[RADIOCARBON, VOL. 35, NO. 2, 1993, P. 271–276]

CARBON ISOTOPIC COMPOSITION OF DEEP CARBON GASES IN AN OMBROGENOUS PEATLAND, NORTHWESTERN ONTARIO, CANADA

RAMON ARAVENA[1], B. G. WARNER[2], D. J. CHARMAN[3], L. R. BELYEA[4]
S. P. MATHUR[5] and HENRI DINEL[6]

ABSTRACT. Radiocarbon dating and carbon isotope analyses of deep peat and gases in a small ombrogenous peatland in northwestern Ontario reveals the presence of old gases at depth that are 1000–2000 yr younger than the enclosing peat. We suggest that the most likely explanation to account for this age discrepancy is the downward movement by advection of younger dissolved organic carbon for use by fermentation and methanogens bacteria. This study identifies a potentially large supply of old carbon gases in peatlands that should be considered in global carbon models of the terrestrial biosphere.

INTRODUCTION

Northern peatlands play an important role in the cycling of atmospheric trace gases. Recent estimates suggest that about 65% of all methane (CH_4) emissions from natural peatlands originate in northern regions (Harriss *et al.* 1985; Matthews & Fung 1987; Crill *et al.* 1988; Gorham 1991). These estimates are based on measurements of surface fluxes, but little is known about the internal carbon dynamics of peatlands. Recent studies using theoretical models have shown that decomposition of organic matter is a continuous long-term process in these systems (Clymo 1984, 1991; Warner, Clymo & Tolonen 1993). High concentrations of CH_4 and CO_2 at depth in peatlands (Dinel *et al.* 1988; Brown, Mathur & Kushner 1989; Claricoates 1990; Mathur, Dinel & Levesque 1991; Buttler *et al.* 1991; Romanowics, Siegel & Glaser 1991) support these findings. The fate of these gases is virtually unknown, and specifically, their export by groundwater has not been considered. Thus, accurate estimates of future contributions to atmospheric CO_2 and CH_4 pools by peatlands will depend on our understanding of the natural carbon dynamics of these systems. Of particular importance are the pathways for production and efflux of the gaseous components, and coupling of these pathways with those in the surrounding environment.

In this paper, we present preliminary findings on the use of carbon isotopes to investigate carbon sources for gases and carbon transport in peatlands. This work is part of ongoing research employing an integrated approach of examining the hydrological, geochemical and ecological characteristics of northern peatlands to understand carbon-cycling processes.

STUDY SITE

The study site is a small ombrogeneous peatland about 180 ha[2], situated 6 km north of the town of Rainy River on the Minnesota-Ontario border in northwestern Ontario, Canada (48°47′ N; 94°33′ W; Fig. 1). The peatland has developed in a small, shallow basin lacking any surface outlets. The basin became available for peatland development after deglaciation and withdrawal of proglacial Lake Agassiz by *ca.* 9.5 ka BP, but it remained dry until *ca.* 4.6 ka BP (Belyea 1991; B. G. Warner,

[1]Centre for Groundwater Research and Wetlands Research Centre, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
[2]Wetlands Research Centre and Department of Geography, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1
[3]Department of Geographical Sciences, University of Plymouth, Plymouth, Devon PL4 8AA, United Kingdom
[4]School of Biological Sciences, Queen Mary and Westfield College, London E1 4NS, United Kingdom
[5]75 Foxleigh Crescent, Kanata, Ontario, Canada K2M 1V6
[6]Centre for Land and Biological Resources Research, Research Branch, Agriculture Canada, Ottawa, Ontario, Canada K1A 0C6

