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Minimizing Net Greenhouse Gas Sources from Mangrove and Wetland Soils

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Abstract. Mangrove and wetland soils are regarded as potentially large sinks of carbon, and hence a possible contributor to offsetting fossil fuel emissions. But they may also be globally significant sources of greenhouse gases (GHG), whose emissions must be balanced against carbon sequestration. Here we review measurements of GHGs from wetland and mangrove soils and the key factors controlling the processes producing and consuming them, as a guide to minimizing net sources. Carbon dioxide (CO_2) fluxes from mangrove and wetland soils derive from root respiration and microbial organic matter oxidation. Despite very high organic matter content of wetland soils, CO_2 fluxes are fairly low because lack of oxygen (O_2) forces organic matter decomposition into energetically inefficient anaerobic pathways. Carbon dioxide fluxes are highest when soils are aerated, during drainage, low tides, or dry seasons. Mangrove soils provide the largest CO_2 sinks when permanently flooded. Methane (CH_4) is produced only under anaerobic conditions, and consumed by aerobic soils, so emissions are highest when soil is flooded, the opposite to CO_2. However, CH_4 formation is suppressed by traces of sulfate (SO_4^{2-}), which is almost entirely provided by seawater in coastal sediments. Methane production is very low in mangrove soils, except for mangroves with high freshwater influence, unless decomposition is so intense that SO_4^{2-} is used up near the surface. Nitrous oxide (N_2O) production is widely regarded as due to anaerobic denitrification, but in fact this process is a sink for the gas because N_2O is almost as efficient a terminal electron acceptor as O_2. Nitrous oxide largely comes from micro-aerophilic nitrification. Nitrous oxide sources are maximal under low O_2 concentrations and fall in fully aerobic soils, while anaerobic soils are sinks for N_2O. Nitrous oxide fluxes are highest when soils are partially aerated due to drainage, low tide, dry seasons, or plant roots that pump O_2 into soils, while peat soils consume N_2O when fully submerged. Fertilisation with ammonium (NH_4^+) greatly increases N_2O formation, while nitrate (NO_3^-) fertilisation has a much smaller effect. To minimize greenhouse gas releases from mangrove soils, they should be submerged in salt or brackish water, not fertilised beyond the plant's immediate nitrogen uptake needs, and mangrove species that pump the least O_2 into root rhizosphere soil should be used. Because few data are available, more measurements of GHG fluxes are needed to quantify their release to the atmosphere under a wide range of field conditions, in order to identify the management conditions that maximize carbon sequestration and minimize GHG emissions.

1. Introduction

Large scale efforts to plant mangrove forests as an atmospheric carbon sink to mitigate global warming must not only maximize storage of carbon as both vegetation and soil carbon, but must minimize greenhouse gas (GHG) emissions from sediments. If GHG emissions are large, they may offset or even exceed the global warming reduction effects of carbon removal into mangrove biomass and peat. The carbon-rich sediments of wetlands and swamps have long been recognized as significant global sources of GHG, so it is natural to assume that mangroves are as well, because they accumulate large amounts of carbon in peat sediments. However, there are few direct GHG flux data from such habitats. In this paper we review measurements of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions from wetland soils and their microbiological source and sink mechanisms. We show that wetland CO_2 emissions are relatively low in general, and that mangrove CH_4 releases are generally small, unlike those from freshwater wetlands. Wetlands are a major global source of N_2O. The mechanisms of N_2O production and consumption have been largely misunderstood. Insight into microbiological N_2O sources and sinks, and the factors that control them, allow management steps to be proposed that can greatly reduce GHG emissions from reforested mangroves.

