates to the water column in the Black Sea reached the atmosphere. The oxidation and dissolution rates of CH_4 in ocean water are dependent on the water temperature, the level of CH_4 saturation in the water column, seep rate, and bubble size. As these factors may change under different climate conditions, the fraction of the CH_4 released into the water column that reaches the atmosphere is likely to be affected.

Another factor that affects CH_4 emissions from marine geologic seeps is sea level, which determines the amount of water through which the CH_4 emitted on the sea floor must pass before reaching the atmosphere. For this reason, a decrease in sea level is likely to lead to an increase in CH_4 emissions from marine seepage, while an increase in sea level would lead to a decrease in CH_4 emissions (Boles et al., 2001). More importantly, changes in sea level can cover or reveal near-shore sources. Converting a previously marine source into a terrestrial source would significantly increase emissions as the overlying ocean water was removed, while conversion of a terrestrial source into a marine one would decrease emissions. Hence, Luyendyk et al. (2005) also proposed that greater exposure of continental shelves due to lower sea level during glacial periods could have increased the amount of geologic CH_4 emitted directly to the atmosphere from continental sources relative to today's emission rates.

8.3 Current Global Emissions

Initially, global emissions of CH_4 from geologic terrestrial sources (primarily magma-producing volcanoes) were estimated relative to measured sulfur emissions from these sources, as these were much better known (e.g., Houweling et al., 1999; Simpson et al., 1999). However, as recent observations have shown, magmatic volcanoes likely account for only a small fraction of total geologic CH_4 emissions each year.

Instead, systematic measurements in recent years combined with more sophisticated upscaling procedures have clearly shown that, on a global scale, CH_4 emissions from petroliferous, sedimentary areas are far more important than emissions from geothermal regions. Individual features, including both MVs and larger areas with active degassing fault lines, can produce on the order of tens to hundreds of tonnes of CH_4 per year (Castaldi and Tedesco, 2005; Etiope et al., 2004a,b, 2007a; Yang et al., 2004).

Global estimates of CH_4 emissions from the individual source types listed in Section 8.1.1 are provided below and summarized in Table 8-1. Table 8-2 summarizes global-scale bottom-up geologic CH_4 emissions estimates.

8.3.1 Mud Volcanoes in Petroliferous Sedimentary Regions

Currently, estimates of global and annual emissions of CH_4 from MVs require extrapolation of a limited number of site-specific emission measurements and eruptive characteristics to MV regions around the world. This introduces a significant amount of uncertainty into global estimates (Table 8-1).

Annual emissions from individual MVs cover a wide range. Single vents or craters of small MVs (from 1 to 5 meters in height) can produce on the order of tens of tons each year. A single large MV, consisting of tens or even hundreds of vents, can emit hundreds of tons per year. Eruptions of MVs can release thousands of tons of CH_4 in just a few hours.

Methane emissions from MVs are not produced solely by visible craters and vents; significant amounts of gas are also released as diffuse degassing from the soil. The amount of gas released into the atmosphere by this type of microseepage, calculated for the whole MV area, is often comparable to or even larger than the output from the vents themselves (Etiope and Milkov, 2004; Etiope, 2005; Hong and Yang, 2007). Annual average CH_4 flux for MV areas, including both microseepage and vents but excluding episodic eruptions, ranges from 100 to 1,000 tons per square kilometer.

Due at least in part to the relatively large assumptions that must be made when estimating global values from spatially and temporally variable sources, particularly from submarine MVs, global estimates of emissions of CH_4 from MVs have been the source of much debate over the past few years (Kopf, 2003, 2005; Milkov and Etiope, 2005). Kopf (2002) first estimated total CH_4 emissions to the atmosphere from terrestrial and marine MVs to lie between 0.08 and 1.29 Tg/year. The estimates, which depended on volcano size (small, medium, large) and minimum and maximum CH_4 flux rate estimates averaged from the literature, ranged from 0.197 to 123 Tg CH_4/year, most of which is attributed to marine MVs (Kopf, 2003). According to these estimates, emissions from terrestrial MVs would be negligible when compared to marine emissions. Kopf (2003) does note that much of the CH_4 emitted from marine MVs may not reach the atmosphere (instead being precipitated at the sea floor, oxidized in the water column, or dissolved into the water column), but does not provide an estimate of the atmospheric emissions. Kopf's findings were challenged by Milkov and Etiope (2005), who argued, based on their survey of terrestrial MV regions and associated emissions, that Kopf had used a smaller, not a larger, sample size than previously, and had committed a number of mathematical errors that led to a best estimate of CH_4 emissions from all terrestrial MVs together that was lower than the emissions actually measured at individual locations in Sicily, eastern Azerbaijan, and eastern Romania (Etiope et al., 2002, 2004a,b).

Alternate estimates for CH_4 released from onshore and shallow offshore MVs range from 10.2 to 12.6 Tg CH_4/year (Dimitrov, 2002b), neglecting any dissolution or oxidation that may occur in the water column, and 33 Tg CH_4/year, composed of 15.9 Tg CH_4/year during quiescent periods and 17.1 Tg CH_4/year during eruptions (Milkov et al., 2003). Of the 33 Tg CH_4/year total emissions, 6 Tg CH_4/year are estimated to directly enter the atmosphere from onshore and shallow offshore MVs and the remaining 27 Tg CH_4/year are emitted to the water column from deep-water MVs. The only global estimate based on experimental measurements and emission factors is that proposed by Etiope and Milkov (2004), of 6 to 9 Tg CH_4/year.

As increasing numbers of MV locations are identified both on and offshore, and measurements of CH_4 emissions made during quiescent and eruptive periods are accumulated, global estimates of MV emissions will continue to be refined and the uncertainty reduced.

8.3.2 Seepage in Petroliferous Sedimentary Regions

In contrast to emissions from MVs and other macroseepage features, terrestrial microseepage rates from sedimentary basins characterized by underground petroleum and gas reservoirs have been directly measured for only a limited number of individual locations. These include regions in Italy (Etiope et al., 2007b), Greece (Etiope et al., 2006), Romania and Azerbaijan (Etiope et al., 2004a,b), the United States (Klusman et al., 2000; Klusman, 2003), and the former Soviet Union (Voitov, 1975; Balakin et al., 1981).

Fluxes directly measured or visually estimated from 50 gas seeps in 11 countries show annual emissions between 5 and 100 tons of CH_4 per year for gas seeps with a diameter greater than 1 meter (Etiope et al., 2008b). Up to 2,000 tons per year can be emitted from large seeps with diameters exceeding 1 to 2 meters. In a seep site, however, gas is not released only through macroseepage from the vents. Large amounts are also produced by microseepage through the surrounding soil over broader areas on the order of 10^3 to 10^4 square meters. The large areas are due to the fact that a macro-seep is generally the primary expression of a larger gas-bearing fracture system.

Numerous gas flux surveys show that the amount of gas released from the surrounding soil can be up to 3 times greater than that from the vent alone (Etiope et al., 2004a,b, 2006, 2007a; Hong and Yang, 2007). Using this methodology, Etiope et al. (2008b) estimate emissions for about 12500 macro- and micro-seeps worldwide of about 3–4 TgCH_4 per year (Etiope et al., 2008b).

Global microseepage rates are extrapolated based on the area of known continental areas overlying sedimentary basins, multiplied by areal averaged emission rates derived from observations such as those listed above. Preliminary models suggested that the hydrocarbon-prone sedimentary basins in a dry climate produce a mean microseepage flux of 4.4 mg CH_4 per square meter per day (Klusman et al., 1998; 2000). Assuming 90 percent consumption at this microseepage rate in dry soil gives a global annual emission estimate of at least 7 TgCH_4 per year.

Global "potential" microseepage of 14 to 28 Tg CH_4/year has been estimated by Etiope (2005) on the basis of the global area covered by Total Petroleum Systems (the system commonly used in petroleum geology, which includes all elements of gas production, accumulation, and seepage, the area of which can be estimated from specific maps) and a limited flux data-set. More recently, Etiope and Klusman (2009) have refined global estimates of annual emissions from terrestrial seepage to lie between 11 and 25 Tg CH_4/year based on 563 measurements from a range of hydrocarbon-prone basins in the United States and Europe.

8.3.3 Submarine Seepage

CH_4 emissions from marine seeps have also been estimated for a limited number of locations. These include Coal Oil Point, Santa Barbara, California (Hornafius et al., 1999; Clark et al., 2000; Washburn et al., 2005); the Cascadia Continental Margin (Collier and Lilley, 2005); the Black Sea (Dimitrov, 2002a; Schmale et al., 2005; Kessler et al., 2006; Wallmann et al., 2006); the continental shelf of the U.K., including Torry Bay, Firth of Forth, Scotland (Judd et al., 1997, 2002b); and the Costa Rican coast (Mau et al., 2006). In Europe, the most intense and largest gas bubble plumes, visible even from the sea surface, occur in the coastal areas, from inter-tidal zones to 200–300 meters of depth along the coastlines of Bulgaria, Romania, Ukraine and Georgia. Emission estimates from these areas, although rough and incomplete, cannot be ignored (Etiope, 2008).

Kessler et al. (2006) estimated basin-wide flux of CH_4 from seeps and clathrates to the water column in the Black Sea using $^{14}C\text{-}CH_4$ source partitioning. The approach was based on calculation of gas diffusion in water, but was not representative of the entire Black Sea area as it only partially accounted for direct emission from bubbles in coastal zones. Emissions from seeps and clathrates were estimated to be 3.6 to 4.28 Tg CH_4/year to the water column, and 0.05 to 0.21 Tg CH_4/year to the atmosphere (Kessler et al., 2006). This would correspond to a CH_4 transmission efficiency (i.e., the fraction of CH_4 emitted to the water column that reaches the atmosphere) of 1.4 to 4.9 percent.

In comparing this estimate to those of Kvenvolden (33 to 60 percent; Kvenvolden et al., 2001; Kvenvolden and Rogers, 2005), the nature of the CH_4 seepage must be considered. A greater fraction of CH_4 will reach the atmosphere during more rapid upwelling flow and when larger bubbles are produced during eruptive episodes such as blowouts (Leifer et al., 2004, 2006). Both factors reduce CH_4 loss to the water column during bubble transport. Therefore, transient "eruptive" emissions are more likely to transport CH_4 to the atmosphere than background emissions because bubbles are larger meaning that they dissolve more slowly, and a greater fraction of CH_4 remains in bubbles at surface; upwelling flows are produced, accelerating bubble transport to the surface (Leifer and Clark, 2002); and plume water becomes saturated, reducing net transport of CH_4 out of bubbles (Leifer et al., 2000, 2004; Leifer and Judd, 2002).

Leifer and Clark (2002) describe characteristics of the bubble plume from a marine seep field located offshore from Coal Oil Point, Santa Barbara, California, and found that, based on three seeps of different sizes, bubbles were about 90 percent CH_4 at the base of the plume, but only 60 percent CH_4 at the surface due to dissolution of CH_4 into the water column. Using a bubble model, MacDonald et al. (2002) found that only bubbles of a certain intermediate size (about 4 to 5 millimeters) could reach the surface; smaller bubbles dissolved rapidly and larger bubbles broke into smaller bubbles, which would dissolve.

Several approaches have been used to produce global emissions estimates for submarine seepage into the ocean and atmosphere. The estimates of Hovland et al. (1993) are based on a review of case studies representing different geographic and oceanographic environments, while Judd (2004) estimates emissions to the atmosphere from marine seepage based on previously published estimates rather than new calculations. Hornafius et al. (1999) extrapolated their Coal Oil Point emission estimates to the high-seepage-potential areas of the world's continental shelves. Kvenvolden et al. (2001) took two approaches to estimating CH_4 seepage to ocean and atmosphere, based on findings of a workshop held to assess the magnitude of marine CH_4 seepage: (1) a review and synthesis of published estimates and (2) an estimate based on total availability of CH_4 for seepage from all global geologic sources and assumptions regarding the half-life of the geologic reservoir.

From these estimates, extrapolations have been made that approximate global emissions from marine seepage. These estimates range from 8 to 65 Tg CH_4/year emitted to the ocean, with an estimated 10 to 30 Tg CH_4/year reaching the atmosphere from marine seeps. The average, 20 Tg CH_4/year, is the current consensus value for emissions from submarine sources reaching the atmosphere (Kvenvolden et al., 2001; Judd, 2004). Table 8-1 summarizes these emission estimates.

8.3.4 Volcanoes, Vents, and Other Geothermal Sources

Emissions of CH_4 from magmatic volcanoes were originally estimated through relating CH_4 to measured sulfur emissions (e.g., Lacroix, 1993). In this way, the amount of CH_4 produced by magma-producing volcanoes on land was estimated to lie between 0.8 and 6.2 Tg CH_4/year, averaging about 4 Tg CH_4/year.

Based on this work, some inverse modeling studies have mistakenly grouped all geologic emissions into a "volcanic" category, estimating its magnitude at 3.5 ± 3 Tg CH_4/year (e.g., Houweling et al., 1999), or 7 Tg CH_4/year for a "misc. ground" category that includes volcanoes and hydrothermal vents (Harder et al., 2007). However, as noted previously, these estimates are likely both too high for an individual volcanic source and too low for a total geologic source.

A simple calculation based on the average ratio of CO_2 to CH_4 emissions from volcanoes, assuming a global volcanic CO_2 flux of 300 Tg per year, suggests a global CH_4 source of less than 1 Tg per year. This suggests that volcanoes are not an important CH_4 source (Ryan et al., 2006; Etiope et al., 2007b). Overall, Etiope et al. (2007b) concludes that magmatic volcanoes are not a major source of CH_4 emissions on an annual basis, although individual eruptions may sporadically produce globally significant amounts.

Geothermal systems, often independent of active volcanoes, are much more important, as recently shown by bottom-up estimates in Europe (Etiope, 2008). Etiope et al. (2007a) estimate regional geothermal emissions for Europe alone (primarily due to emissions from geothermal regions in Italy, Greece, and Iceland) on the order of 0.1 Tg CH_4/year.

Other minor geological sources include natural exhalation from coal-bearing rocks (influenced by mining activities), and degassing from crystalline basement and mantle; but no global estimates of atmospheric emissions from these sources have been proposed as yet.