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press

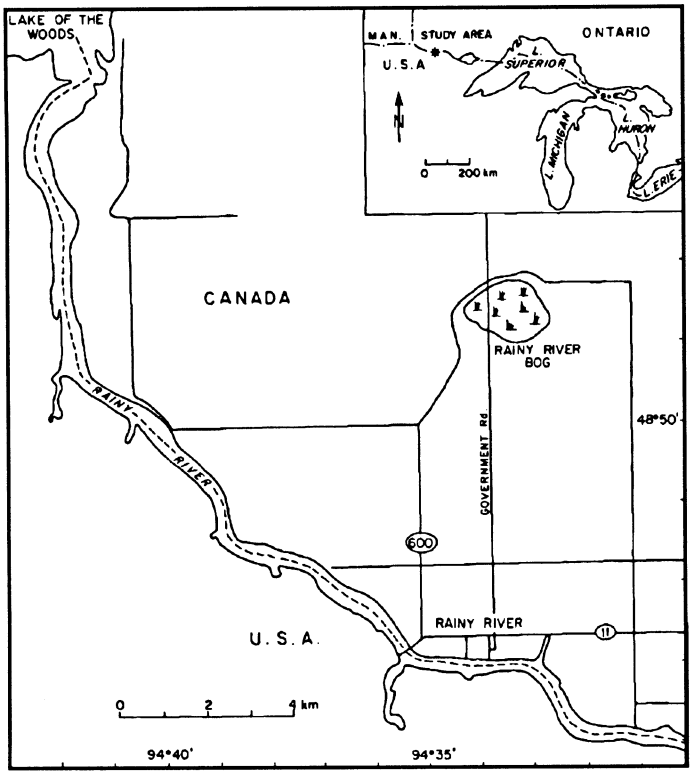

Fig. 1. Location of study area

unpublished data). Hydrological conditions after this time promoted peatland inception through primary peat formation. The modern vegetation consists of an open shrub peatland community with well-developed microtopography of *Sphagnum fuscum*, *S. angustifolium* and *Cladina* lichens. Closed *Picea mariana* forest occurs in some areas of the peatland.

Material and methods

Seven bulk peat samples were collected from a 208-cm-deep sequence from the western (oldest) part of the peatland for ^{14}C analysis. Peatland gases and water samples were collected at three depths in the profile, 65–85, 102–122 and 150–170 cm from the surface, at the end of the summer. The water table was positioned at 60 cm during sampling. Gases were collected with a stainless steel probe described by Dinel *et al.* (1988).

For analyses of ^{14}C and ^{13}C, CO_2 and CH_4 were separated and purified cryogenically. CH_4 was converted to CO_2 by passing the gas with a helium oxygen mixture through copper oxide heated to 850°C. A background of <0.5% modern carbon was obtained using commercial ^{14}C-free methane for the whole conversion process. ^{14}C analyses on gases were done by accelerator mass spectrometry (AMS) at the IsoTrace Radiocarbon Facility, University of Toronto, Canada. Peat ^{14}C dates were obtained by liquid scintillation counting (LSC) at the Environmental Isotopes Laboratory, University of Waterloo. All ^{14}C dates were normalized to $\delta^{13}C = -25$ ‰. All ages are reported to ± 1 σ. Tritium (^3H) was analyzed on water samples by LSC with a counting error of ± 8 TU (direct counting) and ± 0.8 TU (electrolytic enrichment), respectively.

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press

RESULTS AND DISCUSSION

Carbon Isotope Data

^{14}C dates obtained on peat samples indicated that the peat carbon began accumulating at least 4.6 ka BP in the peatland basin. The application of a model of peat growth (Clymo 1984) to the record of peat accumulation at the site suggests that decay occurs throughout the anoxic layer of the peat mass (Belyea 1991).

^{14}C dates on both species of gas at each depth were of comparable age, but about 1–2 ka younger than the enclosing peat (Table 1). Gas and peat ^{14}C ages should have agreed if the sole carbon source for gas production was the enclosing peat, without input of younger carbon from the overlying strata. The ombrogeneous character of the peatland suggests two alternative explanations for the discrepancies between gas and peat ages. First, CO_2 and CH_4 that had been produced closer to the surface from younger carbon may have been transported downward in peatland waters and mixed with older gases produced at depth. Alternatively, and more likely, dissolved organic carbon (DOC) originating from younger peat may have infiltrated deeper strata and provided fermentation and methanogen bacteria with a carbon source younger than the enclosing peat. Recent studies do not support the first hypothesis. They show deeper peat layers more highly saturated with methane than peat layers closer to the surface (Dinel *et al.* 1988; Brown, Mathur & Kushner 1989; Claricoates 1990; Mathur, Dinel & Levesque 1991; Buttler *et al.* 1991). In either case, the gas ages represent an average estimate of the ages of carbon sources used in gas production.