2. Factors controlling major GHG production and fluxes in wetlands

We base our recommendations on hundreds of direct measurements of CO_2, CH_4, and N_2O emissions fluxes from wetland soils that we have made from freshwater wetlands [1], inter-tidal salt marshes [Goreau, unpublished data], and mangroves [de Mello, unpublished data] under a wide range of water levels with and without fertilization, other published data from mangroves, marine waters, and marine sediments [2-11], and a critical review of the thermodynamic and microbial mechanisms of production and consumption of these gases as a function of the chemical and physical parameters that control them in freshwater wetlands, soils, oceans, and marine sediments.

2.1. Carbon dioxide

Carbon dioxide fluxes from soils are generally thought to result primarily from decomposition of organic carbon, and should therefore be directly proportional to the amount of soil carbon, its biochemical composition, and its rate of microbial oxidation. Microbial decomposition rates are directly controlled by oxygen (O_2) levels, temperature, and by organic matter content and composition, modulated by diffusion rates, which are affected by soil water content and permeability. These factors regulate potential biogeochemical pathways leading to GHG emissions, the thermodynamic efficiency of oxidation-reduction couples, and competition for electrons by acceptors. Little appears to be known about rates of mangrove root respiration, which is hard to measure separately from that of the surrounding sediments, which may be affected by root dissolved organic carbon exudates, and by root pumping of oxygen into sediments. However, CO_2 fluxes from forest soils in the Amazon were shown to decrease by 80% immediately following deforestation and addition of all the vegetation carbon to the soil [12], indicating that the most tropical rainforest soil CO_2 release is derived from root respiration rather than soil carbon decomposition [13]. Because similar measurements have not been made in mangroves, there are few data that allow separation of soil-atmosphere CO_2 fluxes into plant respiration and microbial decomposition. Root respiration may be an important component, possibly even dominant as in rain forests, but its magnitude remains unknown without direct measurements that isolate it from soil microbial sources. Much further work is needed to partition mangrove soil CO_2 fluxes into rapidly recycled root respiration and the much slower cycling decomposition sources. In addition there are soil CO_2 sinks from uptake by autotrophic organisms, including algae, cyanobacteria, photosynthetic bacteria, and methane, sulfur, and ammonium-oxidizing eubacteria and archaebacteria. Little is known about the magnitude or signficance of such CO_2 sinks, but they are likely to be fairly small and rapidly recycled within the sediment.

Despite the high amount of carbon in Everglades wetland peat soils and warm temperatures, CO_2 releases from wetland peats were found, surprisingly, to be much lower than those from drier soils at higher elevations in South Florida prairie and forest habitats [1]. Waterlogged carbon-rich soils quickly have their O_2 removed by aerobic microbial heterotrophs and re-oxidation of reduced iron, manganese, and sulfur compounds produced deeper in the sediments (Kristensen, this volume), and so become anoxic below a thin surface layer, often only a millimeter or so thick, below which anaerobic decomposition of organic matter takes place. Anaerobic oxidation is much less efficient thermodynamically than aerobic decomposition, due to the much larger free energy change that takes place when O_2 is the terminal electron acceptor compared to most alternate acceptors, so anaerobic decomposition is much slower. The result is that anaerobic habitats have lower CO_2 emissions than aerobic soils, even though they have much higher carbon content. In fact, the high carbon content of waterlogged soils is the result of the greatly reduced rate of organic carbon decomposition, allowing it to accumulate and form peat soils.

Mangrove and wetland soils are therefore expected to have relatively low CO_2 fluxes to the atmosphere compared to forests on aerobic soils [1] unless they are exposed to O_2 by canal drainage or groundwater pumping, are exposed to air at high tides, or are coarse grained (sand rather than peat) with high O_2 permeability. In addition, CO_2 release from mangrove peats should be lower than from freshwater wetland peats because of the higher amount of woody litter with high carbon and low nitrogen and phosphorus content (i.e., high C:N and C:P ratios), and because of the much higher content of lignin and tannins. Compared to freshwater marsh vegetation, mangrove carbon is much more resistant to oxidation and may inhibit many microbial decomposers.

