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**METHANE FLUXES FROM A TROPICAL PEATLAND IN BRUNEI DARUSSALAM**A. Hoyt<sup>1\*</sup>, S. Pangala<sup>2</sup>, L. Gandois<sup>3</sup>, A. Cobb<sup>4</sup>, F. M. Kai<sup>4</sup>, X. Xu<sup>5</sup>, V. Gauci<sup>2</sup>, Y. Mahmud<sup>6</sup>, A. S. Kamariah<sup>7</sup>, J. A. Eri<sup>8</sup> and C. F. Harvey<sup>1</sup><sup>1</sup>*Massachusetts Institute of Technology, Parsons Laboratory, USA*<sup>2</sup>*Department of Environment, Earth & Ecosystems, The Open University, United Kingdom*<sup>3</sup>*Université de Toulouse, UPS, INP, EcoLab (Laboratoire Ecologie fonctionnelle et Environnement), France*<sup>4</sup>*Singapore-MIT Alliance for Research and Technology, Singapore*<sup>5</sup>*Department of Earth System Science, University of California Irvine, USA*<sup>6</sup>*Brunei Heart of Borneo Centre, Brunei Darussalam*<sup>7</sup>*Universiti Brunei Darussalam, Brunei Darussalam*<sup>8</sup>*Brunei Forestry Department, Brunei Darussalam*

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**SUMMARY**

Emissions of methane (CH<sub>4</sub>) from tropical wetlands are highly uncertain. Although tropical peatlands are warm, wet, anoxic environments, limited CH<sub>4</sub> emissions have been observed. We examine CH<sub>4</sub> production and transport in a pristine tropical peatland in Borneo to determine the rate and carbon source of CH<sub>4</sub> production. First, we use the <sup>14</sup>C composition of dissolved CH<sub>4</sub>, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) within the peat porewater to identify the source of CH<sub>4</sub> production. In contrast to the peat, which ages with depth to nearly 3000 cal BP, DOC is of contemporary origin throughout the peat column, to depths of 4.5m. The <sup>14</sup>C content of CH<sub>4</sub> and DIC are nearly identical, and are intermediate between the DOC and peat <sup>14</sup>C content. Thus, despite the presence of modern C throughout the peat profile, peat decomposition is an important source of CH<sub>4</sub> production. Next, we use the δ<sup>13</sup>C of CH<sub>4</sub> and DIC to identify the mechanism of CH<sub>4</sub> production. Within the peat profile, CH<sub>4</sub> and DIC concentrations increase with depth and DIC becomes increasingly enriched in <sup>13</sup>C. The δ<sup>13</sup>C of CH<sub>4</sub> is relatively uniform with depth, resulting in a δ<sup>13</sup>C fractionation between DIC and CH<sub>4</sub> of 55-70‰ (α<sub>C</sub>CO<sub>2</sub>-CH<sub>4</sub> = 1.06-1.07). This fractionation suggests CO<sub>2</sub> reduction is the dominant pathway for CH<sub>4</sub> production at the site. These trends are similar to those observed in northern peat bogs. Finally, we use information on site hydrology, CH<sub>4</sub> and DIC concentrations, isotopic compositions and fluxes to build a model of CH<sub>4</sub> production and transport. This model allows us to partition CH<sub>4</sub> losses from the peat due to diffusion, tree-mediated transport, and lateral transport. We find that lateral transport of dissolved CH<sub>4</sub> may be a more important pathway than previously considered.

**INTRODUCTION**

Southeast Asia is home to the world's largest proportion of tropical peatlands (Page *et al.* 2011). In these ecosystems, anaerobic conditions allow carbon to accumulate over thousands of years. Across Southeast Asia, these forested peatlands are rapidly being drained and deforested, releasing stored carbon to the atmosphere (Hooijer *et al.* 2012; Miettinen *et al.* 2012). Tropical peatlands play an important role in the global carbon cycle, and can be sources of both carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) to the atmosphere (Couwenberg *et al.* 2010; Hooijer *et al.* 2010).