TABLE 1. ^{14}C Ages for Bulk Peat and CO_2 and CH_4 Gases from the Rainy River Peatland, Northwestern Ontario

Depth (cm)	Water	Peat		Gases			
	^{3}H (TU)	$\delta^{13}C$ ‰ (PDB)	^{14}C age (BP)	$\delta^{13}C$ ‰ (PDB)		^{14}C age (BP)	
				CO_2	CH_4	CO_2	CH_4
50–51		−27.4	1520 ± 70				
71–73		−25.6	1780 ± 70				
65–85	34 ± 8.0			−12.4	−74	760 ± 70	640 ± 70
100–101		−26.9	2460 ± 80				
102–122				−5.9	−63	470 ± 70	540 ± 70
129–130		−27.5	2690 ± 70				
155–156		−27.8	2990 ± 70				
150–170	46 ± 3.0			−1.4	−61	1150 ± 70	1200 ± 90
181–182		−27.4	3440 ± 70				
208–209		−29.0	4600 ± 70				

^{3}H analyses on water accompanying the gases (Table 1) indicate the presence of ^{3}H of thermonuclear origin in the peat pore water at a depth of at least 150–170 cm. Thermonuclear ^{3}H in Canadian precipitation reached peak values of 3400 TU in 1963, and values have steadily decreased to around 40 TU since 1985. Precipitation before the start of thermonuclear tests in 1950 have ^{3}H concentrations less than 5 TU (Robertson & Cherry 1988). Gorham and Hofstetter (1978) have also reported the presence of thermonuclear ^{3}H at a depth >2.0 m in a raised peatland in nearby Minnesota. We have found high concentrations of thermonuclear ^{3}H at 140 cm depth in 4500-yr-old peat in northeastern Ontario (Charman, Aravena & Warner 1992). ^{3}H at depth in the Rainy River peatland further confirms the possibility of transport of young carbon from the shallow

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press

part of the peatland. Similarly, atmospheric carbon enriched in thermonuclear ^{14}C (McNeely 1988) has accumulated as peatland organic matter since 1950, thereby providing a carbon source enriched in ^{14}C for transport downwards and gas production deep within the peatland. This is confirmed by ^{14}C data on near-surface peat at Rainy River that range from 101 to 111 pMC (Belyea & Warner 1993).

The other possibility that could explain the apparent age discrepancy between gases and peat carbon is transport of younger carbon from shallow depths induced by the sampling apparatus. Gas collection is carried out by a small vacuum created in the sampling chamber. This pressure differential could induce gas movement through the outer part of the gas probe. This possibility can be evaluated using the $\delta^{13}C$ results obtained on the CO_2 and CH_4 gases.

These data show a trend toward depleted $\delta^{13}C$ values for CO_2 with values of −1.5‰ at 150–170 cm depth, changing to values of −12.4‰ at the shallowest sampling depth (Table 1). We observed a similar trend, decreasing from −60‰ to −74‰ in the CH_4 samples. These isotopic changes have been reported in peat (Landsdown, Quay & King 1992) and in marine sediments (Claypool & Kaplan 1974), and can be attributed to isotopic effects occurring during CH_4 production. One parameter used to estimate the importance of acetate fermentation and CO_2 reduction for CH_4 production is the relation

$$\alpha_c = \frac{(\delta\,^{13}C_{CH_4} + 1000)}{(\delta\,^{13}C_{CO_2} + 1000)} \quad . \qquad (1)$$

Previous estimates suggest that α_c values <0.95 are typical of marine environments where CO_2 reduction is the main carbon pathway, as opposed to freshwater environments characterized by α_c >0.95 where acetate fermentation is the main carbon pathway (Whiticar, Faber & Schell 1986). However, α_c values <0.95 have been reported recently for wetland gases (Landsdown, Quay & King 1992). Their results show that CO_2 reduction can also be an important mechanism in wetland environments. α_c values for Rainy River gases range from 0.937 to 0.942 in agreement with data reported by Landsdown, Quay and King (1992). Thus, the ^{13}C gas depth profiles are clearly controlled by methanogenesis and do not support a mixing scenario between shallow and deeper gases. Transport of younger shallow carbon by the sampler seems unlikely, and should not cause the ^{14}C age discrepancies between gases and peat at this site. Definitive information about transport of carbon and carbon sources for gases in peatlands requires a thorough evaluation of the internal carbon dynamics of whole peatland systems.

