Title

Methane transport from the active layer to lakes in the Arctic using Toolik Lake, Alaska, as a case study

Journal

Proceedings of the National Academy of Sciences of the United States of America, 112(12)

ISSN

0027-8424

Authors

Paytan, Adina
Lecher, Alanna L
Dimova, Natasha
et al.

Publication Date

2015-03-24

DOI

10.1073/pnas.1417392112

Peer reviewed

Methane transport from the active layer to lakes in the Arctic using Toolik Lake, Alaska, as a case study

Adina Paytan[a,1], Alanna L. Lecher[a], Natasha Dimova[a,b], Katy J. Sparrow[c], Fenix Garcia-Tigreros Kodovska[c], Joseph Murray[a], Slawomir Tulaczyk[a], and John D. Kessler[c]

[a]Earth and Planetary Science, University of California, Santa Cruz, CA 95064; [b]Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487; and [c]Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627

Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved February 13, 2015 (received for review September 8, 2014)

Methane emissions in the Arctic are important, and may be contributing to global warming. While methane emission rates from Arctic lakes are well documented, methods are needed to quantify the relative contribution of active layer groundwater to the overall lake methane budget. Here we report measurements of natural tracers of soil/groundwater, radon, and radium, along with methane concentration in Toolik Lake, Alaska, to evaluate the role active layer water plays as an exogenous source for lake methane. Average concentrations of methane, radium, and radon were all elevated in the active layer compared with lake water (1.6×10^4 nM, 61.6 dpm·m^{-3}, and 4.5×10^5 dpm·m^{-3} compared with 1.3×10^2 nM, 5.7 dpm·m^{-3}, and 4.4×10^3 dpm·m^{-3}, respectively). Methane transport from the active layer to Toolik Lake based on the geochemical tracer radon (up to 2.9 g·m^{-2}·y^{-1}) can account for a large fraction of methane emissions from this lake. Strong but spatially and temporally variable correlations between radon activity and methane concentrations ($r^2 > 0.69$) in lake water suggest that the parameters that control methane discharge from the active layer also vary. Warming in the Arctic may expand the active layer and increase the discharge, thereby increasing the methane flux to lakes and from lakes to the atmosphere, exacerbating global warming. More work is needed to quantify and elucidate the processes that control methane fluxes from the active layer to predict how this flux might change in the future and to evaluate the regional and global contribution of active layer water associated methane inputs.

methane | Arctic lakes | active layer | radioisotope tracers | permafrost

Methane is a powerful greenhouse gas estimated to be responsible for approximately one-fifth of man-made global warming, and its concentration has been increasing (1). The largest natural source of methane is wetlands (2), including a major component from northern high-latitude regions containing permafrost (3). Observations in the Siberian Arctic show high rates of methane release from both the coastal seabed and land-based permafrost soils (4, 5). Previous research has also documented extensive methane release from Arctic lakes, primarily via ebullition, with significant spatial variability within and between lakes (6, 7). Methane in Arctic lakes forms by microbial production (methanogenesis) in the water column and/or within anaerobic lake sediments (8). However, it is possible that some fraction of the observed methane is not produced within the lakes but is rather transported to the lakes from external, land-based sources through subterranean groundwater discharge (SGD) (9) (Fig. 1). Specifically, water in the active layer (the surficial layer of the soil system above the permafrost that thaws every summer) could be transported into lakes and rivers during the thaw season (May–August) (10). Groundwater in some temperate climate regions can be highly enriched in methane (11), and groundwater discharge contributions to the methane budget of the coastal ocean and lakes in temperate climate have been reported (12, 13). This conduit of methane transport may be particularly important in regions where organic-rich soils and anaerobic conditions promote methane production in the soil, such as in the Arctic (14). SGD occurs everywhere at the land–water interface in lakes, rivers, and the ocean, and evidence of water flow through the active layer in permafrost-dominated regions is found in springs, in open water reaches and base flow of rivers, in talik, and in the distribution of halophytic vegetation (15, 16). Methane fluxes sourced from land into lakes and coastal waters in the Arctic have not been directly measured. The organic-rich soils and anaerobic conditions in the active layer in the Arctic are prime conditions for methane production, and this methane could be transported to lakes and coastal waters.