Table 8-1. Estimates of Methane Emissions from Individual Geologic Sources

Annual Emissions *(Tg CH_4/Year)*	**Sources Included**	**Reference**
Mud Volcanoes		
10	Terrestrial and shallow water	Dimitrov, 2002b
5	Terrestrial and shallow water	Dimitrov, 2003
2–10	Terrestrial	Etiope and Klusman, 2002
5	Terrestrial	Kvenvolden and Rogers, 2005
6–9	Terrestrial and shallow marine	Etiope and Milkov, 2004
6	Terrestrial and marine	Milkov et al., 2003
Other Macroseepage		
3-4	Terrestrial seeps excluding MVs	Etiope et al., 2008b
Microseepage		
>7	Terrestrial diffuse	Etiope and Klusman, 2002
14–28	Terrestrial diffuse	Etiope et al., 2005
10-25	Terrestrial diffuse	Etiope and Klusman, 2009
Submarine Seepage		
18–48	Reaching the atmosphere	Hornafius et al., 1999
8–65	Emitted to oceans	Hovland et al., 1993
20	Emitted to oceans	Judd, 2004
30–50 20 (10–30)	Emitted to oceans Reaching the atmosphere	Kvenvolden et al., 2001; Kvenvolden and Rogers, 2005
Volcanoes, Vents, and Other Geothermal Sources		
1.7–9.4	Geothermal and volcanic	Lacroix, 1993
2.5-6.3 <1	Geothermal Volcanic	Etiope and Klusman, 2002; Etiope et al., 2008b

8.3.5 Global Emissions

Despite the relatively large uncertainty in emissions estimates from individual geologic sources, more recent bottom-up estimates of global emissions are relatively consistent (Table 8-2). The most complete estimate of global CH_4 emissions from geologic sources has been made by Etiope et al. (2008b), who estimates total global geologic emissions of 42 to 64 Tg CH_4/year, broken down into emissions of 6 to 9 from MVs (Etiope and Milkov, 2004), 10 to 25 from microseepage (Etiope, 2005), 2.5 to 6.3 from geothermal flux (Etiope and Klusman, 2002), about 20 from submarine seeps (Kvenvolden et al., 2001), and less than 1 Tg CH_4/year from magma-producing volcanoes. When these additional, documented sources are included, the geologic CH_4 budget increases to 42 to 64 Tg/year.

Table 8-2. Global Estimate of Methane Emissions from Geologic Sources

Annual Emissions ***(Mt CH_4/yr)***	**Sources Included**	**Reference**
Bottom-Up Estimates (based on extrapolation of observed emission rates and number of geologic features worldwide)		
30–70	Terrestrial and marine mud volcanoes and vents, microseepage, and geothermal regions	Etiope and Klusman, 2002
35–45	Terrestrial and marine mud volcanoes and vents, low estimate of microseepage, and geothermal regions	Etiope and Milkov, 2004
40–60	Terrestrial and marine mud volcanoes and vents, microseepage, and geothermal regions	Etiope, 2004
16–40 7-20	Terrestrial (not including microseepage) and submarine to the ocean Terrestrial (not including microseepage) and submarine to the atmosphere	Judd et al., 2002a
40	Macroseepage, microseepage, mud volcanoes, and miscellaneous	Kvenvolden and Rogers, 2005
53 (42-64) 30-80	Best guess Extended range (all geologic sources)	Etiope et al., 2008a
Top-Down Estimates (based on inverse modeling studies using isotopic ratios to constrain the global methane budget)		
20[a]	All natural “fossil” sources (terrestrial, marine)	Ferretti et al., 2005
55–70[b]	Includes natural geologic sources and abandoned coal mines	Lassey et al., 2007a
85	May include unresolved anthropogenic fossil emissions > current estimate of 90 Tg/yr	Etiope et al., 2008b

[a] An *a priori* estimate that was held constant to estimate the contribution of biomass burning emissions to the global CH_4 budget over the last two millennia. Authors acknowledge actual magnitude could be much larger.

[b] Value inferred from Lassey et al. (2007a) estimate of a 30 percent contribution of fossil emissions to the global budget and a previous fossil source estimate of 90 to 120 Tg CH_4/year from Ehhalt et al. (2001) based on a 20 percent contribution from fossil methane, for a total budget of 560 Tg CH_4/yr.

The largest uncertainty lies in estimating submarine emissions. In the Etiope (2004) budget, marine geologic emissions are estimated at 20 Tg CH_4/year, based on the estimated range of 10 to 30 Tg CH_4/year (Judd, 2004) resulting from theoretical assumptions described in Kvenvolden et al. (2001). In contrast, estimates of onshore emissions are based on direct measurements and upscaling procedures based on standard concepts of emission factors as applied to both homogeneous areas (for diffuse emissions such as microseepage) and point sources (for individual macroseepage features such as MVs).

In terms of other estimates of global CH_4 emissions from geologic sources, Judd et al. (2002a) estimate total geologic CH_4 emissions of 16 to 40 Tg CH_4/year, with 6.6 to 19.5 Tg CH_4/year reaching the atmosphere, while Kvenvolden and Rogers (2005) estimate total geologic CH_4 emissions to the atmosphere of 45 Tg CH_4/year. (Kvenvolden and Rogers' figure is broken down as 25 Tg CH_4/year from macroseeps, 7 Tg CH_4/year from microseeps, 5 Tg CH_4/year from MVs, and 8 Tg CH_4/year from miscellaneous sources including magmatic volcanoes.) Global geologic CH_4 emissions estimated using these methods are summarized in Table 8-2.

New analyses by Lassey et al. (2007a) that combine isotopic records with a mass-balance modeling approach (as described in Lassey et al., 2007b) find that fossil CH_4 likely contributed 30 percent of the global budget for 1986 through 2000. Reconciling this estimate with current bottom-up CH_4 budgets requires several significant adjustments to conventional wisdom regarding the relative magnitude of individual CH_4 sources. These adjustments include requiring a substantially larger natural source of fossil CH_4, of similar magnitude to the emission estimates provided in Table 8-2. Thanks to this work, global budgets are now beginning to be reconciled with bottom-up estimates of CH_4 emissions from geologic sources as isotopic analyses confirm the likely existence of a geologic source of fossil CH_4 significantly larger than previously thought. Estimates of natural fossil emissions either used (Ferretti et al., 2005) or estimated (Lassey et al., 2007a; Etiope et al., 2008b; Schaefer and Whiticar, 2008) by inverse modeling and isotopic analyses are summarized in Table 8-2.

Based on the bottom-up estimates presented in Table 8-2, combined with the isotopic and modeling analysis of Lassey et al. (2007a,b), it is therefore likely that average annual geologic CH_4 emissions from both terrestrial and marine sources could lie within the most recent range of 42 to 64 Tg CH_4/year estimated by Etiope et al. (2008b). Incorporating the additional uncertainty in sub-oceanic emissions expands this range to 32 to 74 Tg CH_4/year, which we present here as the best-available estimate of present-day emissions of CH_4 from both terrestrial and submarine geologic sources.

8.4 Future Emission Scenarios

As noted previously, relatively few climate- or human-related factors are hypothesized to be capable of influencing emissions of CH_4 from geologic sources. Long-term changes in geologic CH_4 emissions and potential causes for these changes inferred from ice core records may have implications for future emissions, however.

Etiope et al. (2008a) hypothesize that the large-scale extraction of natural gas and oil from underground reservoirs, over the last century or two, may have decreased geologic CH_4 emissions by reducing underground pressure that had previously been forcing gases up to the surface. This suggestion is supported by Hornafius et al. (1999), who compared sonar measurements of bubble plumes near an oil platform in Santa Barbara Channel from 1973 and 1995. They estimated an 80 percent reduction in seepage over that time, likely due to oil and gas extraction from nearby locations. These past changes suggest that continued fossil fuel extraction, particularly in areas with significant geologic CH_4 emissions, could reduce surface emissions of CH_4 from that region's soils, fissures, and vents.

Over longer time periods, it has been suggested that geologic CH_4 emissions may be higher following deglaciation events, as seismic activity increases (Etiope et al., 2008a). Given that the deglaciation of Greenland and Antarctica may already be underway, this link suggests a potential positive feedback in the future whereby crustal rebound in these regions could trigger increased seismic activity, increasing regional CH_4 emissions from the Earth's crust *if* these regions lie above petroleum and gas deposits where significant amounts of CH_4 gas would be stored.

Judd et al. (2002a) and Luyendyk et al. (2005) suggest a mechanism by which submarine emissions could have been higher during ice ages. Due to lower sea levels, a greater number of marine sources—including fissures, vents, and hydrates—were directly exposed to the atmosphere. Greater exposure of continental shelves due to lower sea level during glacial periods would increase the amount of geologic CH_4 emitted directly to the atmosphere from continental sources relative to modern emissions. Given that global sea level has already increased almost 20 centimeters since pre-industrial times, and is projected to increase by at least that much—if not more than five times that—by the end of the century (Rahmstorf, 2006), this would suggest a possible decrease in geologic CH_4 emissions that reach the atmosphere if sources currently located in coastal regions were inundated. Higher sea levels would also be likely to decrease seabed CH_4 seepage due to an increase in the hydrostatic pressure. This would discourage upward gas migration. Furthermore, the proportion of seabed seepage gas surviving passage through the water column decreases as the water depth increases (Judd et al., 2002a).

Hill et al. (2006) estimate a three- to fourfold increase in CH_4 emissions (0.3 to 0.4 Tg CH_4/year) from the Santa Barbara Channel during the deglaciation relative to modern emissions (>0.10 Tg CH_4/year). The authors estimate global marine seepage source of 90 Tg CH_4/year during the deglaciation, although they note that this would require the unlikely synchronous response of CH_4 seeps around the world. Etiope et al. (2008a) expand on this to hypothesize that global emissions from geologic sources during the Quaternary could contribute to increased CH_4 concentrations during the late Quaternary. This assumes that greater exposure of continental shelves due to lower sea level during glacial periods would increase the amount of geologic CH_4 emitted directly to the atmosphere from continental sources relative to modern emissions, and that pre-industrial emissions from geologic sources were greater than modern emissions because petroleum exploitation has reduced emissions from associated seeps.

While geologic CH_4 emissions have very likely changed in the past and are likely to continue to change in the future, these mechanisms are too speculative to use as a basis to estimate even the potential sign of future changes in geologic CH_4 emissions. However, they do serve as an important reminder that even emissions from seemingly stable sources are not necessarily impervious to the consequences of human interference with the climate system.

8.5 Areas for Further Research

Although emissions of CH_4 from a wide variety of geologic sources are now well-documented, much work remains to be done in extrapolating site-specific and time-limited observations to refine global and annual estimate of CH_4 emissions from these sources. Issues range from in situ observational techniques (including units of measurement) to the statistical methods and geographical data used to extrapolate local-scale observations to estimate the global average contribution of these sources to the global total.

For example, much of the CH_4 seepage through submarine seeps and MVs is consumed within the sediment by anaerobic oxidation (Niemann et al., 2005, 2006; Wallmann et al., 2006). What is not well known is the overall or average oxidation rate of CH_4 for all sources. For submarine emissions, the oxidation rate is highly dependent on the residence time of the CH_4 in the water column, the size of the CH_4 bubbles, the rate of CH_4 release, and the CH_4 saturation in the surrounding waters. For terrestrial emissions, the oxidation rate is dependent on the bacterial populations (either methanogenic, methanotrophic, or both) present in the layers of soil through which the gases must pass before being released into the atmosphere. In order to obtain an accurate account of the CH_4 flux into the atmosphere from these geologic sources, a better understanding of *in situ* CH_4 dissolution, oxidation, and production rates is needed.

The primary area where additional research is required, however, is to better quantify macro-seep emission factors, spatial and temporal distributions of macro-seeps (including, for example, the number of active seeps and the frequency of MV eruptions), and the extent of micro-seeps over dry land areas. As microseepage is one of the largest contributors to geologic CH_4 emissions, it is particularly important to develop refined estimates of its emission factors and active areas.

Specific uncertainties relate to identifying:

- The number of MVs around the world.
- The area of faulted land producing a net CH_4 flux into the atmosphere.
- The frequency of eruption events characterized by significantly higher emission rates.
- Spatial and temporal variations in emission rates.
- CH_4 oxidation rates in both ocean water and soils, which determines the transfer efficiency through the water column for marine sources and sedimentary layers for continental sources.
- Terrestrial microseepage emission rates.

The uncertainties described above all relate to improving the ability of bottom-up budget analyses to accurately assess global CH_4 emissions from geologic sources. In addition to increasing the number of measurement studies and the identification rates of these geologic features and regions with the aim of improving bottom-up estimates, however, top-down techniques combining observations with mass-balance analyses and isotopic modeling also show significant potential to constrain the magnitude of global CH_4 emissions from geologic sources. Recent analyses (Lassey et al., 2007a,b; Etiope et al., 2008b) find that fossil sources contribute approximately 30 percent of the global budget. This implies that a fossil geologic source of the magnitude suggested initially by Etiope and Klusman (2002), refined by Etiope (2004) and Etiope et al. (2008b), is plausible.

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Chapter 9. Wildfires

Wildfires are fires in unmanaged forests, grasslands, savannas, and shrublands (Aalde et al., 2006a). These fires can be ignited by lightning strikes or started accidentally by humans, but do not include deliberate controlled burns for land clearing activities. As they burn, wildfires release a number of greenhouse gases, particulates, and other air pollutants. Incomplete combustion of biomass, consisting of both living and dead organic matter, is the primary source for emissions of CH_4 from wildfires. In contrast to CH_4 emissions, N_2O emissions from wildfires depend not only on the combustion conditions but also on the nitrogen content in the biomass being burnt. Wildfires are typically a very small source of N_2O, as they are fairly low-temperature fires (in comparison to fossil fuel combustion), thus limiting the conversion of atmospheric nitrogen (N_2) to fixed nitrogen.

In most studies of the global CH_4 or N_2O budget, natural sources such as wildfire emissions are either assumed to remain constant over time or lumped together with a larger biomass burning source, the majority of which is deliberate or planned burning. Together, these assumptions have limited estimates of historical changes in wildfire emissions, as well as projections of how they might be altered in the future under conditions of changing climate.

The previous EPA report (U.S. EPA, 1993) does not discuss wildfires, perhaps because they were not considered to be of sufficient magnitude or one of the primary natural sources most likely to be sensitive to climate. However, a number of observational and modeling studies have now shown wildfire frequency and intensity to be highly dependent on climate. Shifts in climate and weather patterns establish the conditions necessary for wildfire ignition and spread.

Similarly, in earlier IPCC Assessment Reports (e.g., Ehhalt et al., 2001) a natural wildfire source was not distinguished from the larger, primarily deliberate or planned anthropogenic biomass burning source. In the most recent IPCC report (Denman et al., 2007), a table summarizing eight individual estimates of the CH_4 budget shows only two studies that provide values for a natural wildfire source: 5 Tg CH_4/yr (Houweling et al., 2000), and 2 Tg CH_4/yr (Wuebbles and Hayhoe, 2002).

N_2O emissions from wildfires were not considered in either of the latest IPCC reports (Ehhalt et al., 2001; Denman et al., 2007), nor do there appear to be any peer-reviewed estimates of the contribution of wildfire to the global N_2O budget in the scientific literature.

9.1 Description of Emission Source

Although emissions from wildfires may be virtually indistinguishable from controlled burns, an important distinction must be made between natural (accidental) and anthropogenic (deliberate) fires. According to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (Aalde et al., 2006b), "A wildfire is any unplanned and uncontrolled wetland fire which, regardless of ignition source, may require suppression response." Fires that are the result of accidental ignition that occur on unmanaged lands are "natural" (i.e., not included in the anthropogenic inventory), while fires that result from either accidental or deliberate ignition on managed lands are considered "anthropogenic." Almost 90 percent of all biomass burning is considered to be deliberately human-initiated. Much of it occurs in the tropics, where savanna and forest fires are driven by land clearing for agriculture and the need for fuelwood. Prescribed burning for forest management and agricultural waste burning is also prevalent in temperate-boreal regions.