Tropical peatlands would seem to offer ideal conditions for methanogenesis; they are warm, wet, organic-rich environments. However, tropical peatlands are reported to have much lower CH<sub>4</sub> fluxes than temperate and boreal peatlands. These fluxes range from negligible at low water levels to up to 3 mg CH<sub>4</sub>/m<sup>2</sup>/h at high water levels (Couwenberg *et al.* 2010). One possible reason for the low CH<sub>4</sub> fluxes is that environmental conditions, such as the organic substrate (e.g. high lignin content) in tropical peatlands may be unfavorable to methanogens (Calvert *et al.* 1991; Gandois *et al.* 2013, 2014). Morphological adaptations by trees that transport oxygen into the root zone may also suppress methane production (Adji *et al.* 2014). Alternatively, aerobic oxidation near the peat surface may consume most of the produced CH<sub>4</sub> before it escapes the peat, resulting in lower apparent CH<sub>4</sub> production rates.

Existing data on CH<sub>4</sub> emissions from tropical peatlands comes from studies based on chamber measurements, which predominantly capture diffusive fluxes (Adji *et al.* 2014; Arai *et al.* 2014; Furukawa *et al.* 2005; Hadi *et al.* 2001, 2005; Inubushi *et al.* 1998, 2005; Jauhainen *et al.* 2005; Melling *et al.* 2005). Focus on these diffusive fluxes neglects the importance of other possible CH<sub>4</sub> pathways. For example, in addition to aerobic oxidation near the peat surface, CH<sub>4</sub> could be oxidized anaerobically (Gupta *et al.* 2013; Smemo & Yavitt 2011) at the peat-clay interface where sulfate concentrations are higher. Alternatively, CH<sub>4</sub> could leave the peat through ebullition, tree transport (Pangala *et al.* 2013) or lateral transport (Figure 1). Despite the importance of hydrology in peatland carbon cycling and the documented importance of advection in peatlands (Chanton *et al.* 2008; Corbett *et al.* 2013), advection of dissolved gas is not considered a primary CH<sub>4</sub> transport pathway (Chanton 2005). As a result, advective transport of dissolved CH<sub>4</sub> has never been quantified from a tropical peatland, but could play an important role in CH<sub>4</sub> cycling.

Here we use measurements of CO<sub>2</sub> and CH<sub>4</sub> in a pristine tropical peatland to assess the relative roles of different transport pathways. We present data on dissolved gas concentrations and isotopic compositions. We use this data to inform a reactive transport model that considers both vertical and lateral transport in a peatland. We then quantify the relative fluxes of diffusive and advective pathways under a range of scenarios and find lateral transport is the dominant transport pathway at this site. Finally, we use the isotopic composition of the dissolved gases to provide insight into the source and production pathway for methanogenesis.

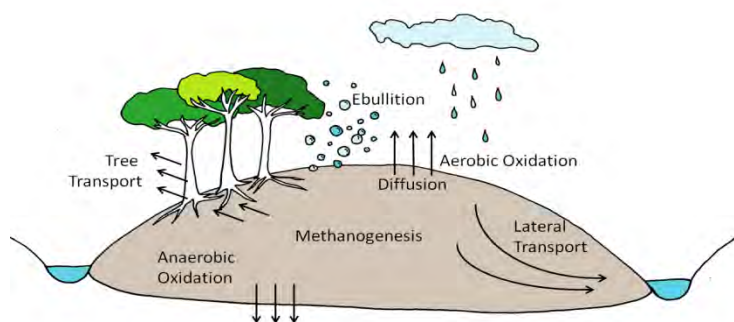


Figure 1: Chamber measurements capture diffusive methane (CH<sub>4</sub>) fluxes from the peat surface. There are many alternative CH<sub>4</sub> transport pathways.

## METHODS

**Study site** - Samples were collected from the Mendaram peat dome in the Ulu Mendaram Conservation Area, Belait District, Brunei Darussalam, on the island of Borneo. This is a pristine peat swamp forest characterized by *Shorea albida* (Anderson 1983). Porewater samples were collected from the pristine sites I and III as described in Gandois *et al.* (2014).