Results and Discussion

Toolik Lake is an Arctic lake (1.5 km^2) situated in the continuous permafrost zone in the northern foothills of the Brooks Range, Alaska (68°38'N, 149°36'W; elevation 720 m). The region is affected by rapidly growing thermokarst features, a testimony to decaying near-surface permafrost due to recent climate changes (17). There are more than 2 million Arctic lakes, which cover a large fraction of the surface area north of 45°N (18, 19), and methane input from the active layer into these lakes could be important. Methane, radon, and radium concentrations were determined concurrently in lake water, river water entering the lake, and groundwater, in July 2011 and August 2012; limited sampling in a few other lakes was also conducted in the summer of 2014. Naturally occurring ^{224}Ra ($t_{1/2}$ = 3.6 d) and ^{222}Rn ($t_{1/2}$ = 3.8 d) isotopes are well recognized as valuable geochemical tracers of water that has been in contact with rocks and soil (20, 21) and have been used to quantify groundwater discharge

Significance

Methane, a greenhouse gas, contributes to global warming. We show that methane-rich water from the seasonally thawed active layer in the Arctic flows into Toolik Lake, Alaska. This may be an important previously unrecognized conduit for methane transport and emissions in Arctic lakes. The controls on methane input from the active layer are fundamentally different than those affecting methane production within lakes, and the response of these processes to climate and environmental change is also distinct. The accuracy of predictions of methane emissions and ultimately the extent of climate change that can be expected in the Arctic depend on a better understanding of methane dynamics in the region, including the controls over methane production and transport processes within the active layer.

Author contributions: A.P., A.L.L., N.D., and J.D.K. designed research; A.P., A.L.L., N.D., K.J.S., F.G.-T.K., J.M., S.T., and J.D.K. performed research; A.P. and J.D.K. contributed reagents/analytic tools; A.P., A.L.L., N.D., K.J.S., F.G.-T.K., J.M., S.T., and J.D.K. analyzed data; and A.P., A.L.L., N.D., K.J.S., F.G.-T.K., and J.D.K. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

[1]To whom correspondence should be addressed. Email: apaytan@ucsc.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1417392112/-/DCSupplemental.

Table 1. The ^{224}Ra, ^{222}Rn, and methane average concentrations and range of concentrations measured in the active layer, lake water, and rivers at Toolik Lake

Tracer analyzed	Active layer water	Lake water	Primary inflow	Secondary inflow
		2011		
^{224}Ra, dpm·m^{-3}	58.5	3.3	10.1	10.4
	12.3–161.7	1.3–10.9		
	$n = 7$	$n = 11$	$n = 1$	$n = 1$
^{222}Rn, dpm·m^{-3}	4.1×10^5	5.7×10^3	not sampled	not sampled
		$0.6–19.7 \times 10^3$	not sampled	not sampled
	$n = 2$	n = 291	not sampled	not sampled
[CH_4], nM	3.5×10^4	1.3×10^2	not sampled	4.3×10^2
	6.3×10^2–1.5×10^5	4.7×10^1–2.7×10^2	not sampled	
	$n = 6$	$n = 34$	not sampled	$n = 1$
		2012		
^{224}Ra, dpm·m^{-3}	63.2	6.9	6.4	0.8
	7.2–186.2	2.2–14.9	5.4–7.4	
	$n = 13$	$n = 18$	$n = 2$	$n = 1$
^{222}Rn, dpm·m^{-3}	4.9×10^5	2.9×10^3	17.9×10^3	13.9×10^3
	$4.8–5.1 \times 10^5$	$0.3–7.3 \times 10^3$	$9.0–22.4 \times 10^3$	$7.5–17.6 \times 10^3$
	$n = 4$	$n = 388$*	$n = 125$*	$n = 29$
[CH_4], nM	8.1×10^3	1.4×10^2	1.1×10^2	5.3×10^1
	1.2×10^1–4.6×10^4	2.2×10^1–8.2×10^2	9.5×10^1–1.2×10^2	
	$n = 16$	$n = 50$	$n = 3$	$n = 1$

*Rn values include measurements from both survey and time series records.