The remaining 10 percent of fires, classified as "natural wildfires," are attributed to natural causes, such as lightning, and accidental human ignition. These natural fires occur predominantly in the mid- and high-latitude temperate-boreal ecosystems (for example, boreal forest fires in Alaska and Canada in summer 2004 and Siberian forest fires in summer 2003; Levine, 1999, and references therein; Lavoué et al., 2000). Natural fires are also prevalent in arid, heavily populated regions that are dominated by shrublands (for example, the southern California wildfires in October 2007 and the Mediterranean wildfires in August 2007). In this report, EPA estimates emissions from natural lightning-ignited and uncontrolled human-initiated biomass burning only, referred to from now on as wildfires.

As the general fire and emission characteristics of anthropogenic and natural fires are identical, the discussion below pertains to both types of biomass burning. However, in this report EPA summarizes estimates of wildfire emissions only.

Emission of various gases and particles in the smoke from fires depends on the composition of the biomass burned, and on combustion conditions (Andreae and Merlet, 2001). Biomass typically contains about 45 percent carbon by weight, with the remainder being hydrogen and oxygen (~55 percent) (Levine, 2000; Levine et al., 2004; Andreae and Merlet, 2001). Trace amounts of nitrogen and sulfur are also present depending on the nature of biomass. Under conditions of complete combustion, burning of organic matter proceeds via oxidation that mainly produces water vapor (H_2O) and carbon dioxide (CO_2), according to the following reaction:

$(CH_2O) + O_2 \rightarrow CO_2 + H_2O$,

where CH_2O represents the average composition of organic matter (Levine et al., 2000; Levine, 2004). However, combustion is not a single-stage process but proceeds in three stages that determine the ultimate proportions of the chemical species emitted (Levine et al., 2000; Levine, 2004). The first stage involves pyrolysis accompanied by the emission of organic volatile compounds in the form of white smoke. In the second stage, high-temperature flaming combustion occurs that converts reduced substances to simple oxidized species, including CO_2, H_2O, and N_2O. Other intermediate species such as CO and CH_4 are also released at this stage, depending on the chemical and physical interactions in the flame. Finally, after the flaming combustion stops, low-temperature smoldering begins, which emits large amounts of incompletely oxidized volatile organic compounds. The majority of non-CO_2 chemical species including CO, CH_4, NO_x, non-methane hydrocarbons, and various volatile organic compounds and particles are emitted during this final smoldering stage of combustion. Experimental data indicate a linear relationship between N_2O emissions and the nitrogen content of the biomass being burned (Lobert et al., 1991).

Open vegetation fires are dynamic fires; hence, all three combustion types are present at any given time. However, their proportions vary over time, with flaming dominating in the earlier part of the fire and smoldering during the later part. For forest fires, the flaming phase in given location typically lasts for an hour or less, while the smoldering phase may last up to a day or longer depending on the fuel type, moisture content, weather conditions, etc. (Andreae and Merlet, 2001). For savanna grassland and agricultural waste fires, the flaming phase lasts only a few minutes, while the smoldering phase lasts up to an hour (Levine et al., 2000; Andreae and Merlet, 2001). Thus, the type of ecosystem burning, the amount of biomass burned, the phase of combustion, and the evolution of emissions with changing fire conditions in various ecosystems are all important pieces of information required to determine the contribution of wildfires emissions to the total global CH_4 budget. Knowledge of the nitrogen content in the biomass being burned is also required, in addition to all of these factors, to estimate wildfire N_2O emissions.

Factors influencing emissions from wildfires are described in Section 9.2. Estimates of current and future wildfire CH_4 and N_2O emissions are described in Sections 9.3 and 9.4, respectively. Finally, areas of further research are outlined in Section 9.5.

9.2 Factors That Influence Emissions

Wildfire emissions depend on the frequency and strength of wildfires, which are in turn determined by several factors, including:

- The type of vegetation present in a region.
- The frequency of lightning (not associated with heavy rainfall) that triggers the fires.

- The frequency of dry periods or droughts, which would create optimal conditions for wildfire (this is particularly important for arid regions when drought follows a wet period that has allowed vegetation to grow).
- The frequency of other weather conditions—such as extreme wind events—that would help the fires to spread.
- The presence of humans in the region, whose inadvertent activities—from dropping a burning match to neglecting to extinguish sparks blown from a campfire—can begin a wildfire.
- Other human factors that can limit the area burned, including firefighting, breaks in vegetation and flammable structures due to human clearing, etc.

Sections 9.2.1 to 9.2.3 discuss how these factors modulate wildfires and their emissions under broad categories.

9.2.1 Type of Vegetation

The type of vegetation burned determines the dominant combustion process, which in turn controls the level of CH_4 and N_2O emitted. Forest fires dominated by smoldering emit more CH_4 and less N_2O than do savanna and grassland fires that are mostly flaming. For example, the estimated average amount of CH_4 emitted per area burned of tropical forest fires is three times that of the CH_4 emitted when burning savanna and grassland (Andreae and Merlet, 2001).

Emissions from types of vegetation burned are estimated in terms of emission factors. Due to the large difference in combustion processes or fire characteristics from one ecosystem to another, emission factors are usually estimated specifically for the type of vegetation burned (Delmas, 1994; Andreae and Merlet, 2001). Emission factors are discussed in detail in Section 9.3.1.

9.2.2 Influence of Weather and Climate

Weather and climate strongly affect forest wildfires, specifically the area burned by fires (Swetnam, 1993; Flannigan and Wotton, 2001). Weather is defined here as short-term processes that result in variations in atmospheric conditions ranging from minutes to the length of a fire season, while climate refers to processes that influence the atmosphere over time periods of years to decades, longer than a fire season. The connection between weather and climate and the area burned by forest fires is discussed below.

9.2.2.1 Weather

Once lightning triggers a fire in a forest with dry flammable biomass, synoptic weather conditions that produce strong winds, low relative humidities (dry conditions), and above-normal temperatures can cause a fire to rapidly spread. Forest fires tend to be concentrated in summer months, when these weather conditions are most prevalent.

Early studies of synoptic-scale weather conditions associated with large wildfires in the eastern half of the United States indicate that nearly 80 percent of fires are associated with a cold front, either before or after passage of a dry cold front. Analysis of the relationship between meteorological variables and monthly area burned by wildfires in Canada suggest that severe fire months were independent of rainfall amount but significantly dependent on rainfall frequency, temperature, and relative humidity.

Furthermore, since large forest fires are not constrained to the surface but extend many kilometers into the atmosphere, the atmosphere's vertical structure can also have a significant impact on fire growth and behavior. A dry and unstable atmosphere enhances the growth of forest fires by promoting erratic fire behavior and fire spread. Thus, day-to-day weather can dramatically influence fire behavior and area burned.

9.2.2.2 Climate

Variations in large-scale climatic patterns affect the corresponding weather variables and thus also influence wildfires. Climate primarily interacts with fire through its direct effect on fuel moisture. Larger fires usually occur during warm, dry years. However, climate also affects the geographic distribution of vegetation types and site productivity, and thus indirectly influences the intensity, frequency, and size of fires through the types of fuels that are made available and the rates at which those fuels accumulate (Miller and Urban, 1999). Numerous studies have shown that wet years that contribute to fuel accumulation often promote burning in the subsequent dry years (Swetnam and Betancourt, 1990; Heyerdahl et al., 2002; Westerling et al., 2003).

El Niño Southern Oscillation

The Southern Oscillation (SO) reflects the monthly or seasonal fluctuations in the air pressure difference between Tahiti and Darwin. It occurs at irregular intervals, from two to seven years. The warm phase of SO, referred to as El Niño, is characterized by warm sea surface temperatures in the eastern and central equatorial Pacific Ocean, high pressure over the tropical western Pacific, and low pressure on the southeastern Pacific near the coast of South America. The opposite phase of SO, known as La Niña, is characterized by higher surface pressures in the eastern Pacific and lower sea surface temperatures along the equator.

El Niño events tend to produce increased rainfall and widespread flooding along coasts of northern Peru and Ecuador, and severe drought conditions in parts of Southeastern Asia and Northern Australia. In the United States, El Niño events are associated with warm and wet winters in upper Midwestern states, the Northeast, and Canada, while the central and southern California, northwest Mexico, and the southwestern United States are wetter and cooler than normal. La Niña events are typically associated with weather conditions opposite to those of El Niño events.

More recent work has linked spatial and temporal variability in fire activity to inter-annual and inter-decadal climate variations caused by variations in hemispheric and even global-scale atmospheric circulation patterns. The most well-known source of climatic fluctuations is the El Niño Southern Oscillation, or ENSO (see text box).

Several researchers have studied the relationship between fire occurrence in various parts of the world and variations in weather patterns associated with ENSO or ENSO-like atmospheric circulation. Following are results from recent studies that highlight the influences of variations in large-scale climatic patterns on fire regimes:

- Correlation of the 300-year record of fire activity for the southwestern United States with an index for the Southern Oscillation showed that large areas tend to burn after dry springs associated with La Niña events, while smaller areas burn after wet springs associated with El Niño events that increase vegetation growth (Swetnam and Betancourt, 1990).
- El Niño years are characterized by dry winters and warm spring temperatures in the Pacific Northwest United States. Heyerdahl et al. (2002) assessed the influence of annual variations in climate on fire regimes of pine forests in eastern Oregon and Washington using tree-ring reconstructions of annual total area burned for the years 1687 to 1994. They found that large fires burned during dry years and El Niño years in all watersheds, while small fires burned regardless of variation in these climate parameters. However, large fires also burned during relatively wet years and La Niña years in one watershed they examined, indicating that local factors can override regional climate controls in some locations.
- The direct impact of El Niño was most recently observed in the forested peatlands of Indonesia during the El Niño event of 1997, which caused widespread fires. The fires were initially started to clear forests for agriculture, but soon became uncontrolled because of severe drought conditions in the region owing to El Niño (Siegert et al., 2001).

- Using satellite-derived burn areas, Baltzer et al. (2005) also suggests a relationship between fire severity and the positive phase of the Arctic Oscillation (see text box) in Siberia.
- Fauria and Johnson (2006) studied the large lightning fires in Canada and Alaska during 1959–1999 and found a relationship between their occurrence and both the Arctic Oscillation and ENSO on an interannual scale, with a frequency of 2 to 6 years.

While the above analyses illustrate important relationships between wildfire severity, frequency, and large-scale climate variations, these studies are constrained by the fire data being influenced by human interventions as well.

The Arctic Oscillation

"Arctic Oscillation" refers to opposing atmospheric pressure patterns in northern middle and high latitudes. The oscillation is characterized by a "negative phase" with relatively high pressure over the polar region and low pressure at mid-latitudes (about 45 degrees north), and a "positive phase" in which the pattern is reversed.

The positive phase is characterized by wetter weather in Alaska, Scotland, and Scandinavia; drier conditions in the western United States and the Mediterranean; and warmer weather in Eurasia. Weather patterns in the negative phase are generally opposite to those of the positive phase.

9.2.3 Human Influence

Human activities also influence the frequency and intensity of wildfires, and therefore impact wildfire emissions as well. Human settlement, transportation, and recreation patterns determine where people live and where they travel to. This in turn sets the spatial pattern for accidental ignitions. The higher the human presence in an area already predisposed for fire conditions by climate and weather patterns, the more likely an accidental ignition is.

Residential development also affects wildfire probability. Human settlement along the urban-forest perimeter limits the possibility for controlled burns or natural fires to remove highly flammable dead material and underbrush. Fuel builds up; when a wildfire eventually does occur, more fuel is available and so the fire often ends up spreading further than it would have if allowed to happen naturally earlier. Residential areas also affect the path of wildfires. They provide breaks in natural vegetation as well as additional flammable materials. Here in the United States and in many other industrial nations, the presence of homes—particularly vacation expensive homes—is also a determining factor whether or not resources are spent on combating a given fire, or if it is allowed to burn itself out.

Prescribed burning or controlled burning in unmanaged lands is sometimes used for forest management. Benefits include protecting trees from insects and disease, improving habitat for wildlife species, and decreasing the risk of future larger, uncontrolled fires. In dry and windy conditions with high flammable fuel loads, controlled fires can sometimes get out of control, causing a wildfire event.

Given the complexity of these interactions, it is difficult to evaluate and quantify the human influence on wildfire emissions on a global scale. However, it is important to note that they do exist and are likely important.

9.3 Current Global Emissions

Wildfire emissions are generally estimated using the relationship first given by Seiler and Crutzen (1980) and described in detail in more recent studies (Delmas, 1994; Levine, 2000, 2004; Levine et al., 2000; Liousse et al., 2004). This relationship is also used to calculate emissions from prescribed fires and wildfires in managed lands (Aalde et al., 2006a). Gas or aerosol emissions (M_x) are calculated as:

$$M_x = EF_x \times M_{biomass},$$

where EF_x is the emission factor defined as the amount of any species x released per amount of dry matter consumed in units of g/kg, and $M_{biomass}$ is the amount of biomass burned in mass units. Sections 9.2.1 and 9.2.2 discuss the methods to calculate these parameters and the factors that influence them.

9.3.1 Estimating Emission Factors

According to Andreae and Merlet (2001), the emission factor of carbon species from biomass burning can be expressed as:

$$EF_x = \frac{M_x}{M_{biomass}} = \frac{M_x}{M_C}[C]_{biomass} \cong \frac{[x]}{\Sigma\left([C_{CO_2}]+[C_{CO}]+[C_{CH_4}]+[C_{VOC}]+...\right)}[C]_{biomass},$$

where M_x is the mass of species emitted, M_C is the mass of carbon emitted, $[C]_{biomass}$ is the carbon content in the biomass burned, $[x]$ is the concentration of species in the smoke, and $[C_{CO2}]$, etc., are the concentrations of the various carbon species in the smoke. Both the carbon content of the biomass burned and the carbon budget of the fire are difficult to measure in the field but can be easily determined in the laboratory. A fuel carbon content of 45 percent is usually assumed when fuel and residue data at the ground are not available.

The emission ratio relates the emission of a species to the emission of a reference gas, for example, CO_2 or CO, and can be used to derive species-specific emission factors. Emission ratios are given by dividing the excess species concentration in a fire plume by the excess concentration of a simultaneously measured reference gas. The "excess" concentrations are obtained by subtracting the ambient background concentrations from the concentrations measured in the burn plume. For example, following Andreae and Merlet (2001), the emission ratio of CH_4 relative to CO_2 in molar units is

$$ER_{CH_4/CO_2} = \frac{\Delta CH_4}{\Delta CO_2} = \frac{(CH_4)_{smoke} - (CH_4)_{ambient}}{(CO_2)_{smoke} - (CO_2)_{ambient}}$$

and the emission ratio of N_2O relative to CO_2 is given by

$$ER_{N_2O/CO_2} = \frac{\Delta N_2O}{\Delta CO_2} = \frac{(N_2O)_{smoke} - (N_2O)_{ambient}}{(CO_2)_{smoke} - (CO_2)_{ambient}}$$

The calculation of emission ratios requires only simultaneous measurements of the species of interest and the reference gas in the smoke plume and in the background air. Furthermore, knowledge of the fuel composition and the amounts of fuel burned is not needed, thus making emission ratios suitable for field studies, particularly airborne plume measurements.