**Porewater sampling and analysis** - Porewater was sampled from throughout the peat profile to capture trends with depth from the surface to 5.5m deep in the peat. Sampling was conducted using a portable Inox pushpoint piezometer (MHE products, USA) and PVC sampling wells. Samples were collected to determine the concentrations of the major elements, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and dissolved CH<sub>4</sub> concentrations, and for isotopic analysis. pH and electrical conductivity were also measured.

**$\delta^{13}\text{C}$  and  $^{14}\text{C}$  isotope analysis** - Porewater gases for  $^{14}\text{C}$  analysis of CO<sub>2</sub> and CH<sub>4</sub> were collected in April and August 2014. Porewater was pumped using a peristaltic pump and flushed through a sealed 1L glass bottle for 1-4 hrs to accumulate sufficient gas volume, with timing depending on concentration. Dissolved gases were trapped in the bottle as they degassed. CO<sub>2</sub> and CH<sub>4</sub> were separated during analysis. Collected gases were transferred via syringes to pre-evacuated serum vials sealed with butyl rubber septa.  $^{14}\text{C}$  analysis was conducted at University of California Irvine. Samples for analysis of  $^{14}\text{C}$  content of DIC were analyzed at NOSAMS and collected following the standard NOSAMS protocol.

## RESULTS

**Model Description & Performance** - Existing models of CH<sub>4</sub> production and transport within the catotelm represent various subsets of the following processes: methanogenesis, methane oxidation, diffusive transport, ebullition and

vertical advection (Steinmann *et al.*, 2008; Shoemaker & Schrag, 2010; Corbett *et al.*, 2013). However, none of these models includes lateral advection. We present a new model which accounts for both downward and lateral advection of porewater and dissolved gases. It uses a steady-state 1D reactive transport model with a non-uniform vertical velocity to capture the both vertical and lateral advection as well as diffusive transport. It generates not only concentration profiles, but also models the profiles of  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  of both  $\text{CO}_2$  and  $\text{CH}_4$ . By modelling  $^{12}\text{C}$ ,  $^{13}\text{C}$  and  $^{14}\text{C}$  individually, we capture the fractionation caused not only by methanogenesis, but also as a result of advective and diffusive transport. The steady-state model successfully replicated the observed concentration profiles and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and  $\text{CH}_4$  measured in the peat profile within the variability of the measurements. These fits were achieved using parameters based on literature values and data from the site. The only free parameter was the  $\text{CH}_4$  production rate, which was adjusted to  $0.045 \text{ mol/m}^3/\text{yr}$  in order to match the observed  $\text{CH}_4$  concentrations.

**Methane,  $\text{CO}_2$  and DOC concentrations** - Despite significant spatial heterogeneity,  $\text{CH}_4$  concentrations in all samples increased with depth, from  $<0.1 \text{ mM}$  near the surface to maximum concentrations of  $1.5 \text{ mM}$  just above the mangrove peat boundary. A decrease in concentrations was observed in the deepest samples from the mangrove peat, which has a substantial mineral fraction and higher sulfate concentration. There was significant spatial heterogeneity. Short-term temporal heterogeneity was not as dramatic; repeat sampling in the same location after a few days later showed only small changes in the concentration.

**$\delta^{13}\text{C}$  of  $\text{CH}_4$  and DIC** - The  $\text{CH}_4$  and DIC both became increasingly enriched in  $^{13}\text{C}$  with depth. Shallow DIC at 10-20cm had a  $\delta^{13}\text{C}$  signature of  $-26\text{‰}$  to  $-27\text{‰}$ , similar to that of the vegetation, dissolved organic matter and peat ( $-28\text{‰}$  to  $-31\text{‰}$ ) (Dommain *et al.* 2015; Gandois *et al.* 2014). Deeper samples were increasingly enriched, to a maximum of  $+2.0\text{‰}$  at 5.5m. The  $\delta^{13}\text{C}$  of  $\text{CH}_4$  was much more depleted, but followed a similar trend, with values ranging from  $-90\text{‰}$  to  $-70\text{‰}$ , with the most depleted values near the surface. The  $\delta^{13}\text{C}$  fractionation between DIC and  $\text{CH}_4$  was relatively uniform with depth, ranging from  $55\text{‰}$ - $70\text{‰}$  ( $\alpha_{\text{C}\text{CO}_2\text{-CH}_4} = 1.06\text{-}1.07$ ). This apparent  $\alpha_{\text{C}}$  is within the range typical of the  $\text{CO}_2$  reduction pathway (Chanton *et al.* 2005; Whiticar 1999).