Carbon Dynamics in the Peatland

The role of advection and dispersion as transport mechanisms for carbon in peatlands is not well known; however, recent hydrological studies in northern Minnesota have shown that advection plays a significant role in the groundwater flow regime of peatlands (Chason & Siegel 1986; Siegel & Glaser 1987). Carbon transport by diffusion could also occur in peatlands because DOC concentration profiles in peatland pore water show high concentrations near the surface, decreasing with depth (McKnight, Thurman & Wershaw 1985).

Significant quantitites of CO_2 and CH_4 at depth in peatlands have been documented previously (Dinel *et al.* 1988; Brown, Mathur & Kushner 1989; Claricoates 1990; Mathur, Dinel & Levesque 1991; Buttler *et al.* 1991; Romanowics, Siegel & Glaser 1991), but the ultimate fate of these deep gases remains a mystery. ^{14}C dates on CH_4 emitted from peatland surfaces suggest that recent carbon is not the only source involved in the production of these gases (Wahlen *et al.* 1989).

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press

Clearly, at least some old gas leaves the deep peat reservoir *via* surface evolution, but another fraction may remain trapped in void spaces, and eventually will be transported out of the peatland by water. The efflux of dissolved CO_2 and CH_4 *via* surface and groundwater regimes has been effectively ignored in previous considerations of peatland carbon dynamics; so too, the nature of the carbon source (peat or DOC) and the translocation of carbon sources dissolved in peatland waters. These processes are linked intimately to the dynamics of water movement in peatland systems, especially in the deeper anaerobic zone. Recent studies have shown that active groundwater movement occurs in peatland systems, and these systems can behave as recharge or discharge areas (Chason & Siegel 1986; Siegel & Glaser 1987). The origins and dynamics of peatland gases are evidently far more complex than previously recognized.

These complexities have important implications for predicting future concentrations of atmospheric trace gases. Carbon isotope mass balance models of CH_4 generation currently consider only two carbon sources: a modern carbon pool derived from recent biogenic sources, and a fossil (^{14}C-free) pool derived from coal and natural gas (Wahlen *et al.* 1989; Lowe *et al.* 1988; Manning *et al.* 1990). We have shown that old peat of northern peatlands is another potentially large carbon source whose isotopic signal is masked by that of the modern carbon pool. Our preliminary results suggest that peatland waters may play an important role in translocation and cycling of carbon gases and their organic precursors. Although we have come a long way from the early view that peatlands function indefinitely as carbon sinks, much remains to be learned about the carbon dynamics of these systems.

Acknowledgments

This work was funded by the Natural Sciences and Engineering Research Council of Canada. This is Centre for Land and Biological Resources Research Contribution 92-60.

References

Belyea, L. R. (ms.) 1991 Dynamics and implications of peat accumulation in a northwestern Ontario peatland. M. Sc. thesis, University of Waterloo.

Belyea, L. R. and Warner, B. G. (ms.) 1993 Dating of the near-surface layer of a peat deposit from Northwestern Ontario, Canada. Submitted to *Oikos*.

Brown, A., Mathur, S. P. and Kushner, D. J. 1989 An ombrotrophic bog as a methane reservoir. *Global Biogeochemical Cycles* 3: 205–213.

Buttler, A. J. Dinel, H., Levesque, M. and Mathur, S. P. 1991 The relation between movement of surface water and gaseous methane in a basin bog with a novel instrument. *Canadian Journal of Soil Science* 71: 427–438.

Charman, D. J., Aravena, R. and Warner, B. G. 1992 Carbon dynamics and accumulation in a forested peatland in northeastern Ontario, Canada. Abstract. *Program, Carbon and Peatlands Symposium*, Nottingham, England, British Ecological Society.

Chason, D. and Siegel, D. I. 1986 Hydraulic conductivity and related physical properties of peat, Lost River peatland, northern Minnesota. *Soil Science* 142: 91–99.

Claricoates, J. (ms.) 1990 Gas production during peat decay. Ph.D. thesis, Queen Mary and Westfield College, London.