2.2. Methane

Methane has a global warming potential about 20 times higher than CO_2 [14]. Methane production by eubacteria and achaebacteria is possible only under anoxic conditions. Because CH_4 formation, by either fermentation or by reduction of carbon dioxide by hydrogen, has a very small free energy change, it can only take place at extremely low redox potential, after all more energetically favorable terminal electron acceptors (such as O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} etc.) have been exhausted [15]. As long as traces of these remain, CH_4 generation is suppressed, being restricted to locally reduced microsites in freshly decomposing organic matter. In general, methanogenesis and sulfate reduction take place in spatially separated habitats, but in some cases where they appear to be concurrent they may be taking place in separate microhabitats in rapidly decomposing organic matter, such as fecal pellets of crabs and other marine organisms. A possible exception lies in tightly coupled symbiotic bacterial consortia, where thermodynamically unlikely reactions can take place if another symbiotic partner such as methane oxidizing bacteria rapidly removes the product of the reaction that could otherwise not occur (E. DeLong, Pers.

Comm.). The extent to which this takes place in mangroves sediments is unknown, and use of 16S libraries of the ribosomal RNA of entire microbial communities is needed to resolve it (the definitive way of identifying all of the microbes present, of which only about one percent can be successfully cultured and studied).

In freshwater peat wetlands energetically favored electron acceptors such as O_2, NO_3^-, Fe^{3+}, Mn^{4-}, and SO_4^{2-} are generally low in concentration and quickly exhausted, so CH_4 production is very high. Consequently, natural wetlands, artificial wetlands (e.g., rice paddies and forests drowned by dams), and anoxic sites in the guts of ruminant animals and termites are the major global sources of atmospheric CH_4 [14]. Measurements of CH_4 fluxes along elevation gradients in Florida show that the waterlogged and flooded swamps are the largest sources of CH_4 to the atmosphere [1], but that CH_4 is consumed from the atmosphere when surface soils are drained, whether by human activity or seasonal water table fluctuations [1]. Aerobic methane oxidizing bacteria in surface soils feed off CH_4 derived from lower soil horizons below and from the atmosphere above. Freshwater wetlands are therefore significant atmospheric CH_4 sources only when anoxic up to near the surface during high water table conditions, and are much smaller sources or even sinks during dry seasons, or when drainage lowers the water table.

While mangroves might also be thought to be significant CH_4 sources like freshwater wetlands, this is not generally found to be the case. Reported measurements of CH_4 fluxes from mangroves range from negative to moderately high values, with most being low and many being undetectably small [5-11; Alongi, this volume]. Since some of these were based on concentration measurements in water that could have been flushed or drained from inland or other portions of mangroves, rather than *in-situ* flux measurements, it is hard to be certain where the CH_4 was produced. However the warm conditions and high decomposition rates in mangroves make it likely that much of this may be produced deep in the sediment column where sulfate has been depleted. Measurements of CH_4 fluxes from mangroves of Sepetiba Bay, Brazil, found no flux of CH_4 to the atmosphere [de Mello, unpublished data], and the same was found in salt marsh soils [Goreau, unpublished data]. Seawater contains very large amounts of sulfate (SO_4^{2-}), and even small traces of SO_4^{2-} are able to outcompete and inhibit the CH_4 producing pathways for electrons released by organic matter decomposition, even in slightly brackish waters [Kristensen, this volume]. No CH_4 production can take place until SO_4^{2-} is almost completely used up, which takes place only deep in the sediment column (or in diffusion-limited microsites) unless decomposition is so intense that all SO_4^{2-} is consumed by sulfate-reducing bacteria near the sediment surface. Even though aerobic CH_4 oxidizers are unable to live in anoxic soils, anaerobic CH_4 oxidation can take place deep in sediments by coupled reduction of SO_4^{2-} as an alternate electron acceptor [15, 16]. Consequently, almost all CH_4 produced deep in the sediment is consumed as it diffuses upwards, so CH_4 fluxes to the atmosphere may be negligible even where there is high production in sediments, unless sulfate depletion takes place very close to the surface or the CH_4 can escape through crab burrows or vascular passages in plant roots and stems. It is only in places with very strong vertical SO_4^{2-} reduction gradients that significant amounts of CH_4 are able to escape from soils or sediments [9]. Because decomposition rates generally increase at high temperatures, CH_4 release to the atmosphere is most likely under the warmest conditions. Latitudinal gradients and seasonal changes are likely to significantly affect CH_4 emissions.