**Radiocarbon dates** - We used the  $^{14}\text{C}$  content of peat, DOC, DIC, and dissolved  $\text{CH}_4$  to identify the carbon source for methanogenesis. Consistent with the gradual accumulation of organic matter, the peat ages with depth to nearly 3000 cal BP (Dommain *et al.* 2015). In contrast, DOC is of contemporary origin throughout the peat column, to depths of 4.5m, indicating flushing of the peat profile with recharge originating as rainwater on the peat surface (Gandois *et al.* 2014). The  $^{14}\text{C}$  content of  $\text{CH}_4$  and DIC are nearly identical, and are intermediate between the DOC and the peat  $^{14}\text{C}$  content.  $\text{CH}_4$  and  $\text{CO}_2$  are of contemporary origin near the surface and increase in age with depth to over 1500 years at 4.5m. Throughout the profile, the ages of  $\text{CH}_4$  and  $\text{CO}_2$  from the same sample were within 15% of each other, with  $\text{CH}_4$  at most depths slightly older than the  $\text{CO}_2$ . The ages of the  $\text{CO}_2$  were also similar to DIC ages sampled at the same location one year earlier. Samples taken at different times all followed the same depth trends.

## DISCUSSION

### **Importance of lateral transport**

Aquatic fluxes are a new and important consideration for the tropical peatland carbon budgets, which has not been as extensively researched as that of northern peatlands. Recent work has demonstrated the importance of lateral fluxes of DOC in tropical peatlands (Gandois *et al.* 2013; Moore *et al.* 2011; Moore *et al.* 2013). However, dissolved gas fluxes have not been quantified in tropical peatlands. Our data suggests the additional importance of including dissolved gas fluxes in the carbon budget.

Our results suggest that lateral flux of dissolved  $\text{CH}_4$  plays an important role in tropical peatlands. This is consistent with the hydrology of these peat domes. Coastal peatlands in Southeast Asia experience large amounts of precipitation, much of which runs off the peat surface or flows through the upper few centimeters of the peat. However, some also flows into the deep peat itself, as documented by the presence of DOC of contemporary origin present in the deep peat (Corbett *et al.* 2013; Gandois *et al.* 2014). This downward flow is eventually obstructed by the underlying marine clay, which is relatively impermeable to flow. In order to maintain downward flow from the peat surface in the presence of an impermeable boundary, lateral flow must occur. This flowing water carries dissolved gases with it, which are then released to adjacent streams.

The lateral flow of water and dissolved CH<sub>4</sub> in the peat is controlled by the recharge rate into the peat. The relative importance of diffusive and lateral CH<sub>4</sub> fluxes therefore depends on the rate of water recharging the shallow peat. Figure 2 captures this dependence over a range of recharge rates, assuming a constant rate of CH<sub>4</sub> production. In the absence of recharge, CH<sub>4</sub> concentrations build up within the peat profile, leading to higher diffusion rates. Alternatively, if the peatland experiences rapid flushing, dissolved CH<sub>4</sub> will be transported laterally, immediately following production, leading to negligible diffusive fluxes.

In the Mendaram peat dome, the lateral flux of CH<sub>4</sub> dominates. At our calculated recharge rate of 0.2m/yr, we expect ~20 times more CH<sub>4</sub> to be transported laterally out of the peat column than out of the surface through diffusion (Figure 2). This suggests that current estimates significantly underestimate the amount of CH<sub>4</sub> produced by tropical peatlands. However, the fate of this CH<sub>4</sub> is still unknown. This dissolved CH<sub>4</sub> will be transported to the margins of peatlands, most commonly rivers or drainage canals. There we expect it to degas to the atmosphere or potentially be oxidized before it is released. Further measurements are required to determine the importance of this pathway as a source of methane to the atmosphere.