Emission factors, on the other hand, allow the most straightforward calculation of trace gas and aerosol emissions when the amount of biomass burned is known. Therefore, experimental values of emission ratios are usually converted to emission factors to determine regional or global-scale fire emissions. The following equation is used to convert molar emission ratios (Andreae and Merlet, 2001):

$$EF_x = ER_{(X/Y)} \frac{MW_X}{MW_Y} EF_Y,$$

where $ER_{(X/Y)}$ is the emission ratio of species x relative to the reference species Y, MW_X and MW_Y are the molecular weights of the species x, and Y, and EF_Y is the emission factor of the reference species. The emission factor for N_2O calculated in this way therefore represents the fraction of burned fuel nitrogen emitted as N_2O, and is independent of the fuel nitrogen content (Delmas et al., 1995), which would otherwise represent a key uncertainty in the estimate.

Emission factors are highly dependent on the fire regime (type of vegetation burned, combustion conditions). Fires dominated by smoldering, such as forest fires, generally have higher emission factors for reduced species such as CH_4. In contrast, dominantly flaming fires, such as savanna, grassland, and shrubland fires, have fairly low emission factors for reduced species and high emission factors for oxidized species including N_2O (contingent on nitrogen content of the biomass). For example, the estimated average CH_4 emission factor for tropical forest fires is three times that of the CH_4 emission factor for burning savanna and grassland (Andreae and Merlet, 2001).

For this reason, emission factors are usually estimated specifically for the different types of vegetation burned (Delmas, 1994; Andreae and Merlet, 2001). Uncertainties in emission ratios (factors), however, still arise due to lack of sufficient field data, sampling conditions with a tendency to over-represent one mode of combustion over the other (for example, ground-based sampling tends to over-represent smoldering emissions that remain closer to the ground while airborne sampling may be biased towards emission from the flaming phase that are lofted to higher altitudes), and differences in the types of measurements (tower vs. ground-based vs. aircraft measurements). Furthermore, emission factors vary as the fire season progresses, due to changing moisture conditions. The seasonality in emission factors is usually not reported in the literature. Instead, only annual average emission factors are tabulated.

Early estimates of emission factors for CH_4 from biomass burning and wildfires were synthesized by Delmas (1994) from various experimental studies. Extremely limited information exists on the emission factors for N_2O (Lobert et al., 1991; Andreae and Merlet (2001). Andreae and Merlet (2001) updated the previous compilation of emission factors for CH_4 along with emission factors for approximately 100 other relevant species, including that for N_2O, with information from recent large- and small-scale experimental studies. Emission factors from Andreae and Merlet (2001) have also been recommended for calculating biomass burning emissions by Aalde et al. (2006a). The most recent estimates of CH_4 and N_2O emission factors for various types of wildfires and biomass burning are shown in Table 9.1. To calculate global wildfire emissions, the emission factors for savanna and grassland, tropical forest, and extratropical forest fires are combined with estimates of the amount of biomass burned by natural fires in each of these categories. The methodologies to estimate the amount of biomass burned are discussed below.

Table 9-1. Methane and Nitrous Oxide Emission Factors for Different Types of Wildfires and Biomass Burning (from Andreae and Merlet, 2001)

Type of Biomass Burning	Emission Factor (g/kg)	
	Methane	Nitrous Oxide
Savanna and grassland	2.3 ± 0.9	0.21 ± 0.10
Tropical forest	6.8 ± 2.0	0.20
Extratropical forest	4.7 ± 1.9	0.26 ± 0.07
Biofuel burning*	6.1 ± 2.2	0.06
Charcoal making*	10.7	0.03
Charcoal burning*	6.2 ± 3.3	0.20
Agricultural residues*	2.7	0.07

* Not relevant for wildfires

9.3.2 Estimating Amount of Biomass Burned

The amount of biomass burned annually (*M*) is by far the most difficult quantity to determine, and hence the most uncertain. Annual values are usually obtained by a relationship originally given by Seiler and

Crutzen (1980) and applied in several other studies (Delmas, 1994; Levine, 1999, 2004; Levine et al., 2000; and Liousse et al., 2004):

$$M = A \times B \times \alpha \times \beta ,$$

where A is the area burned (m^2), B is the average biomass per unit area in a particular ecosystem (kg m^{-2}), α is the fraction of the average above-ground biomass burned relative to the total average biomass B, and β is the burning efficiency of the above-ground biomass.

Large uncertainties exist in the four parameters required to calculate M. Burn area (A), a critical parameter, is particularly difficult to estimate because of the high spatial and interannual variability in this factor at continental to global scales (Giglio et al., 2006).

Early estimates of burn area were based on statistics from the Food and Agriculture Organization or national survey data (Hao and Liu, 1994). Although remote sensing products (i.e., satellite observations) have been used to monitor fires since the late 1970s, it is only recently that remote sensing has been used to generate maps of annual burned area at the global and regional scales (Grégoire et al., 2003; Liousse et al., 2004; Simon et al., 2004; Giglio et al., 2006). The two most evaluated and frequently used satellite-derived burn area products are the GLOBSCAR product collected by the Along Track Scanning Radiometer (ATSR) (Simon et al., 2004) and the GBA-2000 product generated from data collected by the SPOT-VEGETATION instrument (Grégoire et al., 2003; see text box).

GLOBSCAR and GBA-2000

The GLObal Burn SCARs (GLOBSCAR) project was initiated in 2001 as part of the European Space Agency (ESA) Data User Programme, for production of global incremental monthly maps of burnt areas using daytime data from year 2000 of the Along Track Scanning Radiometer (ATSR-2) instrument onboard the ESA ERS-2 satellite. The final GLOBSCAR products are distributed through VITO's GEOSUCCESS web server (http://www.geosuccess.net/).

The Global Burnt Area-2000 initiative (GBA2000) was launched by the Global Vegetation Monitoring unit of the European Commission's Joint Research Centre in partnership with several other institutions around the world, with the specific objective of producing a map of the areas burnt globally for the year 2000, using the medium resolution (1 km) satellite imagery provided by the SPOT-Vegetation system, and to derive statistics of area burnt per type of vegetation cover. The GBA-2000 product can be downloaded from http://www.grid.unep.ch/activities/earlywarning/preview/ims/gba/.

While these efforts demonstrate the feasibility of using satellite products to determine the global area burned, there are still uncertainties and shortcomings in the satellite-derived burned-area information (Hoelzemann et al., 2004; Simon et al., 2004). Specifically, two major shortcomings are: (1) the area estimates do not differentiate between fires in different ecosystems, and (2) the area estimates do not make a distinction between anthropogenic biomass burning and natural wildfires. The second shortcoming makes it particularly difficult to assess CH_4 emissions from wildfires (as highlighted below). Future efforts by the remote sensing community are directed towards addressing these shortcomings and further refining the data (van der Werf et al., 2004, 2006).

Climate/weather parameters (discussed in Section 9.2.3) induce significant temporal (season-to-season, year-to-year) variability in burned areas. Most of the temporal variability occurs in fires in the tropics, followed by the boreal and temperate forests (Dwyer et al., 2000; van der Werf et al., 2006).

Early studies incorporated seasonal variability in emissions using surrogates such as seasonal rainfall patterns, cultural practices, vegetation types, and surface ozone for the presence of biomass burning. For example, Hao and Liu (1994) derived monthly distributions of the amount of biomass burned in the tropics by assuming that high surface ozone concentrations during the dry season were a result of these fires. Cooke et al. (1996) investigated the seasonality in biomass burning emissions for Africa using satellite data and compared their results with that of Hao and Liu (1994). Their analysis showed that the inventory of Hao and Liu (1994) tended to underestimate the intensity of the peak months of burning, and indicated that seasonal variation in surface ozone concentrations is *not* a good proxy for seasonality in emissions on a regional and continental scale.

The first global assessment of the seasonal variability of fire occurrence using satellite data was performed by Dwyer et al. (2000). Their analysis concluded that the strongest variability in biomass burning is that associated with the movement of the dry season in the tropics from the northern to the southern hemisphere. Intense burning in Africa, north of the equator, occurs from October to February, transitioning to July through September for regions south of the equator. The most intense burning in Central America and southern Asia occurs in April and May. The burning season runs from May to August in most regions of the northern hemisphere'1s temperate and boreal biomes, while in the temperate regions of the southern hemisphere, the burning season is from December to March.

Biomass density or the available fuel load is an equally important parameter required to estimate the amount of biomass burned. Early estimates of fuel load were based on compilations of ecosystem-specific biomass load obtained from field measurements (Hao and Liu, 1994; Lavoué et al., 2000). Recently, vegetation models that simulate the global carbon cycle have been used to derive the biomass density of vegetation susceptible to fire on a global scale (Hoelzemann et al., 2004; van der Werf et al., 2004). The accuracy of simulated fuel loads depends on how well the vegetation model simulates the global carbon cycle. The simulated ecosystem-specific fuel loads are compared with published values to evaluate and validate the models. However, direct comparison of modeled fuel loads with literature values is difficult because it is usually unclear what value (total biomass load, aboveground biomass density or the available fuel load) is being reported in the published literature. Furthermore, the coarse resolution of vegetation models (typically $0.5^{\circ} \times 0.5^{\circ}$ or $1^{\circ} \times 1^{\circ}$ grid cell) is unable to capture the spatial heterogeneity in fuel loads within a grid cell.

Finally, combustion efficiency is estimated based on field observations in different ecosystems (Delmas, 1994). The biomass density and the combustion efficiency are only known to within ±50 percent (Liousse et al., 2004).

9.3.3 Estimating Current Methane and Nitrous Oxide Emissions

As stated previously, it is extremely difficult to distinguish between burned areas from natural wildfires and those burned by anthropogenic fires. This makes it difficult to isolate wildfire emissions relative to the global total from all biomass burning. Estimates of wildfire CH_4 emissions are currently based on the assumption that about 10 percent of the global biomass burning is natural (Levine, 1999), although of course this proportion is likely to vary year to year. No published estimates of global wildfire N_2O emissions are available. Therefore, EPA has applied the same assumption to provide a "best-guess" estimate for global wildfire N_2O emission. This estimated value is likely to be highly uncertain and should therefore be used with caution.

Globally, wildfires are estimated to emit between 2 and 5 Tg CH_4/yr (Denman et al., 2007; Houweling et al., 2000; Wuebbles and Hayhoe, 2002). These emissions are not for a specific year but are climatological averages. The estimate of Houweling et al. (2000) is based on the work of Chappellaz et al. (1993), who assumed that of the 50 Tg CH_4/yr (based on Fung et al., 1991) emitted from biomass burning, 10 percent is released from wildfires.

Lobert et al. (1999) give estimates of carbon emissions from different types of vegetation feedstock, including forest wildfires (mainly in temperate and boreal forests) representative of the early 1990s. The database of the area and amount of biomass burned in each category was compiled from various sources (Logan and Yevich, unpublished manuscripts, 1998, cited in Lobert et al., 1999). Total global carbon emissions from forest wildfires are estimated to be 265 Tg C/yr. Applying a factor of 1/0.45 to convert this value to mass of fuel burned and then combining with CH_4 emission factors for extratropical forests from Table 9-1 suggests annual global wildfire CH_4 emissions of ~3 Tg CH_4/yr (Table 9-2). This estimate coincides with the CH_4 emissions from extratropical forests derived by Andreae and Merlet (2001) based on the same source of biomass burning estimates. Based on the similar methodology using the N_2O emission factors summarized above, EPA also estimates global wildfire N_2O emissions to be approximately 0.1 Tg N/yr, although no reference for this value is available in the peer-reviewed literature. Given the methodological problems associated with estimating the amount of biomass burned in wildfires, a valid statistical error analysis of the emission estimates cannot be performed.

Global burned area derived from sophisticated satellite products combined with updated/refined data for other parameters has been used recently to estimate global fire emissions (Hoelzemann et al., 2004; Ito and Penner, 2004; van der Werf et al., 2004, 2006). As noted previously, no distinction is made between natural and anthropogenic emissions in these studies; however, we can again apply the assumption that 10 percent of global biomass burning emissions are from wildfires. Ito and Penner (2004) used the GBA-2000 data product supplemented by ATSR hot spot data from the World Fire Atlas as inputs into a global emissions model to calculate global biomass burning emissions for various chemical species including CH_4 (32.2–55.2 Tg CH_4/yr) for the year 2000. Wildfire CH_4 emissions estimated from their study would therefore range from 3.2 to 5.5 Tg CH_4/yr, which is within the range of emissions provided in previous studies (Table 9-2). Hoelzemann et al. (2004) used the GLOBSCAR burned-area product supplemented with data from the World Fire Atlas to produce estimates of emissions from global wildland fires for the year 2000. Their estimate for global biomass burning CH_4 emissions was 12 Tg CH_4/yr, resulting in global wildfire CH_4 emissions of 1.2 Tg CH_4/yr. These estimated emissions are significantly lower than others, a fact attributed primarily to discrepancies in the burned area estimated using GLOBSCAR. Finally, van der Werf et al. (2006) used a satellite-driven global vegetation model to estimate global fire emissions for 1997 through 2004. Using their estimate of global CH_4 emissions of 15 Tg CH_4/yr for the year 2000 yields wildfire emissions of 1.5 Tg CH_4/yr. Like the Hoelzemann et al. study, the van der Werf et al. study produces a CH_4 emissions estimate that appears to be too low; the reason for this discrepancy is not clear.

Because the above studies did not provide any estimates for N_2O emissions from biomass burning, it is not possible to apply the same assumptions to estimate wildfire N_2O emissions as done for CH_4.

Table 9-2. Estimates of Wildfire Methane and Nitrous Oxide Emissions

Reference	Base Year	Methane Emissions (Tg CH_4/yr)	Nitrous Oxide Emissions (Tg N/yr)
Houweling et al. (2000)		5.0	
Wuebbles and Hayhoe (2002)		2.0	
Lobert et al. (1999)	1990s	3.0	0.1
Hoelzemann et al. (2004)*	2000	1.2	
Ito and Penner (2004)*	2000	3.2-5.5	
van der Werf et al. (2006)*	2000	1.5	

* Derived from these studies as 10 percent of global total biomass burning emissions

Because of the large temporal variability in burned areas, significant variability is introduced in year-to-year wildfire emissions as well. Duncan et al. (2003) performed the first comprehensive analysis of the interannual and seasonal variability of fire emissions on the global scale. They applied remotely sensed data for fire counts and for smoke-related aerosols to estimate both the seasonal and the interannual variation of biomass burning for six regions of the world: Southeast Asia, Indonesia and Malaysia, Brazil, Central America and Mexico, Canada and Alaska, and Asiatic Russia. They found significant interannual variability in carbon monoxide emissions from biomass burning, especially in Indonesia and Malaysia, Brazil, Southeast Asia, and the boreal regions. The largest CO emissions resulted from uncontrolled forest wildfires during the last two decades and were often associated with ENSO-induced droughts. Their conclusions can also be applied to CH_4, as both CH_4 and CO are emitted under similar combustion conditions, particularly during the smoldering phase of the fire (see Section 9.1).