As a result of high SO_4^{2-} content of surface mangrove soils (except for mangroves growing in soils with strong freshwater and river influence), habitats dominated by saltwater probably have very little CH_4 production. Along the saltwater to freshwater gradient methane production will largely take place deep in high salinity soils and sediments along the coast or in hypersaline evaporative inland habitats, and will likely be consumed before it can diffuse to the atmosphere. The lower the salinity the sooner the sulfate will be exhausted and the closer to the surface methane production can occur. There is a strong inverse relationship of methane release along increasing salinity gradients [Kristensen, this volume)], so only mangroves planted in freshwater influenced habitats are likely to produce signficant CH_4. Examples are inland sides of mangroves receiving terrestrial groundwater flow, and gallery forest mangroves growing along rivers and estuaries (common in South and Central America). Such sites should therefore be avoided for mangrove reforestation, which should focus on the marine end of the freshwater-marine continuum.

Mangrove roots may greatly increase CH_4 fluxes by transport through vascular channels [9], but this may be counter-balanced to some degree by root releases of oxygen into the rhizosphere [7], reducing methane production and increasing populations of methane oxidizing bacteria. A previously unknown chemical mechanism for CH_4 production from plant leaves and stems has recently been discovered [17], and may be a globally significant atmospheric source of CH_4. No information is yet available of its importance in mangrove ecosystems, and measurements need to be made to determine if it is significant. If so, it will need to be included in the vegetation mass balance of GHGs.

2.3. Nitrous oxide

Nitrous oxide has a global warming potential about 300 times higher than CO_2 [14], and its pathways of production and consumption are much more complicated. Misunderstanding of these pathways has held back progress for many years. Almost all textbooks describe the major source of N_2O as denitrification, an obligately anaerobic heterotrophic process in which bacteria use nitrate (NO_3^-) as a terminal electron acceptor after O_2 is exhausted. The NO_3^- is reduced in sequential stages to nitrite (NO_2^-), nitric oxide (NO), N_2O, and finally molecular nitrogen (N_2). For a long time denitrification was thought to be the only source of atmospheric N_2O, and since it could only take place in anoxic waters and sediments, wetlands were thought to be a major global source of N_2O. Also, it was thought that the only sink for N_2O was ultraviolet photodissociation in the stratosphere above the ozone layer, and that N_2O found in waters, soils, and the atmosphere was in the process of being transported from anaerobic sediment towards the upper atmosphere.

This view was completely overturned with the discovery in the 1970s that N_2O (and NO) is in fact a product of nitrification [18-21], an obligately aerobic autotrophic process in which ammonium (NH_4^+) is oxidized first to NO_2^- by one group of bacteria, and then NO_2^- oxidized to NO_3^- by another group. Nitrous oxide was shown to be a by-product of NH_4^+ oxidation to NO_2^-, and the bacteria responsible for this process were found to require O_2 but to grow fastest at very low concentrations of O_2 (microaerophilic) [20, 21]. The first archaebacterium capable of ammonium oxidation has just been described [22], but it is not yet known if it also produces N_2O like its bacterial analogues. Nitrification, an aerobic and autotrophic process, is effected by different organisms and in completely different habitats than denitrification, which is anaerobic and heterotrophic. It was found that denitrification in anoxic environments consumed N_2O completely, rather than making it as previously thought, and in fact would consume all the N_2O added even at levels hundreds of times higher than ambient [21]. Everglades soils were found to produce large amounts of N_2O when NH_4^+ fertilizer was added, but only when surface soils were aerated because the water table was low [1]. Smaller amounts of N_2O were released from NO_3^- only when it was added to the soil surface during flooding [1]. Similar patterns were later found in mangrove soils [2-4] and waters [Upstill-Goddard et al. this volume; Barnes et al. this volume].