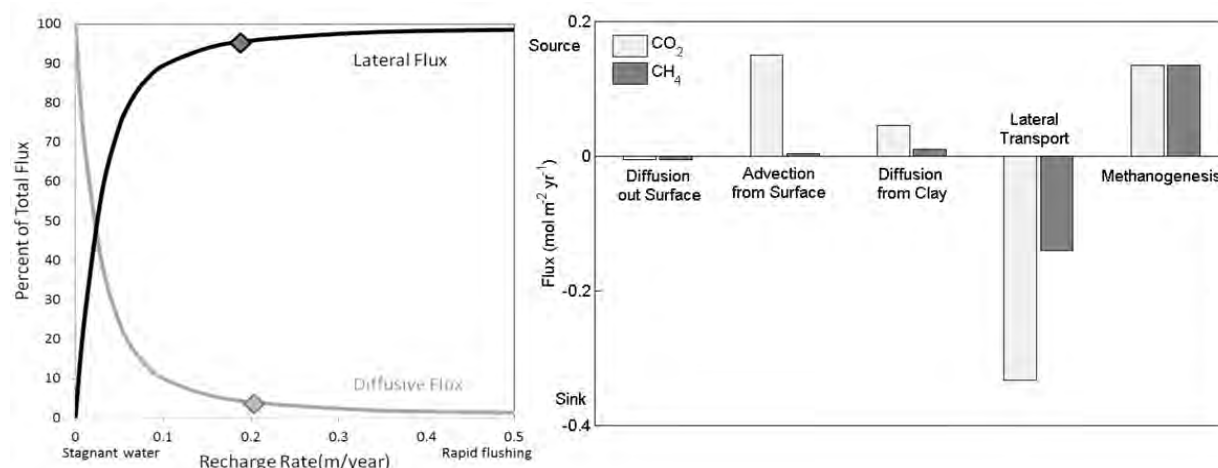


Figure 2: (a) Dependence of lateral and diffusive flux on recharge rate. Diamonds show recharge value of 0.2m/yr appropriate to our site. (b) Modeled production and fluxes of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) show the important role of vertical advection and lateral transport.

## CONCLUSION

We found that only a small fraction of the CH<sub>4</sub> produced in the deep peat escapes by diffusion, with other pathways playing a more important role. We collected field data and used it to improve our understanding of CH<sub>4</sub> production and transport within a tropical peat dome. We used the carbon isotopic composition of CH<sub>4</sub> and CO<sub>2</sub> to determine the source and pathway of CH<sub>4</sub> production. We coupled these findings with a model based on the site hydrology to evaluate the production and transport of CH<sub>4</sub> within the peat. Our results show that advection plays an important role in tropical peatlands, and that only a small proportion of the CH<sub>4</sub> produced in the deep peat diffuses out the peat surface. At this site, flow is much greater than production, so an order of magnitude more CH<sub>4</sub> is transported through the system by lateral transport than by diffusion. As a result, current estimates of CH<sub>4</sub> production in tropical peatlands are likely to be significantly underestimated. However, shallow porewater CH<sub>4</sub> data suggests that oxidation plays an important role in the root zone. Much of the CH<sub>4</sub> transported laterally is likely oxidized before it reaches the atmosphere. More detailed seasonal data on oxidation is required to fully evaluate the CH<sub>4</sub> fluxes to the atmosphere from tropical peatlands. Finally, although near-surface processes such as tree transport are not assessed here, they are anticipated to further increase total CH<sub>4</sub> fluxes from the ecosystem. A focus on chamber measurements means that current studies may account for <10% of the total CH<sub>4</sub> produced in the peat. This highlights the important role of hydrology in governing the carbon cycle in tropical peatlands.

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