throughout the world (22). Methane concentrations, as well as ^{224}Ra and ^{222}Rn activities, in water collected from the active layer are at least an order of magnitude higher than those observed in Toolik Lake water (Table 1 and Tables S1 and S2). Measurements of ^{224}Ra and ^{222}Rn in Toolik Lake indicate that water high in Ra and Rn (from the active layer) is discharging into the lake. This is consistent with a water balance estimate that noted an unidentified flow of water to the lake contributing 3.64×10^4 m^3·d^{-1} (23). Water input calculations using Rn mass balance ($2.1 \pm 1.3 \times 10^4$ m^3·d^{-1} and $1.6 \pm 0.6 \times 10^4$ m^3·d^{-1}, in 2011 and 2012, respectively) suggest similar input rates, and Ra modeling also produces results of similar magnitude (Table 2 and *SI Text*). Estimates of methane fluxes to Toolik Lake determined by multiplying the average active layer methane concentrations (3.5×10^4 nM and 8.1×10^3 nM in 2011 and 2012, respectively) by the Rn based water discharge rate estimates range from 2.9 to 0.5 g·m^{-2}·y^{-1} in 2011 and 2012 respectively (Table 2 and *SI Text*). The range in flux reflects differences in average methane concentrations in the active layer as well as differences in water discharge from the active layer between the years. These rates are comparable in magnitude to reported methane emissions from Toolik Lake to the atmosphere [~2 g·m^{-2}·y^{-1} (24)] (Table S3).

Good correlation between ^{222}Rn and methane in the lake water (Fig. 2) and the enrichment of both gases close to the lake shoreline, where the active layer interfaces with the lake and where water from the active layer may enter the lake, are consistent with the transport of methane to the lake from this source (Fig. 3). We did not observe bottom water enrichments in methane or ^{222}Rn in water depth profile sampling conducted during our campaigns (in 2011, surface water ^{222}Rn was 9.2×10^3 dpm·m^{-3} with methane concentrations of 93 nM, while bottom water ^{222}Rn was 9.0×10^3 dpm·m^{-3} with methane concentrations of 87 nM; in 2012, water ^{222}Rn was 5.8×10^3 dpm·m^{-3} with methane concentrations of 132 nM, while bottom water ^{222}Rn was 3.1×10^3 dpm·m^{-3} with methane concentrations of 73 nM), indicating that sediments in Toolik Lake are not a major source of these gases, at least during the sampling period; Ra was also not enriched at depth (Table S1). Indeed, Cornwell and Kipphut (25) found very low organic matter sedimentation rates and low dissolved oxygen consumption rates within Toolik Lake sediments, suggesting that the methane in Toolik Lake may be from a different origin. Similar spatial distribution patterns of methane, showing highest concentrations close to the lakeshore, have been seen in other Arctic lakes (9, 26, 27). While other explanations for this spatial distribution are possible (e.g., active slumping of organic-rich soil along the shoreline or wave-induced methane release), this is also consistent with the allochthonous input from the active layer as we propose here, which may contribute to the total lake methane inventory. This methane has the potential to be emitted to the atmosphere from the lake surface.

Methane input rates to the lake from the active layer depend on the SGD flux and on methane concentrations in the active layer water. The former is a function of the hydrogeology (aquifer recharge, porosity, permeability, and hydraulic head) of the different lake watersheds, and the latter is a function of methane production in the active layer. Elevated methane concentrations occur naturally in anoxic conditions via biogenic production in organic-rich soils. In the Arctic, organic soil carbon storage in near-surface permafrost can be substantial and can

Table 2. Water and methane discharge from the active layer determined using Table 1 ^{222}Rn values

Method	Active layer water discharge, m^3·d^{-1}	Associated methane flux, g·m^{-2}·y^{-1} (1)
Whalen and Cornwell, 1985 water budget "undefined flow"	3.64×10^4	NA
2011 ^{222}Rn mass balance	$2.1 \pm 1.3 \times 10^4$*	2.9
2012 ^{222}Rn mass balance	$1.6 \pm 0.6 \times 10^4$*	0.5

NA, not available.

*The estimates and attributed uncertainties are based on average ^{222}Rn concentration from three moorings deployed during each of the sampling campaigns around the perimeter of the lake and thus representative of the spatial heterogeneity in groundwater discharge to Toolik Lake, not on the method analytical precision.