The reason why this happens is clear thermodynamically. Nitrous oxide is one of the most energetically efficient electron acceptors, releasing almost as much free energy as O_2 [15, 21]. As a result dentrifying bacteria consume all the N_2O they can get, making anoxic environments sinks of N_2O rather than the sources that were previously thought. Wetlands will produce large amounts of N_2O wherever NH_4^+ is exposed to O_2 in the upper layers of the soil, and consumes it in anaerobic layers below. The rate of production is greatest where soils are drained, during the dry season, during low tide, and when soils are fertilized with NH_4^+ [1-4, 8]. After wetland soil is flooded, it consumes N_2O from the atmosphere at very low rates [1]. Several anaerobic nitrification pathways are now known, in which NH_4^+ is oxidized using iron, manganese, NO_2^-, or NO_3^- instead of O_2, based on chemical, microbiological, and genome sequencing studies [23-27]. Such pathways will not be net producers of N_2O to the atmosphere since any N_2O produced will be reduced to N_2 by denitrifying bacteria because it is the energetically favored electron acceptor. This rate may be sensitive to sediment pH. The salinity of the water will not make a difference as it does for CH_4, because all of these pathways take place at a redox potential higher than that of SO_4^{2-} reduction, which therefore cannot compete with them for electrons.

Unlike CO_2 fluxes that are highest under aerobic conditions, and CH_4 that is highest under anaerobic conditions, N_2O fluxes are highest under intermediate and fluctuating oxygenation, and are extremely spatially and temporally variable [1]. Nitrous oxide production from wetlands (including mangroves) can therefore range from negative (consumption from the atmosphere) to the highest emission values recorded in any ecosystem, depending on the physical and chemical conditions [1]. This makes N_2O the hardest of the greenhouse gases to control, and the most crucial and demanding aspect of minimizing greenhouse warming potential from planted mangroves. Poor management, such as overfertilizing mangroves on drained sandy soils, will result in large fluxes of N_2O to the atmosphere. Because these fluxes can vary rapidly in space and time, many more measurements of N_2O flux under the full range of natural and management conditions are needed to prepare quantitative guides to the best conditions for maximizing carbon sinks and minimizing N_2O fluxes from mangrove plantations. A funded program is critically needed for such research to optimize mangrove management with the least impact on the atmosphere and climate.

Some qualitative guides follow directly from understanding of the sources and sinks of N_2O. The most important thing is to minimize nitrification. This is best done by planting mangroves in soils that are carbon rich, fine grained, and have minimal exposure to O_2 due to large tidal and seasonal variations in water level, or drainage. If nitrogen fertilizer is added to increase mangrove growth rates and CO_2 uptake from the atmosphere, it would be best if this is added in the form of NO_3^- rather than NH_4^+. If NH_4^+ is added it should be done in a way that it is released directly to the plant at high tide, does not exceed plant uptake rates, and is not broadcast over the soil away from the plants where nitrifying bacteria can compete for it. This seems to be the case for the method used in Eritrea [G. Sato, personal communication].. A further consideration is that many aquatic plants are capable of pumping O_2 into roots and into adjacent soil. Mangrove species that are capable of doing this (probably including many species with vertical aerial roots and pneumatophores rising from sediment) could create zones of intense nitrification and N_2O production in soil around their roots. Nitrous oxide fluxes need to be measured around all species of mangroves to see which species are most effective at oxygen translocation to sediments from the roots, and species with the highest rate of sediment oxygen pumping should be avoided in reforestation projects.