Significant interannual variability in fire CH_4 emissions was also demonstrated by van der Werf et al. (2006), who investigated the temporal variability in fire emissions during the eight-year period from 1997 to 2004 using satellite data coupled with a biogeochemical model. Their analysis showed that burning in forests, as opposed to savanna ecosystems, was highly variable from year to year and that this variability combined with high fuel loads contributed to high variability in observed emissions.

Given the large spread in CH_4 emission values and the significant uncertainties in their estimates, EPA estimates a present-day source to be bounded by the estimates of 2 and 5 Tg CH_4/yr as summarized by Denman et al. (2007).

9.4 Future Emission Scenarios

As discussed in Section 9.2.3, wildfires and climate/weather are intimately linked. Hence, any changes in climate conditions are likely to influence the fire regime (Swetnam, 1993; Westerling et al., 2006). In particular, warmer, drier, and windier conditions resulting from future climate changes are predicted to increase the frequency and severity of wildfires, particularly temperate-boreal fires (Price and Rind, 1994; Torn and Fried, 1992; Piñol et al., 1998; Brown et al., 2004; Fried et al., 2004, 2008; Levine, 2004; Lenihan et al., 2006; Miller and Schlegel, 2006; Westerling and Bryant, 2006; Pitman et al., 2007), in many locations. This would result in greater release of trace gases including CH_4 and possibly N_2O as well, depending on the nitrogen content of the vegetation.

Studies of the potential impact of climate change on wildfire relate fire characteristics, such as fire severity, frequency, and burn areas, with climate variables simulated for different climate scenarios by general circulation models (GCMs). For example, Torn and Fried (1992) examined the impact of a doubling of atmospheric CO_2 on wildfire area burned and the frequencies of escaped fires in northern California using climate variables from three GCMs combined with daily weather records and mechanistic models of fire behavior and fire suppression. They found increased burn areas and fire frequencies in grasslands of northern California in response to a doubled CO_2 climate. The magnitude of those increases, however, strongly depended on the vegetation type, choice of the GCM scenario, and choice of climate forcing variables. Recent research applying either an advanced version of the modeling system of Torn and Fried (Fried et al., 2004) or other sophisticated models using GCM projections of climate variables (Torn et al., 1998; Lenihan, 2006; Miller and Schlegel, 2006; Westerling and Bryant, 2006; Fried et al., 2008) all suggests increases in fire frequency and intensity in various parts of California with warmer temperatures as well as drier and windier conditions.

Using a fire model combined with the Goddard Institute for Space Studies GCM, Price and Rind (1994) show a possible 44 percent increase in wildfires ignited by lightning in the continental United States for an equilibrium doubling of carbon dioxide, with a 78 percent increase in the area burned by these fires. Their study also found that in the tropics, where most fires are human-initiated today, future climate change could potentially result in large increases in tropical wildfires. This was recently observed in the case of extensive and widespread tropical forest and peat fires that swept throughout Kalimantan and Sumatra, Indonesia, between August and December 1997. The fires initially resulted from burning from land clearing and land-use change. However, severe drought conditions following El Niño caused the initially controlled, anthropogenic fires to become large uncontrolled wildfires (Levine, 2004, and references therein). About 2.5 Tg CH_4 was emitted from the 1997 Indonesian fires alone, which is equivalent to the estimated total global wildfire emissions (Table 9-2).

Stocks et al. (1998) investigated the fire danger levels in Russian and Canadian boreal forests under equilibrium-doubled CO_2 climate using climate outputs from four GCMs. Results from all four models indicated large increases in the areal extent of extreme fire danger in both the countries under doubled CO_2 climate. Applying two different approaches, Beer and Williams (1995) and Pitman et al. (2007) concluded that fire risk over Australia is primarily driven by warming and reductions in relative humidity (dry conditions), thus making the region very vulnerable to fires under future climate changes.

In summary, future climate change is likely to increase the frequency of weather conditions associated with high wildfire risks in many regions of the world. Climate change has the potential to affect multiple elements of wildfires, including fire behavior, ignition, fire management and vegetation fuels. The complex interactions between each of these factors will determine future spatial and temporal distribution of wildfires and their emissions in response to climate change.

Currently, no scenarios for future CH_4 emissions from global wildfires exist in the literature. Efforts are, however, directed toward developing models that can predict/forecast wildfire events and can therefore be used to estimate emissions. Two types of models are currently being applied to predict wildfires.

- **Statistical modeling approach:** This approach uses statistical correlations to relate wildfire activity to various fire-danger predictors. These predictors may be climate factors (for example, seasonal temperature, precipitation, or relative humidity) or indices of large-scale climate variations (for example, the Southern Oscillation Index). For example, Preisler and Westerling (2007) have developed a statistical model to estimate the probability of a large fire event given a list of fire danger predictors. Using historical fire occurrence and fire weather predictors, the authors demonstrate the utility of this statistical tool for estimating one-month-ahead forecasts for large wildfire events in the western United States. Additionally, most of the studies described above apply statistical approaches to relate changes in climate variables to fire activity. While useful in forecasting/predicting fire danger for a region, these models cannot be used directly to predict gas or particle emissions from wildfires, either on a regional or a global scale.
- **Fire module within a dynamic vegetation model:** This approach involves including representation of fire dynamics within a global dynamic vegetation model that can be run using climate outputs from a GCM (offline) or coupled to a GCM (online). Fire dynamics are included in the vegetation models using simple and robust parameterizations of relevant processes (fuel availability, susceptibility to fire, and an ignition source). Fire-vegetation models are capable of simulating the inter-related effects of climate change on vegetation dynamics, biomass, hydrology, fire frequency and emissions on regional to global scales (Lenihan et al., 1998, 2003, 2006; Bachelet et al., 2001; Thonicke et al., 2001; Mouillot et al., 2002; Arora and Boer, 2005). These models provide a consistent framework for the simulation of changes in the amount of biomass burned and, therefore, emissions in response to current and future climates.

9.5 Areas for Further Research

With the advent of the satellite era, significant progress has been made—particularly over the last decade—toward understanding wildfire emissions. Current understanding of CH_4 emissions from wildfires is still limited, while that for N_2O is still primitive. Progress, however, can be made with further research.

Below are highlighted the areas that need to be addressed in order to significantly improve estimates of current and future CH_4 emissions from wildfires.

- The area and amount of biomass burned are the most important parameters required to accurately estimate wildfire CH_4 and N_2O emissions. However, these remain poorly constrained. A further complication is the difficulty in distinguishing between biomass subjected to natural, uncontrolled fires and human-initiated fires for land clearing. Further work on this topic is therefore a high priority.
- Emission factors are in general uncertain because of many experimental, instrumental, and methodological factors discussed in Section 9.3.1. However, emission factors for N_2O are at best "best guesses" at this point. Field and laboratory studies are needed to better constrain emission factors for both CH_4 and N_2O.
- Burned area estimates from different satellite sensors using different approaches have recently become available. These estimates demonstrate the strong potential of satellite-derived information that can be used to derive fire emissions. However, there are significant differences between estimates of burn areas derived from different approaches as evident from the studies of Hoelzemann et al. (2004), Ito and Penner (2004), and van der Werf et al. (2004) for the year 2000. These differences highlight the need for continued validation and intercomparison of different burned area products.
- Uncertainties in biomass density or available fuel load also induce uncertainties in emission estimates. Traditionally, compilations of ecosystem-specific fuel loads from different field experiments were used to derive global-scale emissions. More recently, global vegetation models have been used to simulate carbon/nitrogen pools within the vegetation on a global scale. However, large differences exist between simulated and observed fuel loads, possibly due to mismatch in scale between the measurements at the plot level and the much coarser model grid, as well as lack of data and biases in the literature values. This highlights the need for more observations on a global scale to validate the model results.
- Human activities, such as population growth and infrastructure development, are likely to influence wildfires. For example, human settlements near forested areas could increase anthropogenic ignition, resulting in high fire frequencies and high emissions. The impact of human activities on wildfires needs to be assessed in conjunction with the influence of climate change to better constrain the response of natural fire regimes to future global changes.

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Chapter 10. Vegetation

This chapter addresses recent evidence of aerobic CH_4 emissions from plants and vegetation types that have not generally been included in emissions inventories to date. Unflooded ecosystems, such as upland tropical forest, tropical savannas, and well-drained boreal forests, are not generally considered potential sources of CH_4, because drier soils act as an oxidative sink for CH_4. Neither the previous EPA report (U.S. EPA, 1993) nor the most recent IPCC assessment (Denman et al., 2007) includes estimates of CH_4 emissions from well-drained ecosystems in its emissions inventory. However, recent findings suggest that such ecosystems may be a significant unrecognized source of CH_4. Frankenberg et al. (2005) first reported that satellite-based estimates of CH_4 concentrations were higher over tropical forests than would be expected from current inventories of tropical CH_4 sources. The following year, Keppler et al. (2006) reported direct measurements of CH_4 emissions from living plants and plant litter under aerobic conditions, and proposed that forests and other vegetation might be a significant overlooked source of CH_4 to the atmosphere. Together, these findings have prompted recent efforts to explain the high CH_4 concentrations over tropical forests (Frankenberg et al., 2005, 2008; Bergamaschi et al., 2007; Meirink et al., 2008; Schneising et al., 2009), verify the measurements of plant emissions (Dueck et al., 2007; Fedele et al., 2007; Wang et al., 2008; Beerling et al., 2008; Kirschbaum et al., 2008; Bruggemann et al., 2009), identify a mechanism for aerobic plant emissions (Keppler et al., 2008; Vigano et al., 2008; McLeod et al., 2008; Messenger et al., 2009; Nisbet et al., 2009; Wang et al., 2009), refine the estimates of global plant emissions (Houweling et al., 2006; Kirschbaum et al., 2006; Parsons et al., 2006; Butenhoff and Khalil, 2007; Ferretti et al., 2007), and reexamine the potential for ecosystem CH_4 fluxes in forests and other dryland vegetation (Carmo et al., 2006; Crutzen et al., 2006; Sanhueza and Donoso, 2006; Sanhueza, 2007; Sinha et al., 2007).

10.1 Description of Emission Source

Plants have long been recognized as important conduits for CH_4 emissions, transporting CH_4 from anaerobic soils and sediments to the atmosphere (Dacey and Klug, 1979). However, it is only recently that plants themselves have been considered a possible source of CH_4 production (Keppler et al., 2006). Most existing studies of CH_4 flux in unflooded ecosystems focus on the balance between CH_4 production by methanogenic bacteria and CH_4 consumption by CH_4-oxidizing bacteria in soils. Because oxidative consumption exceeds CH_4 production in well-drained soils, unflooded ecosystems are generally inventoried as CH_4 sinks, rather than sources.

Based on their large land area and the strong oxidative capacity of their soils, unflooded tropical forests, tropical savannas, tropical steppes, and boreal forests are among the largest estimated soil sinks for atmospheric CH_4 (Potter et al., 1996). However, recent studies suggest that these unflooded ecosystems may emit CH_4 at the ecosystem level (Carmo et al., 2006; Crutzen et al., 2006; Sanhueza and Donoso, 2006; Sanhueza, 2007; Sinha et al., 2007), and that plants themselves may emit CH_4 through an as-yet-unidentified aerobic process (Keppler et al., 2006; Wang et al., 2008; Bruggemann et al., 2009). The following sections describe evidence of CH_4 emissions from well-drained ecosystems from three sources: indications that bottom-up inventories are underestimating CH_4 emissions over tropical regions (Hein et al., 1997; Houweling et al., 1999; Frankenberg et al., 2005, 2006; Bergamaschi et al., 2007); measurements of direct CH_4 emissions from plants under aerobic conditions (Keppler et al., 2006; Wang et al., 2008, 2009; Bruggemann et al., 2009; but see Dueck et al., 2007; Beerling et al., 2008; Kirschbaum et al., 2008; Nisbet et al., 2009); and direct measurements of ecosystem CH_4 flux (Carmo et al., 2006; Crutzen et al., 2006; Sanhueza and Donoso, 2006; Sanhueza, 2007; Sinha et al., 2007).

10.1.1 Identification of High Methane Concentrations Over Tropical Forests

Frankenberg et al. (2005) first compared global patterns of CH_4 concentrations inferred from satellite-based SCIAMACHY observations to values obtained using an atmospheric transport model and current inventories of CH_4 sources, to show that SCIAMACHY retrievals over tropical forests were up to 4 percent higher than modeled values. This led them to suggest a missing source of 30 Tg CH_4 over the four-month measurement period (August through November 2003). This finding supported earlier inverse modeling studies based on ground-based measurements, which had indicated that source inventories tended to underestimate CH_4 emissions in the tropics (Hein et al., 1997; Houweling et al., 1999).

Later reports (Frankenberg et al., 2006; Bergamaschi et al., 2007) showed that SCIAMACHY retrievals over tropical regions were higher than modeled values throughout the measurement period January 2003 through December 2004, and exhibited strong seasonality, with the greatest discrepancies occurring during August through December. While SCIAMACHY retrievals are prone to some bias (Frankenberg et al., 2006), the high CH_4 concentrations inferred for the Amazon basin are supported by recent aircraft-based measurements (Miller et al., 2007).

Using a new wetland inventory in the transport model redistributed wetland emissions from higher latitudes to the tropics, reducing the discrepancy between SCIAMACHY observations and modeled emissions over the Amazon, particularly during the first half of the year (Bergamaschi et al., 2007). Subsequent analyses have further reduced the discrepancy, particularly the correction of an error that amplified methane concentration estimates in areas with high water vapor abundances (Frankenberg et al., 2008). However, the SCIAMACHY retrievals continue to indicate higher tropical emissions than previously estimated from ground-based observations (Frankenberg et al., 2008; Meirink et al., 2008; Schneising et al., 2009).

10.1.2 Measurement of Methane Emissions From Plants Under Aerobic Conditions

Keppler et al. (2006) first reported CH_4 emissions of 0.2 to 3 nanograms per gram (ng per g) (dry weight) per hour from detached leaves from 19 different species and 12 to 370 ng per g (dry weight) per hour from intact plants representing nine herbaceous species measured under aerobic conditions in the dark. Under natural sunlight, emissions were 3 to 5 times higher, ranging from 1.6 to 15.8 ng per g (dry weight) per hour for detached leaves and 198 to 598 ng per g (dry weight) per hour for intact plants. Because the amount of CH_4 generated was small relative to background CH_4 concentrations, measurements were conducted in static chambers that had been purged with CH_4-free air. Global emissions were then estimated by scaling measured emission rates to annual net primary productivity (NPP), a measure of the total plant matter produced over the course of the year, and taking into account season length and day length for each biome (Table 10-1).

Do plants produce methane?

Since Keppler et al. (2006) first proposed that plants produce methane through a previously unrecognized mechanism, a number of studies have attempted to measure direct CH_4 emissions from living plants under aerobic conditions. The results have been mixed, with some studies confirming aerobic plant emissions (McLeod et al., 2008; Vigano et al., 2008; Wang et al., 2008; Bruggemann et al., 2009; Messenger et al., 2009) and others finding no evidence of plant emissions (Dueck et al., 2007; Beerling et al., 2008; Kirschbaum et al., 2008; Nisbet et al., 2009).