Claypool, G. E. and Kaplan, I. R. 1974 The origin and distribution of methane in marine sediments. *In* Kaplan, I. R., ed., *Natural Gases in Marine Sediments*. New York, Plenum Publishing Co.: 99–103.

Clymo, R. S. 1984 The limits to peat bog growth. *Philosophical Transactions of the Royal Society, London* B303: 605–654.

_____ 1991 Peat growth. *In* Shane, L. C. K. and Cushing E. J., eds., *Quaternary Landscapes*. Minneapolis, University of Minnesota Press: 76–112.

Crill, P. M., Bartlett, K. B., Sebacher, D. I., Harris, R. C., Verry, E. S., Gorham, E., Madzar, L. and Sanner, J. 1988 *Global Biogeochemical Cycles* 2:371–384.

Dinel, H., Mathur, S. P., Brown, A. and Levesque, M. 1988 A field study on the effect of depth on methane production in peatland waters: Equipment and preliminary results. *Journal of Ecology* 76: 1083–1091.

Gorham, E. 1991 Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecological Applications* 1: 182–195.

Gorham, E. and Hofstetter, R. H. 1978 Penetration of bog peats and lake sediments by tritium from atmospheric fallout. *Ecology* 52: 898–902.

Harriss, R. C., Gorham, E., Sebacher, D. I., Bartlett,

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press

K. B. and Febble, P. A. 1985 Methane flux from northern peatlands. *Nature* 315: 652–653.

Lansdown, J. M., Quay, P. D. and King, S. L. 1992 CH_4 production *via* CO_2 reduction in a temperate bog: A source of $\delta^{13}C$-depleted CH_4. *Geochimica et Cosmochimica Acta* 56: 3493–3503.

Lowe, D. C., Brenninkmeijer, A. M., Manning, M. R., Sparks, R. and Wallace, G. 1988 Radiocarbon determination of atmospheric methane at Baring Head, New Zealand. *Nature* 332: 522–525.

Manning, M. R., Lowe, D. C., Melhuish, W. H., Sparks, R. J., Wallace, G., Brenninkmeijer, C. A. M. and McGill, R. C. 1990 The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* 32(1): 37–58.

Mathur, S. P., Dinel, H. and Levesque, M. 1991 The role of methane gas in peatland hydrology: A new concept. *In* Jeglum, J. K. and Oberend, R. P., eds., *Proceedings, Symposium '89, Peat and Peatlands: Diversification and Innovation* 1. Quebec City, Canada: 153–157.

Matthews, E. and Fung, I. 1987 Methane emmission from natural wetlands: Global distribution, area, and environmental characteristics of sources. *Global Biogeochemical Cycles* 1: 61–86.

McKnight, D., Thurman, M. E. and Wershaw, R. L. 1985 Biogeochemistry of aquatic humic substances inThoreau's Bog, Concord, Massachussets. *Ecology* 66: 1339–1352.

McNeely, R. 1988 Radiocarbon dating laboratory. *GEOS* 17: 10–12.

Robertson, W. D. and Cherry, J. A. 1988 Tritium as an indicator of recharge and dispersion in a groundwater system in central Ontario. *Water Resources Research* 25: 1097–1109.

Romanowics, E. A., Siegel, D. I. and Glaser, P. H. 1991 Deep methane in the Glacial Lake Agassiz peatland. Abstract. American Geophysical Union Spring Meeting. *EOS* 72: 80.

Siegel, D. I. and Glaser, P. H. 1987 Groundwater flow in a bog-fen complex, Lost River peatland, northern Minnesota. *Journal of Ecology* 75: 743–754.

Wahlen, M., Tanaka, N., Henry, R., Deck, B., Zeglen, J., Vogel, J. S., Southon, J., Shemesh, A., Fairbanks, R. and Broecker, W. 1989 Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon. *Science* 245: 286–290.

Warner, B. G., Clymo, R. S. and Tolonen, K. 1993 Implications of peat accumulation at Point Escuminac, New Brunswick. *Quaternary Research* 39: 245–248.

Whiticar, M. J., Faber, E. and Schoell, M. 1986 Biogenic methane formation in marine and freshwater environments: CO_2 reduction *vs.* acetate fermentation-isotope evidence. *Geochimica et Cosmochimica Acta* 50: 693–709.

https://doi.org/10.1017/S0033822200064948 Published online by Cambridge University Press