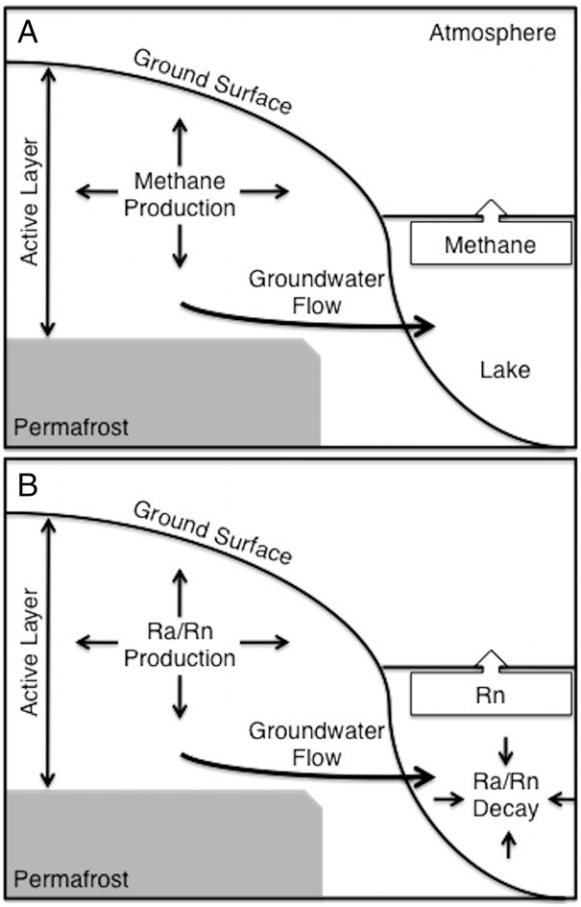

Fig. 1. (*A*) Schematic diagram of active layer water-associated methane flux to Arctic lakes and related climate feedbacks. Warming for more than a century has resulted in various degrees of permafrost thawing. As climate warms, permafrost stability is likely to decrease further. Methane produced in the active layer above the permafrost will be transported and released to receiving waters, eventually reaching the atmosphere and providing a positive feedback to global warming. (*B*) Schematic diagram of Ra and Rn enrichment in the active layer due to production in soil and peat, and their transport via groundwater to the lake where they radioactively decay and Rn-like methane is also released to the atmosphere.

support methane production in the active layer. Although limited, the methane isotope data ($\delta^{13}C = -58.9 \pm 3$) from active layer water samples ($n = 4$) taken around Toolik Lake suggest a biological source, consistent with lake isotope values (26).

Two interesting aspects of our data warrant further consideration; first, while ^{224}Ra and ^{222}Rn in groundwater samples collected at different locations throughout the lake watersheds show relatively consistent activities, methane concentrations in the active layer vary considerably, both spatially and temporally; and second, although all lake water ^{222}Rn and methane data are strongly correlated, the relationship is differentiated into two trends (Fig. 2), depending on sampling location and date. These observations suggest considerable spatial variability in methane production within the active layer. This is likely due to differences in organic matter content, water saturation, temperature, pH, and additional parameters that influence soil methanogenesis (3). Differences in water flow rate, which depends on watershed and soil characteristics, as well as the thickness of the active layer, may also affect the methane input through this conduit, as seen by the ~25% difference in SGD discharge between years (10).

We suspect that active layer water-associated methane input to Arctic lakes is a ubiquitous phenomenon. Our active layer methane input estimates from Toolik Lake are likely lower than in other lakes in permafrost regions due to the small amount of organic matter in the active layer around Lake Toolik compared with other lakes, the relatively large size of the lake (e.g., small shoreline length compared with lake surface area), and the somewhat limited groundwater flow due to the shallow active layer and continuous permafrost in the Northern Arctic region (more SGD is expected farther south in the noncontinuous permafrost regions). However, further investigation must be conducted to verify this hypothesis and identify and quantify the processes that control methane inputs from the active layer to Arctic lakes. Importantly, the controls on methane input to lakes from the active layer are fundamentally different from those impacting in situ methane production rates within the lakes, and the response of these disparate processes to climate and environmental change is also likely to be distinct (28). Future methane and other carbon emissions from the Arctic, as well as the ecological and economic impacts of these sources and their response to climate change remain topics of great interest (3, 29–34). The accuracy of atmospheric methane emissions predictions, and ultimately the extent of climate change that can be expected in the Arctic, depends on a holistic understanding of Arctic methane dynamics, including processes within the permafrost active layer.