The mechanism for aerobic CH_4 production has not been identified, but recent studies link methane emissions to exposure to ultraviolet light (Vigano et al., 2008; McLeod et al., 2008), which may trigger chemical reactions that produce methane from antioxidants commonly found in the mitochondria of living cells (Ghyczy et al., 2008; Messenger et al., 2009).

This approach yielded a global emissions estimate of 62 to 236 Tg CH_4/yr from living plants and 0.5 to 6.6 Tg CH_4/yr from plant litter, which would be equivalent to approximately 10 to 40 percent of the annual total emissions of 582 Tg CH_4/yr estimated by Denman et al. (2007), with tropical forests accounting for about half of the estimated source strength.

A number of studies have attempted to verify Keppler et al.'s (2006) measurements of direct CH_4 emissions from living plants (Dueck et al., 2007; Beerling et al., 2008; Kirschbaum et al., 2008; Vigano et al., 2008; Wang et al., 2008, 2009; Bruggemann et al., 2009; Nisbet et al., 2009) and plant litter (Fedele et al., 2007), with mixed results. Dueck et al. (2007) grew six plant species in air containing ^{13}C-labeled CO_2 (99 atom percent ^{13}C) for nine weeks, and then measured CH_4 emissions from the plants using a high sensitivity laser-based system. Because any CH_4 emitted from the plants would be labeled with ^{13}C, it would be detectable even against background atmospheric CH_4 concentrations. However, emission rates measured from individual plants and from numerous plants grown together were not statistically different from zero. The authors therefore suggested that the CH_4 emissions measured by Keppler et al. (2006) may have simply resulted from diffusion of CH_4 out of air spaces in the plants and soil after the measurement chambers had been flushed with CH_4-free air. Beerling et al. (2008) also failed to detect methane emissions from leaves of rice or corn plants incubated in flow-though chambers, either in the dark or when exposed to photosynthetically active radiation. Nisbet et al. (2009) demonstrated that plants can emit dissolved methane in the transpiration stream, and that small amounts of methane can be produced as a byproduct of the breakdown of plant material under high stress conditions, but showed through a genome analysis that plants do not contain genes linked to the known biological mechanisms for methane formation.

In response, Vigano et al. (2008) and McLeod et al. (2008) conducted a series of follow-up experiments, using both flow-through chambers and static chambers containing both ambient and CH_4-free air, which confirmed CH_4 emissions from plant tissues and structural compounds exposed to UV light and heating. Methane emissions have also been detected by other groups, including Wang et al. (2008), whose examination of 44 species from the Inner Mongolia steppe found that the leaves of seven out of nine woody shrub species produced CH_4 emissions as high as 3.39 ng CH_4/g dry weight/hr, although herbaceous species did not emit measurable levels of plant-derived CH_4. Low levels of methane emission have also been detected in poplar shoot incubated under low-light conditions (Bruggemann et al., 2009).

While the precise mechanism for aerobic CH_4 production by plants has not been identified, the relationship between observed methane emissions and exposure to UV radiation and heat has led to the suggestion that methane production may be linked to the production of reactive oxygen species in response to physiological stress. Aerobic CH_4 production had previously been demonstrated in animal cells and mitochondria exposed to oxidative stress (Ghyczy et al., 2003, 2008). During oxidative stress, overproduction of reactive oxygen species such as hydrogen peroxide (H_2O_2) and the hydroxyl radical (OH^-) can damage vital cell components. Cells produce a number of antioxidant molecules, which protect against cell damage by reacting with and neutralizing reactive oxygen species. Ghyczy et al. (2003, 2008) have demonstrated that a group of antioxidant molecules containing methyl ($-CH_3$) groups can produce CH_4 upon reaction with reactive oxygen species in mammalian cells. The isotopic signature of the CH_4 released in their original study led Keppler et al. (2006) to propose plant pectins as the source of aerobic plant emissions. A later deuterium labeling study suggested that CH_4 was generated from methyoxl groups on the pectin molecules (Keppler et al., 2008). Messenger et al. (2009) recently demonstrated that reactive oxygen species caused the release of methane from plant pectin, and proposed that reactive oxygen species, particularly the –OH radical, causes the release of methane from methoxyl groups in the pectin of plants exposed to UV radiation and other physiological stresses.

10.1.3 Measurement of Ecosystem Methane Flux

Because CH_4 oxidation generally exceeds production in the well-drained soils of upland tropical forests (Potter et al., 1996), tropical savannas (Castaldi et al., 2006), and boreal forests (Whalen et al., 1992), such ecosystems are generally considered sinks for atmospheric CH_4. However, recent studies suggest these ecosystems may be significant sources of CH_4. Static chamber measurements indicate that soil disturbance from selective logging can cause upland forest soils to switch from acting as a CH_4 sink to producing CH_4 at rates as high as 98 to 531 mg CH_4/m^2/day (Keller et al., 2005). Measurements of nighttime canopy concentration profiles yielded emission estimates of 2 to 21 mg CH_4/m^2/day for four upland forest sites in the Amazon basin (Carmo et al., 2006). Similarly, canopy profile measurements indicated emissions of 8.7 mg CH_4/m^2/day for a tropical forest site in Suriname and 8.3 mg CH_4/m^2/day for a boreal forest site in Finland (Sinha et al., 2007). Reexamination of previously published measurements from Venezuelan savanna sites indicates that the savanna ecosystem is an intermittent source of CH_4, with positive fluxes as high as 3.8 mg CH_4/m^2/day (Crutzen et al., 2006; Sanhueza, 2007). Using static chamber measurements, Sanhueza and Donoso (2006) reported higher CH_4 emissions from Venezuelan savanna plots with undisturbed vegetation compared to plots from which live and dead grass biomass had been clipped to just above the soil surface. While they interpret the difference as plant-generated CH_4 emissions, differences in CH_4 flux might also result from differences in soil moisture, soil carbon stocks, and plant-mediated CH_4 transport between disturbed and undisturbed plots.

10.2 Factors That Influence Emissions

Because a possible plant CH_4 source has only recently been suggested and the mechanism for such emissions has yet to be identified, little is known about factors that might control rates of CH_4 emission from plants. Keppler et al. (2006) reported that emission rates increased with temperatures ranging from 30 to 70 degrees Celsius, and were significantly higher in the sunlight than in the dark. The observation that CH_4 emissions continued to increase at such high temperatures suggests that the CH_4 was not produced by enzymatic processes (Kirschbaum et al., 2006). The higher emission rates measured when the incubation chambers were exposed to direct sunlight could indicate that CH_4 production is tied to photosynthetic processes, or flux rate could have simply responded to heating of the incubation chambers by sunlight (Kirschbaum et al., 2006). The relationship between CH_4 emissions and UV exposure suggests the mechanism may involve direct photochemical reactions (Vigano et al., 2008) or biochemical reactions that occur under oxidative stress (Ghyczy et al., 2008; Messenger et al., 2009). As described below, more research is needed to characterize the controls over CH_4 emissions from plants and variation across species and ecosystems.

10.3 Current Global Emissions

Keppler et al. (2006) estimated that plants emit 62 to 236 Tg CH_4/yr, with tropical forests contributing 33.2 to 123 Tg CH_4/yr, or about half of the total. These estimates were developed by scaling the measured emission rates by the annual NPP of each biome, taking into account day and season length (Keppler et al., 2006). The use of NPP as a scaling factor has been criticized for two reasons. First, since NPP measures the accumulation of biomass over the length of the growing season, standing biomass is less than NPP for much of the growing season (Butenhoff and Khalil, 2007; Parsons et al., 2006). Second, NPP is partitioned between aboveground and belowground biomass, and these would likely differ in CH_4 production (Kirschbaum et al., 2006; Butenhoff and Khalil, 2007). As a result, the findings of Keppler et al. (2006) have prompted a number of attempts to better constrain the estimate of global aerobic emissions from plants through both top-down and bottom-up techniques (Houweling et al., 2006; Kirschbaum et al., 2006; Parsons et al., 2006; Butenhoff and Khalil, 2007; Ferretti et al., 2007).

Net primary productivity (NPP) is defined as the net flux of carbon from the atmosphere into primary producers (plants and other photosynthesizing organisms) per unit time. NPP refers to a rate process, i.e., the amount of biomass produced (net primary production) per day, week, or year. Because annual NPP describes the biomass accumulated over the course of the year, the total standing biomass at a given point in time will usually be less than annual NPP.

Specifically, Bousquet et al. (2006) found that adding a plant source of 150 Tg CH_4/yr to the emissions inventory used in inverse modeling simulations could be accommodated by reducing the strength of other sources, such as wetlands and anthropogenic emissions, within the range of their uncertainties. Houweling et al. (2006) found that including vegetation emissions of 125 Tg CH_4/yr in forward modeling simulations explained up to 50 percent of the discrepancy between previous simulations and SCIAMACHY retrievals over the Amazon basin (Frankenberg et al., 2005). However, including vegetation emissions of that magnitude caused the model to overestimate pre-industrial CH_4 concentrations, leading Houweling et al. (2006) to estimate an upper limit of 85 Tg CH_4/yr for vegetation emissions.

Keppler et al. (2006) reported that the CH_4 emitted from plants was enriched in ^{13}C relative to wetland emissions, with mean $\delta^{13}C$ values of -52‰ (per mil) for C3 plants and -46.5‰ for C4 plants. The ratio of ^{13}C, a stable isotope of carbon, to the more common ^{12}C in CH_4 can be related to different sources, which have different characteristic isotopic signatures. Stable isotope ratios are expressed as the ratio of ^{13}C to ^{12}C in a sample, relative to that of a standard reference material, in parts per thousand. This suggested that plant emissions could explain unexpectedly enriched atmospheric $\delta^{13}CH_4$ values obtained from ice cores (Ferretti et al., 2005). However, Ferretti et al. (2007) found that including a large (34 to 121 Tg CH_4/yr) pre-industrial aerobic plant source in mass balance calculations required using unrealistically low biomass burning emissions estimates to accommodate variation in atmospheric $\delta^{13}CH_4$ over the period from 0 to 1700 A.D. (Ferretti et al., 2005). Instead, Ferretti et al. (2007) report "best estimates" of 0 to 46 Tg CH_4/yr for pre-industrial plant emissions and 0 to 176 Tg CH_4/yr for modern plan emissions. Similarly, Schaefer et al. (2006) proposed that plant emissions could help explain unexpectedly enriched $\delta^{13}CH_4$ values at the end of the last glacial period (about 12,000 years ago), when temperatures and atmospheric CH_4 concentrations increased rapidly. More recently, Schaefer and Whiticar (2008) were able to accommodate a modern aerobic plant source of 42 Tg CH_4/yr with a $\delta^{13}CH_4$ value of -51‰ in a detailed budget based on changes in CH_4 concentration and $\delta^{13}CH_4$ between the last glacial maximum and the present.

Table 10-1. Bottom-Up Estimates of Plant Methane Emissions by Biome

Biome	Keppler et al., 2006 (Tg CH_4/yr)[a,b]	Kirschbaum et al., 2006 (Tg CH_4/yr)[c]	Parsons et al., 2006 (Tg CH_4/yr)[b]
Tropical forest	78.2 (33.2–123)	18.8	15.6
Temperate forest	17.7 (7.1–28.4)	3.4	8.0
Boreal forest	3 (1.1–4.1)	2.8	3.6
Mediterranean shrublands	2.7 (1.2–4.3)	1.0	0.8
Tropical savanna and grasslands	29.2 (12.4–45.9)	6.6	8.0
Temperate grasslands	7.4 (2.9–11.8)	1.6	2.0
Deserts	3.8 (1.7–5.9)	0.6	2.2
Crops	7.2 (2.9–11.5)	1.6	2.2
Total	**149 (62.3–236)**	**36.4 (15.1–60.3)**	**42**

[a] Units are teragrams (Tg) of CH_4 emitted per year; a Tg is equivalent to a megaton (Mt), or 1 million metric tons.
[b] Estimated by scaling mean (low to high) emissions measurements by biome NPP.
[c] Estimated by scaling mean emissions measurements from Keppler et al., 2006, by estimated standing leaf biomass.

In contrast to these "top-down" estimates, a number of studies have used "bottom-up" approaches to extrapolate the Keppler et al. (2006) flux measurements to the global scale (Table 10-1). Kirschbaum et al. (2006) used two approaches to estimate global plant emissions: the first based on estimates of standing leaf mass in each biome, and the second based on estimates of photosynthetic productivity for each biome. The leaf-mass approach yielded an estimate of 15 to 60 Tg CH_4/yr, with tropical forests contributing about half the total, and the photosynthesis-based approach yielded an estimate of 9.6 Tg CH_4/yr, with tropical forests contributing about a third of the total plant emissions. Parsons et al. (2006) also used an approach that scaled CH_4 emissions based on standing leaf biomass in each biome, yielding an estimate of 42 Tg CH_4/yr from leafy biomass and an additional 10.7 Tg CH_4/yr from non-leafy biomass, with tropical forests accounting for about half of the total plant source.

Butenhoff and Khalil (2007) used two methods to scale plant emissions: one based on estimates of standing leaf biomass derived from satellite maps of leaf area index (LAI) and a second based on monthly estimates of above-ground net primary production (ANPP). Using Keppler et al.'s (2006) mid-range values of 374 ng CH_4 per gram (dry weight) per hour for sunlit tissue and 119 ng CH_4 per gram (dry weight) per hour for shaded tissue, Butenhoff and Khalil (2007) calculated global plant emissions of 36 Tg CH_4/yr for the LAI method and 20 Tg CH_4/yr for the ANPP method, with tropical forests contributing about a third of the total emissions.

Given the limited number of studies that have attempted to measure CH_4 emissions from plants under aerobic conditions, the conflicting results of those studies, and the fact that an actual physical mechanism by which plants directly produce CH_4 has yet to be identified, a best estimate of global plant emissions must include the possibility of zero emissions (i.e., that plants are in fact not a direct source of CH_4).

If an aerobic plant source is confirmed, additional work will still be required to identify the mechanism of CH_4 production and the environmental and biological controls over emissions rates before plant emissions can be included in process-based models in a meaningful way. Based on the information currently available, in this report EPA estimates a plant CH_4 source of either zero (if plants do not actually emit CH_4) or (if the source is confirmed) 20 to 60 Tg CH_4/yr, a range that captures the agreement between bottom-up estimates. This range is on the low end for current top-down estimates, which generally worked backward from the very large plant source proposed by Keppler et al. (2006) by reducing the estimated contribution from other sources, particularly wetlands.

10.4 Future Emission Scenarios

The recently proposed aerobic plant CH_4 source has not yet been incorporated into simulations of future CH_4 emissions. However, future plant emissions would likely depend on changes in the distribution of different vegetation types, as well as changes in environmental factors that might control emission rates. Current estimates attribute 35 to 50 percent of global plant emissions to tropical forests, with the second largest source, tropical savanna and grasslands, contributing about 20 percent. This suggests that future plant emissions would depend largely on changes in climate and land use in the tropics.