It is important to measure the three major greenhouse gas (CO_2, CH_4, and N_2O) fluxes simultaneously to understand the complete effect of management practices on global warming potential. With the exception of the Everglades study [1], which measured the fluxes of all three GHGs simultaneously, most studies of greenhouse gas emissions from wetlands have measured only a single gas. Much more insight into soil management is gained when all other relevant physical and chemical parameters are measured simultaneously with fluxes of all GHGs. Fertilization experiments followed by measurements of major GHG flux should be performed. Concurrent measurements of reduced sulfur gas emissions, such as hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (OCS), dimethyl sulfide (CH_3SCH_3), and methyl mercaptan (CH_3SH) would also provide great insight because of the strong interactions of the sulfur cycle with CH_4, and because these gases, while not major greenhouse gases, are climatically active gases (CAG) that have profound effects on local and regional climate by providing precursors for smog and cloud condensation nuclei. CAG also include carbon monoxide (CO) and nitric oxide (NO), both of which are produced by combustion but may have biological sources and sinks, in the case of NO also being produced by nitrifying bacteria along with N_2O [28].

3. Management recommendations to minimize soil GHG emissions from planted mangroves

Because the three major greenhouse gases (CO_2, CH_4, and N_2O) are produced and consumed under such different conditions, it may prove impossible to minimize the emissions of all three simultaneously in freshwater wetlands. In mangroves, however, the suppression of CH_4 production by SO_4^{2-} means that total fluxes can be minimized under anaerobic conditions. In order to minimize GHG emissions from mangrove plantations the following guidelines should be followed:

1. Soils should be as waterlogged and saline as possible.

2. Locations with large fluctuations in water table should be avoided, such as locations with large tidal ranges, or seasonal water table variations.

3. Coarse grained sediments low in organic matter should be avoided as high potential N_2O sources.

4. Mangroves should not be planted in places where the soil has been drained by canals or pumps.

5. Plants that pump large amounts of O_2 into root rhizospheres should not be used.

6. Nitrogen fertilization is best done with NO_3^- rather than NH_4^+.

7. Any NH_4^+ fertilization should be applied directly to the plant, not broadcast over the soil, and should not exceed the plant's nitrogen uptake capacity.

8. Ammonium fertilization should be done only when soils are waterlogged, not at low tide. While mangrove fertilization is not common, mangrove growth may benefit from fertilization if soils are nitrogen limited. The fertilization reported by Sato (personal communication) is done in a way that maximizes efficiency of plant uptake and minimizes soil emissions.

9. Because there appear to be very few simultaneous soil emission flux measurements of all GHG gases from mangroves under the full range of management relevant conditions, many further measurements are needed to refine these recommendations.

10. Funding is needed for a targeted program in order to quantitatively refine these qualitative management recommendations in order to minimize the net climatic impact of all three gases simultaneously.

4. Conclusions

Because of their fast growth rate and the rich carbon soils they produce, planted mangroves are potential carbon sinks that may offset fossil fuel production. However, their net GHG balance is critically dependent on the amount of CO_2, CH_4, and N_2O emissions from the soil. Only growing forests are net sinks of CO_2, because forests at steady state have zero net primary productivity since photosynthesis is balanced by respiration and decomposition. The CH_4 and N_2O emission rates are critical, since these gases have one to two orders of magnitude higher greenhouse gas warming potential per molecule than CO_2. Because of the different conditions under which each gas is produced, it is impossible to minimize the emissions of all three gases simultaneously in freshwater wetlands. However saltwater wetlands, like mangroves, can minimize the emissions of all three GHGs simultaneously if they are waterlogged, saline, and if nitrogen fertilization is carefully controlled. The response of GHG and CAG fluxes to changes in environmental and management conditions such as changes in water tables and fertilizer levels can be large and rapid [1],