Materials and Methods

Field Sampling. Lake water, active layer water, and river water samples were collected in August 2011 and July 2012 following standard procedures for ^{224}Ra activities (35, 36), ^{222}Rn activities (37–39), and CH_4 concentration (40, 41). Surface lake water samples were collected from both the interior and perimeter areas of the lake. A deep water sample for Ra analysis was collected at ~14 m above the deepest point of the lake, a localized 25-m-deep basin surrounded by relatively shallow (<3 m) areas, using a submersible pump. Active layer water samples were collected from the perimeter of the lake right at the lake shoreline by installing temporary well points or by digging pits. The depths of the well points and pits were limited by the depth of the active layer (<0.5 m typically from the soil surface to the upper boundary of the permafrost). Water samples were also collected from the thaw bulb below the lake by means of the Toolik Lake Field Station camp water supply well (depth ~15 m below lake). Surface river water samples were collected from the primary and secondary inflows into Toolik Lake. Specific conductivity and temperature were measured with a handheld YSI 85 multiprobe.

Radon Activity. A survey coupling the measurement of ^{222}Rn and CH_4 was conducted in which instruments for the measurement of both gases were

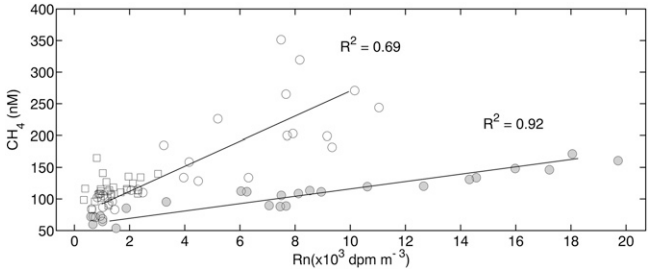

Fig. 2. Correlation between methane concentration ([CH_4]) (nanomolar) and ^{222}Rn activity (10^3 dpm·m^{-3}) concurrent measurements in Toolik Lake during the summers of 2011 and 2012. The data from 2011 (circles) fall on two trends, depending on location. Samples from the east and south sections of the lake fall on the tighter lower trend ($r^2 = 0.92$) with filled symbols; data from the west side of the lake fall on the upper steeper trend ($r^2 = 0.69$) with open symbols. All of the data from 2012 (squares) fall on the steeper trend with the 2011 west lake data. Positive relation is also seen between Ra and CH_4 (e.g., active layer water samples have high concentrations while lake water samples have low concentrations); however, due to the limited number of Ra data points, we did not derive a correlation.