10.5 Areas for Further Research

To date, few published studies have successfully measured direct CH_4 emissions from plants under aerobic conditions (Keppler et al., 2006; Vigano et al., 2008; Wang et al., 2008, 2009; Bruggemann et al., 2009), while others have been unable to detect measurable emissions (Dueck et al., 2007; Beerling et al., 2008; Kirschbaum et al., 2008; Nisbet et al., 2009). These studies' conflicting results indicate that the first priorities for future research should be to verify the findings of Keppler et al. (2006) and identify a mechanism for plant CH_4 emissions. If an aerobic plant CH_4 source is confirmed, experimental work is needed to determine the environmental and physiological controls over emission rates. Measurements should also be taken for a wider range of species to characterize the variation in plant CH_4 production at both the species and ecosystem levels. Until more is understood about the seasonal patterns and controls over emission rates, it will be difficult to accurately quantify the global significance of a possible plant CH_4 source.

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Chapter 11. Terrestrial Arthropods and Wild Animals

The original 1993 report (U.S. EPA, 1993) cited termites as a contributor to natural CH_4 emissions, estimating their global contribution at 20 Tg CH_4/yr (10 to 50 Tg CH_4/yr). However, the report did not discuss this source, and it considered no other type of terrestrial arthropod nor any contributions by wild animals.

In the years since the publication of the 1993 report, additional investigation of CH_4 emissions from termites has resulted in more refined estimates of CH_4 emissions from the various termite species, and suggested that CH_4 may oxidize in termite mounds prior to atmospheric release. In addition, other terrestrial arthropods have been studied to assess whether they generate CH_4 and should be included in any estimates of global emissions. From this new research, termites and other terrestrial arthropods continue to be a small but not insignificant contributor to global CH_4 emissions.

Arthropods

Arthropods are the largest phylum of animals and include insects, arachnids, crustaceans, and others. Arthropods are characterized by the possession of a segmented body with appendages on at least one segment. All arthropods are covered by a hard exoskeleton. Arthropods are common throughout marine, freshwater, terrestrial, and aerial environments.

Wild animals also contribute to global CH_4 emissions, although far less research has been conducted on this source. Much is known about enteric fermentation from domesticated animals, and from this area of study (combined with estimates of wild animal populations), some conclusions can be drawn about the relative contributions from ruminant wild animals.

This chapter reviews the current scientific understanding of terrestrial arthropods and wild animals as sources of CH_4, including the factors that influence emissions and the most recent estimates of current and future global emissions.

11.1 Description of Emission Source

Termites and other terrestrial arthropods produce and emit CH_4 as a result of microbial degradation of the organic matter they ingest. In wild animals, CH_4 emissions are caused by enteric fermentation in ruminants such as bison, deer, elk, mountain goats, and sheep, and also in some smaller rodent species.

CH_4 production from termites was first observed in the 1930s. As research progressed, it became clear that the amount of CH_4 generated varied substantially from species to species. Termites can be divided into two groups: (1) lower termites, which live in a mutualistic relationship with one or more protozoan flagellates that live inside their guts and digest the wood ingested by the termites, and (2) higher termites, which possess anaerobic (methanogenic) bacteria in their guts (Sanderson, 1996). Higher termites have been found to have higher CH_4 emission rates and larger biomasses than lower termites, thereby contributing more to the global CH_4 emissions from this source (Sugimoto and Inoue, 1998).

Certain termites build nests or mounds in which to live. Some groups simply excavate areas in dead wood or make underground nests. The more advanced termites build huge mounds, largely from soil excavated from their underground chambers and cemented with saliva. These are especially common in Africa and Australia. Some nests are open and emit all CH_4 generated by the termites; others are closed (such as subterranean nests) and have a rate of emission close to zero. Some nests have ventilation vents.

CH_4 emitted by the termites in their nests may be partially oxidized by the mound material during emission into the atmosphere. Research conducted by Sugimoto and Inoue (1998) evaluated the emission of CH_4 from various types of termite mounds and developed a set of emission factors defined as CH_4 emitted from the mound divided by CH_4 produced by the termites. These factors were used in combination with estimates of termite populations and biomass to estimate global emissions. For those colonies with mounds, over half (and in some cases up to more than 80 percent) of CH_4 emissions were oxidized by the mound.

Research by Hackstein and Stumm (1994) evaluated whether CH_4 is emitted from other types of arthropods, in addition to termites (*Isoptera*). This research showed that three other groups exhibited CH_4 production: *Diplopoda* (millipedes), *Blattaria* (cockroaches), and *Cetonidae* (flower beetles). Although research is still preliminary, it suggests that these other species, particularly flower beetles, may be significant sources of CH_4.

In animals, CH_4 is produced as part of normal digestive processes. During digestion, microbes resident in the digestive system ferment food consumed by the animal. This microbial fermentation process, referred to as enteric fermentation, produces CH_4 as a byproduct, which can be exhaled or eructated by the animal. The amount of CH_4 produced and excreted by an individual animal depends primarily upon the animal's digestive system, and the amount and type of feed it consumes.

Ruminant animals are the major emitters of CH_4 because of their unique digestive system. Ruminants possess a rumen, or large "fore-stomach," in which microbial fermentation breaks down the feed they consume into products that can be absorbed and metabolized. The microbial fermentation that occurs in the rumen enables them to digest coarse plant material that non-ruminant animals cannot. Ruminant animals, consequently, have the highest CH_4 emissions among all animal types.

11.2 Factors That Influence Emissions

The factors that determine the magnitude of emissions of CH_4 from terrestrial arthropods include the species of arthropod, including the specific type of termite. The highest rates of CH_4 are produced by arthropods with methanogenic bacteria, typically found in higher termites. Environmental conditions such as temperature and humidity also affect the rate of CH_4 generation, as does the population density, termite activity, time of day, and size and type of termite mounds. However, even though different species produce widely different amounts of CH_4, the overall total CH_4 emission remains largely constant. In addition, according to a study by Martius et al. (1996), rainforest clearing and the conversion of primary forest to pasture land did not significantly change the amount of CH_4 emitted by termites.

Emissions of CH_4 from wild animals are influenced by feed quality and feed intake. Because a ruminant digests food in two steps, its food intake is affected by the quality, or digestibility, of the food. The higher-quality food passes through the rumen more quickly and leads to higher intake. However, the lower-quality food tends to generate higher CH_4 emissions (Owensby et al., 1996). Therefore, as available forage changes, the type and quantity of emissions from wild animals is likely to change.

11.3 Current Global Emissions

Table 11-1 presents a summary of global emission estimates for termites, other arthropods, and wild animals. Estimating global emissions of CH_4 from terrestrial arthropods and wild animals has primarily been based on bottom-up calculations using estimates of insect and animal populations, combined with an emission factor based on available measurements of emissions from these systems. These methods contain high levels of uncertainty, since there are limited data available for these calculations.

The AR4 provided a global emissions total for termites of 20 Tg CH_4/yr (Denman et al., 2007), which has been generally agreed upon, with a variation of 50 percent (Sanderson, 1996; Houweling et al., 2000). However, this estimate does not account for the oxidation of CH_4 in the soil mounds surrounding certain termite nests. Research by Sugimoto and Inoue estimated the global CH_4 emitted by termites as 2 to 7 Tg CH_4/yr. The research of Sanderson (1996) and Sugimoto and Inoue (1998) suggests that a range of 2 to 22 Tg CH_4/yr is appropriate.

As mentioned earlier, other research (Hackstein and Stumm, 1994) suggests that there are additional contributions by other types of arthropods that contribute to global CH_4 and these emissions may be as large as 100 Tg CH_4/yr. However, this research is preliminary and has not yet been corroborated by other sources.

Estimates of CH_4 emissions from wild animals range from 2 to 6 Tg CH_4/yr (Leng, 1993, adapted from Crutzen et al., 1986), to more recent estimates of 15 Tg CH_4/yr (Houweling et al., 2000). The global distribution of CH_4 emissions from wild ruminants has been most often approximated using the method described by Bouwman et al. (1997), which assumed that wild animals consume a certain percentage of vegetation, of which a constant fraction is assumed to be emitted as CH_4. The methodology includes assumptions regarding how much vegetation in forested ecosystems consists of consumable grass or leaves, combined with assigning vegetation types on the basis of the land cover.

Table 11-1. Summary of Global Methane Emissions From Arthropods and Wild Animals

Source	Emissions (Tg CH_4/Yr)	Range of Estimate (Tg CH_4/Yr)	Reference
Termites	20	0–40	Houweling, 1999
	20	10–30	Houweling et al., 2000
	20	2–22	Wuebbles and Hayhoe, 2002
	20	18–22	Sanderson, 1996
		1.5–7.4	Sugimoto and Inoue, 1998
Other arthropods		Up to 100	Hackstein and Stumm, 1994
Wild animals	5	0–10	Houweling, 1999
		2–6	Leng, 1993 (adapted from Crutzen et al., 1986)
	15		Houweling et al., 2000

11.4 Future Emission Scenarios

Emissions from terrestrial arthropods (including termites) and wild animals are not expected to change significantly in the future. Changes to land use, which alter the type of plants available for wild ruminants, could affect the diets of these animals and subsequently their rate of enteric fermentation. As human activity encroaches on wildlife ecosystems, the reduced habitat availability will likely cause a decrease in wild animal populations. The habitats for terrestrial arthropods and wild animals are also linked to climate effects resulting in shifting ecosystems (in more northern environments) or drought, which are again likely to decrease populations.

Currently, no scenarios for future CH_4 emissions from this source exist in the literature. However, Owensby et al. (1996) reviewed the impact of increased atmospheric CO_2 on forage quality and the effect on ruminant CH_4 emissions. They found that increased CO_2 reduced nitrogen in the vegetation, and overall negatively affected the quality of forages. Consequently, ruminant intake declined as forage quality decreased. Owensby et al. concluded that wild ruminant diet quality will be affected and growth and reproduction will likely be reduced.

11.5 Areas for Further Research

Much research is needed to improve the bottom-up calculations of CH_4 emissions from terrestrial arthropods and wild animals. Investigation of other arthropods and their potentially significant contributions to global CH_4 is needed, as well as improvements in estimates of current and future populations of these arthropods and whether all CH_4 generated is emitted to the atmosphere.

For wild animals, improvements to the inventories of animal populations and the data available on their diets would contribute to the development of more specific emission factors and confirm the rate of enteric fermentation.

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Chapter 12. Summary and Conclusions

Table 12-1 summarizes the current global estimates of CH_4 and N_2O emissions from natural sources. When compared to the total global sources of CH_4 and N_2O (anthropogenic emissions as identified in the IPCC's Fourth Assessment Report plus natural emissions from this report), natural sources of CH_4 are estimated to contribute about 37 percent of the annual flux of CH_4 to the atmosphere, while natural sources of N_2O are estimated to represent about 64 percent of the global total.

12.1 Summary of Methane Emissions

For some natural sources, such as wetlands, CH_4 emissions are reasonably well understood and have been quantified over some time. Other sources, such as vegetation and terrestrial and marine geologic sources, are potentially significant but are either newly identified or early in the research stages of quantification.

Before the Industrial Revolution, natural wetlands were the dominant source of CH_4 to the atmosphere (Brook et al., 2000; Etheridge et al., 1998). The increase in human population has decreased the relative importance of wetland sources both by increasing anthropogenic sources and by decreasing wetland acreage through drainage and land use change. Both direct and indirect changes in wetland fluxes will continue, because many of the environmental variables such as temperature, rainfall, and vegetation type that control wetland CH_4 emissions are associated with climate. A number of studies have attempted to model wetlands' response to climate change. They calculate that emissions from wet soils will be enhanced more than oxidation in dry tundra and forest soils. As a result, projected CH_4 emissions from northern wetlands are expected to nearly double by the end of the century. Changes in land use, particularly in the tropics, are also likely to significantly alter emissions. Since models point to tropical wetlands as contributing the majority of emissions, understanding change in these regions is critical.

Another potentially significant natural source of CH_4 is natural seeps from geologic sources deep within the Earth's crust. Previous estimates of natural sources have either ignored this source or only evaluated marine seeps (ignoring terrestrial seeps, such as magmatic volcanoes). Current estimates include emissions from mud volcanoes, other macroseepage locations, terrestrial microseepage, and marine seeps. There continue to be large uncertainties in these estimates, the largest of which lies in estimating sub-oceanic emissions. In contrast, estimates of onshore emissions are based on direct measurements and up-scaling procedures based on standard emission factor concepts applied to point sources (for individual macroseepage features such as mud volcanoes) and homogeneous area sources (for diffuse sources such as microseepage). Relatively few climate- or human-related factors are hypothesized to be capable of influencing emissions of CH_4 from geologic sources. Some hypotheses indicate decreased emissions associated with large-scale extraction of oil and gas, and increased emissions following deglaciation events, as seismic activity increases. While geologic CH_4 emissions have likely changed in the past and are likely to continue to change in the future, these mechanisms are too speculative to use as a basis to estimate even the general direction of future changes in geologic CH_4 emissions.

Recent evidence has suggested the possibility of a significant contribution of CH_4 emissions from vegetation, a natural source omitted from previous budget estimates. Previous research classified unflooded ecosystems, such as upland tropical forest and well-drained boreal forests, as CH_4 sinks. However, more recent results suggest that plants may produce methane under aerobic conditions. While the mechanism of plant methane production has not been identified, a number of independent studies have demonstrated measurable methane production, particularly under stressful conditions such as ultraviolet radiation, high temperature, or tissue damage. In contrast, some laboratory and field studies have failed to confirm measurable methane emissions from plants. Given these conflicting results, and the fact that an actual physical mechanism by which plants directly produce CH_4 has yet to be identified, a best estimate of global plant emissions must also include the possibility of zero emissions (i.e., that plants are in fact not a direct source of CH_4).

Other notable natural sources of CH_4 include microbial activity in oceans, estuaries, and rivers, and lakes, as well as in the digestive systems of certain arthropods and wild mammals. Exact estimates still vary widely, however.

12.2 Summary of Nitrous Oxide Emissions

The primary natural sources of N_2O are upland soils and riparian areas, oceans, estuaries, and rivers. Upland soils are well-aerated and generally oxic (Conrad, 1996), and the dry soil conditions favor microbial processes which make dry upland soils a sink for CH_4 and a source of N_2O. In addition, riparian zones have saturated soil conditions and microbially available carbon which contribute to higher rates of production of N_2O than dry upland soils. The vast majority of studies in the past have focused on N_2O emissions from agricultural, not natural, soil sources. Recently, the number of N_2O emissions measurements has increased steadily, allowing for improvements in emission models and budgets, although there are still significant model uncertainties. The prediction of future emissions of N_2O production in soils depends on the changing human activities on these soils, as well as on climate patterns that are shifting as a result of global climate change. The clearing of land for agricultural use has been shown to lead to increased N_2O emissions and a decreased capacity for CH_4 oxidation, for example. Global climate change models show patterns of temperature and precipitation changes worldwide. Because soil moisture is a key determinant of the microbial processes that consume or produce N_2O and CH_4, these shifting climate patterns will determine the fluxes of these greenhouse gases into the future.

The oceans are another major natural source of N_2O to the atmosphere, with N_2O produced primarily in the water column. Emissions of N_2O from other aquatic environments (e.g., estuaries and rivers) are typically classified as largely anthropogenic because the majority of nitrogen entering these systems is believed to be associated with human activities such as agriculture. However, a small portion of these emissions actually reflect the natural movement of nitrogen.

Table 12-1. Current Methane and Nitrous Oxide Emissions From Natural Sources

Source	Methane (Tg CH_4/year)			Nitrous Oxide (Tg N/year)		
	Emissions Estimate[a]	**Range[b]**	**δ^{13}C (‰)[c]**	**Emissions Estimate[a]**	**Range[b]**	**δ^{15}N (‰)[d]**
Wetlands	**170.3**			Negligible		
- Northern/bogs	42.7	24–72	-62			
- Tropical/swamps	127.6	81–206	-58.9			
Upland soils and riparian areas	-30	Not available		6.6	3.3–9.0	-38 to +2
Oceans, estuaries, and rivers	9.1	2.3–15.6	-58	5.4	1.5–9.1	-2 to +12
Permafrost	0.5	0–1		Negligible		
Lakes	30	10–50	-53.8		0.004–0.04	
Gas hydrates		2–9[e]	-62.5			
Terrestrial and marine geologic sources		42-64	-41.8			
Wildfires		2–5	-25	0.1	Not available	
Vegetation		Not a source or 20–60	Not available			
Terrestrial arthropods[f]	20	2–22	-63			
Wild animals	8	2–15	-60.5			
All natural sources	**208**	**See note[g]**	**-57[h]**	**12.1**	**See note[g]**	**8.8[i]**
All sources to the atmosphere (anthropogenic and natural)	566[j]	503–610[k]	-54.5[c]	18.8[l]	8.5–27.7	7[m]
Natural sources as a percent of the total	37%	See note[g]	n/a	64%	See note[g]	n/a

[a] In some cases, a point estimate cannot be provided due to large uncertainty.

[b] Ranges presented here may reflect a compilation of several different estimates. Published estimates vary due in part to uncertainty in estimating the global number of point and diffuse sources and the average annual emissions from each individual source or source area.

[c] Mean value from Whiticar and Schaefer, 2007, and references therein.

[d] Range from Rahn and Wahlen, 2000, and references therein.

[e] The emission estimates for gas hydrates correspond to the flux of methane to the ocean, most of which is likely to be oxidized in the ocean water column.

[f] Estimates for terrestrial arthropods include termites. It is estimated that other arthropods could contribute up to 100 Tg CH_4/year.

[g] Because the relative contributions of emissions from each source to the total budget are not independent of each other (i.e., if one source is at the lower end of its estimated range, another may be at the higher), the ranges cannot be summed.

[h] Lassey et al., 2007.

[i] Based on change from pre-industrial to present as estimated by Röckmann et al., 2003; assuming that pre-industrial emissions are primarily natural.

[j] Mean value for anthropogenic emissions from Wuebbles and Hayhoe, 2002; natural emissions from this work.

[k] Range in total anthropogenic and natural emissions from Denman et al., 2007, and references therein.

[l] Estimates of anthropogenic emissions from Denman et al., 2007; natural emissions from this work.

[m] Observed tropospheric values from Rahn and Wahlen, 2000, and references therein.

12.3 Future Needs

It continues to be difficult to estimate contributions from natural sources, and uncertainties can be large, as evidenced by the large ranges associated with the emissions estimates. Additional research focused on improving our understanding of the processes that result in CH_4 and N_2O emissions should improve current flux estimates and help refine future estimates under altered environmental conditions. High uncertainty in some sources is a result of a lack of basic data – flux measurements may be sparse from some geographic regions and/or seasons. For a number of sources such as wetlands, uncertainties are high in part because these are highly dynamic systems that respond to short-term climate and weather variability with changed emissions. This source of uncertainty will always be present. A number of sources currently rely on inventory-type data to extrapolate small-scale measurements. While this is reasonable for some sources (for example, the number of mud volcanoes is unlikely to change quickly or drastically), this means that they are largely static estimates. Even if modeled, these flux estimates will be limited by the spatial and temporal resolution of the data used for their extrapolation. Reliance on inventory or long-term average data also means that it is difficult to fully take advantage of the accumulating data base of atmospheric mixing ratios and isotopic signatures. These data are highly dynamic and this short-term variability is a crucial part of their utility in inverse modeling approaches. These techniques have proven that they can both help to constrain "bottom up" estimates and provide a way to integrate highly variable natural systems.

For wetlands, the major natural source contributing to CH_4 emissions, research in tropical areas remains sparse and incomplete. Increased work linking emissions to environmental controls, long-term studies to capture seasonality and inter-annual variability, and work on the importance of episodic emissions will help resolve difficulties in modeling these systems. In addition, more work should examine the relationships between CH_4 flux and net primary productivity (the rate at which biomass is produced, for example by photosynthesis), since these relationships appear to be habitat-specific. Because emissions to the atmosphere are a function of the competing processes of CH_4 production and consumption, both processes and their responses to environmental controls must be understood across the landscape. Episodic emissions, which may release a sizeable fraction of annual flux, remain difficult to measure and include in models. Failure to adequately incorporate these fluxes, however, can yield inaccurate and misleading results.

For upland soils and riparian zones, the major natural source contributing to N_2O emissions, more field measurements and improvements in global emissions models are needed. While field measurements of N_2O have increased steadily in the past several years, coverage of global vegetation zones remains incomplete. More measurement data are needed, especially for the dry tropical forest, savanna, tundra, and temperate ecosystems not affected by nitrogen deposition. These measurements should be carried out over extended periods, to help improve our understanding of the complex factors that impact emissions as well as to assess natural variability.

There are many additional areas where research would help improve flux estimates. These are discussed in more detail in the source-specific chapters, but we briefly list a number of them here, where uncertainties are notably high. They include:

- Data from tropical and southern latitude oceans, estuaries, and rivers, as well as estimates of upwelling sources.
- Improvements to permafrost models to account for lateral water movement, dynamic vegetation algorithms, and detailed soil physics.
- Data to quantify lake fluxes, particularly in the Arctic, boreal region, and tropics.
- Better quantification of CH_4 reserves stored as gas hydrates, as well as better estimation of the rate of CH_4 absorption into oceans and CH_4 oxidation in the water column.
- Rates of CH_4 from seeps and mud volcanoes oxidized in sediments, as well as better quantification of the source locations (e.g., number of mud volcanoes, frequency of eruption).
- Activity data for wildfires, including area and amount of biomass, burned area estimates associated with natural wildfires, and additional research on emissions related to different "fuels" (i.e., different types of vegetation).
- Confirmation or rejection of vegetation as a source of CH_4.
- Research that better quantifies the oxidation of CH_4 through termite mounds, confirmation of CH_4 from non-termite terrestrial arthropods, and activity data for arthropods and wild animals.

12.4 Summary

Natural sources make important contributions to the global atmospheric budgets of CH_4 and N_2O. Emissions from these sources will change as a result of increased human activities (e.g., decreasing CH_4 from wetlands through land use changes) and as a consequence of climate change (e.g., increasing frequency and severity of wildfires due to warmer and drier conditions). Although our understanding of the scope of possible changes in emissions has increased significantly in the past few years through model development and improvement, large unknowns remain. There is a potential for very large changes in natural CH4 emissions and the possibility of positive feedbacks between these radiatively important gases and climate means that research and model refinement must continue. As illustrated by recent work suggesting that recent decreases in natural CH_4 emissions from wetlands have temporarily masked increases in anthropogenic emissions (Bosquet et al., 2006), it is impossible to understand the system as a whole if its various components and their links are not understood.

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Appendix A: Glossary

albedo: The fraction of solar radiation reflected by a surface or object, often expressed as a percentage.

anoxic: without oxygen.

anthropogenic: Made by people or resulting from human activities (e.g., emissions that are produced as a result of human activities.

apparent oxygen utilization (AOU): the difference between a measured dissolved O_2 concentration and that expected when at atmospheric equilibrium saturation.

aphotic: having no light.

Arctic Oscillation: refers to opposing atmospheric pressure patterns in northern middle and high latitudes. The dominant pattern of sea-level pressure variation north of 20^{o}N. Pressure variations cause changes in wind patterns and ocean currents. The pattern of alternating high and low pressure thus creates alternating warm and cool temperatures throughout this large region.

arthropods: the largest phylum of animals which includes insects, arachnids, crustaceans, and others. Characterized by the possession of a segmented body with appendages on at least one segment. All arthropods are covered by a hard exoskeleton.

biogeochemical cycle: the biology, geology, and chemistry of the global or regional cycles of the "life elements" carbon, nitrogen, sulfur, and phosphorus with reservoirs including the atmosphere, oceans, sediments, and living organisms.

biome: a distinct ecological community of plants and animals living together in a particular climate.

budget: a balance sheet of all sources and sinks of a reservoir (e.g., all methane into and out of the atmosphere).

clathrate-hydrates: see **"**gas hydrates."

climate change: a change in the state of the climate that can be identified (e.g., by using statistical tests) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer.

controls: variables that affect production and consumption of CH_4 or N_2O.

denitrification: reduction of nitrate or nitrite to molecular nitrogen or nitrogen oxides by microbial activity or by chemical reactions involving nitrite.

ebullition: bubbling.

emissions: the release of a substance (usually a gas when referring to the subject of climate change) into the atmosphere.

ephemeral: short-lived (e.g., a wetland, pond, or spring exists for only a brief period, usually following precipitation or snowmelt).

euphotic: having light.

extratropical: occurring between 30° and 60° latitudes from the equator in both the hemispheres

flux: the amount of material transferred from one reservoir to another per unit time (e.g., methane emissions to the atmosphere, or methane consumption of soils).

gas hydrates: ice-like compounds formed between water and a gas molecule such as CH_4, under high pressure and at temperatures near the freezing point of water.

global warming: an average increase in the temperature of the atmosphere near the Earth's surface and in the troposphere, which can contribute to changes in global climate patterns.

global warming potential (GWP): the cumulative radiative forcing effects of a gas over a specified time horizon resulting from the emission of a unit mass of gas relative to a reference gas.

greenhouse effect: trapping and build-up of heat in the atmosphere near the Earth’s surface (the troposphere).

greenhouse gas (GHG): any gas that absorbs infrared radiation in the atmosphere.

gyre: a relatively stationary region of the open ocean with a circular current created by the Coriolis effect. Gyres are permanent large-scale water circulation features whose circulation tends to isolate them from the rest of the ocean.

ice core: a cylindrical section of ice removed from a glacier or an ice sheet in order to study climate patterns of the past.

isotope: Any two or more forms of an element having identical or very closely related chemical properties and the same atomic number but different atomic weights or mass numbers.

macroseepage: relatively large, visibly detectable, localized emissions from identified geologic features and events such as mud volcanoes and other seeps independent of mud volcanism .

methane (CH_4): a hydrocarbon that is a greenhouse gas with a global warming potential most recently estimated at 25 times that of carbon dioxide.

methanogens: microorganisms (Archaea) that produce methane as a metabolic byproduct in anoxic conditions. Methanogens are anaerobic; most are rapidly killed by the presence of oxygen.

methanotrophs: bacteria that can grow using methane as their only source of carbon and energy.

methylotrophs: bacteria that can grow using reduced one-carbon compounds, such as methanol or methane, as the carbon source for their growth. Some methylotrophs can degrade the methane (see methanotrophs).

microsite: small volume of soil where biological or chemical processes differ from those of the soil as a whole.

microseepage: diffuse fluxes of gaseous hydrocarbons over wide areas.

net primary productivity (NPP): the net production of organic compounds from atmospheric or aquatic carbon dioxide, principally by plants through the process of photosynthesis. It is the difference between the amount of material or energy produced (gross productivity) and respiration (the costs of producing it—cellular respiration and tissue maintenance).

nitrification: Biological oxidation of ammonium to nitrite and nitrate, or a biologically induced increase in the oxidation state of nitrogen.

nitrous oxide (N_2O): a powerful greenhouse gas with a global warming potential of 298 times that of carbon dioxide.

oigotrophic: nutrient-poor, usually having low productivity. Its opposite is "eutrophic," or nutrient-rich.

oxic: containing oxygen.

oxidize: To chemically transform a substance by combining it with oxygen.

peatlands: An environment where partially decayed vegetation matter accumulates to form organic-rich soils (peats), usually in wetlands.

permafrost: soil, sediment, or rock that is continuously frozen (temperature below 0°C) for at least two consecutive years.

pycnocline: a water layer with a large change in density caused by temperature or salinity. When caused by temperature, it is usually called a thermocline. Mixing is impeded across such a layer.

pyrolysis: chemical decomposition of organic materials by heating in the absence of oxygen or any other chemical agents

radiative forcing: a measure of how the energy balance of the Earth-atmosphere system is influenced when factors that affect climate are altered.

reactive N: forms of nitrogen that can be used by living organisms.

redox (short for reduction/oxidation): the relative oxidation status of a soil. Soils with a low redox status have little available oxygen, which limits the types of reactions that can take place.

reduced species: term used to describe the degree of reduction (number of electrons or number of hydrogen atoms) in atoms, molecules, or ions. For example, CH_4 is a reduced compound with relatively little available energy for microbial growth, while CO_2 is oxidized compound that can yield greater energy as it is broken down.

riparian areas: vegetated ecosystems along a waterbody through which energy, materials, and water pass.

shrublands: ecosystems dominated by woody or herbaceous shrubs

sink: a flux of material out of a reservoir.

Southern Oscillation Index (SOI): the normalized pressure difference in surface pressure between Tahiti, French Polynesia, and Darwin, Australia. Positive SOI values of indicate a La Niña event, while negative SOI values indicate an El Niño event.

source: a flux of material into a reservoir.

suboxic: oxygen deficient; may describe the transition zone between the two extremes. Technically, it is often defined as less than or equal to 10 μM (micromoles) O_2.

synoptic scale: scale used with respect to weather systems ranging in size from several hundred kilometers to several thousand kilometers, the scale of high and low pressure systems (frontal cyclones) of the lower troposphere.

thermogenesis: production of a substance (e.g., methane) by thermal breakdown of organic matter.

thermokarst: a pitted land surface that forms as permafrost melts.

thermokarst lake: a body of freshwater formed in a depression by water from thawing.

upland soils: well-aerated soils with lower moisture content than wetland soils.

upwelling: a pattern of coastal and open water oceanic circulation. It is created by persistent winds blowing across the ocean surface. As winds move surface waters, they are replaced by deeper waters that are richer in nutrients and which can support increased phytoplankton growth, which in turn supports higher populations of fish and other consumers.

volatile organic compounds (VOCs): Carbon-containing chemical compounds that can vaporize easily and can play an important role in atmospheric chemistry. Based on their molecular structure, these organic species can be grouped in different classes of compounds, including, aldehydes, alcohols, ketones, acids, etc.

wetlands: areas where water covers the soil, or is present either at or near the surface of the soil all year or for varying periods of time during the year.