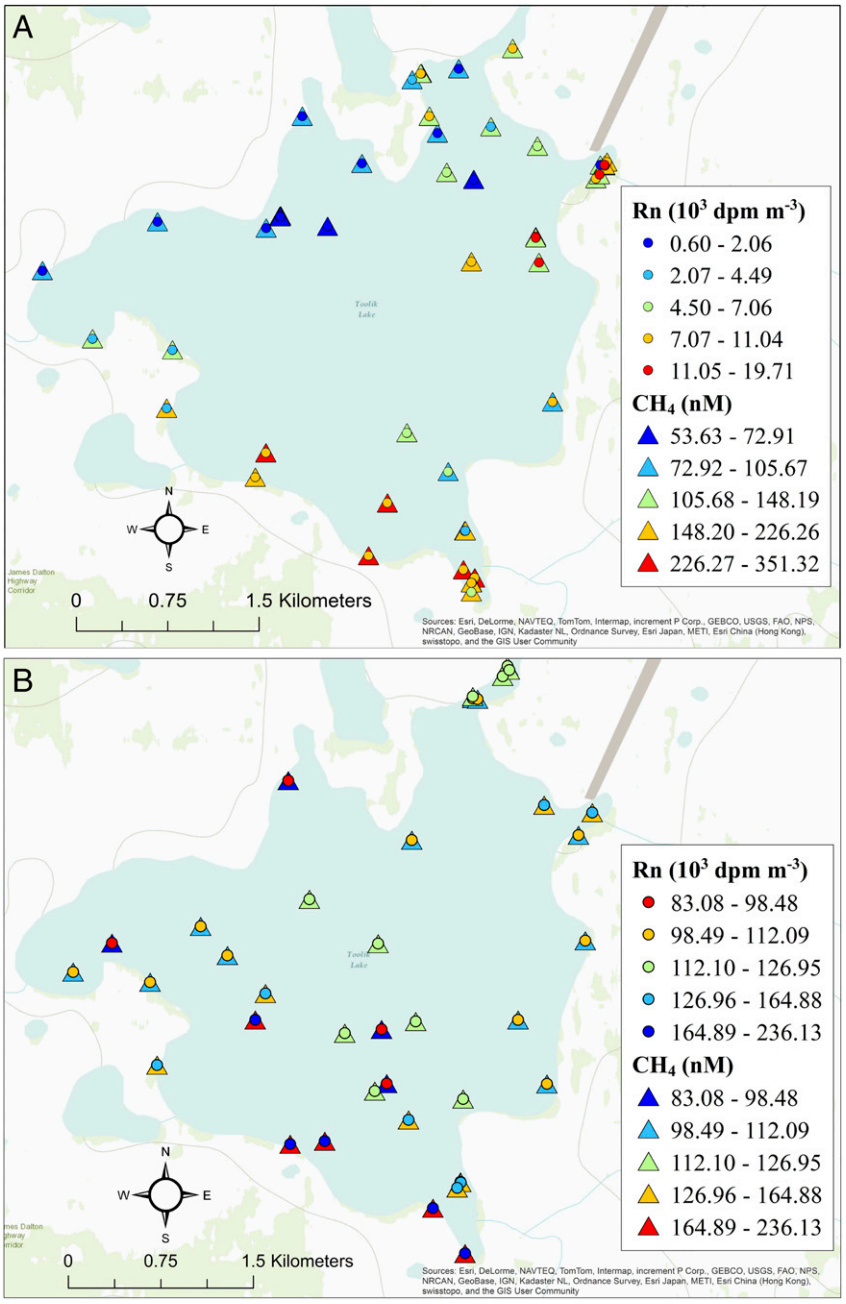

Fig. 3. Maps of methane concentration ([CH_4]) (nanomolar) and ^{222}Rn activity distribution in surface waters of Toolik Lake, Alaska, collected concurrently during surveys in (*A*) 2011 and (*B*) 2012.

mounted on a boat. Data were collected simultaneously for both gases while the boat progressed around the perimeter and through the interior of Toolik Lake.

The ^{222}Rn in both active layer water and surface water was measured using a RAD AQUA Radon-in-air monitor (Durridge Co., Inc.) following procedures outlined in ref. 37. Surface water measurements were conducted both in survey mode (the system was mounted on a boat, and data were collected while driving) and in time series moorings at several locations at the lake. In addition, several depth profiles of ^{222}Rn (coupled with methane analyses) were also sampled each year. Stationary deployment time lengths spanned from a few hours to a few days, and data were collected at 30-min sampling intervals, ensuring <5% measurement uncertainty. To optimize spatial resolution, the survey system was set up to collect data at 10-min intervals, and water pumping flow rates were >6 L·min^{-1}. For depth profiles, water was pumped and equilibrated at each depth for ∼15 min. The ^{222}Rn survey followed the method outlined (38). Three RAD7s were arranged in parallel, all collecting gas from the same water to air exchanger through which lake water was continually pumped from a depth of ∼30 cm.

The ^{222}Rn in the active layer water was also measured from the thaw bulb below the lake using the same automated RAD AQUA system in 10-min time intervals (38). All reported ^{222}Rn concentrations in the active layer water are averages of several consecutive measurements after the system reached full gas/radioactive equilibrium.

Discharge fluxes from the active layer to the lake were calculated using a steady-state excess ^{222}Rn (accounting for any ^{222}Rn production from ^{226}Ra in the lake) mass balance model as described in Dimova and Burnett (37). The main assumptions of the model are that the lake ^{222}Ra used for the calculation is representative of lake average concentrations over short time scales (days to week); the only significant ^{222}Rn source is active layer water (including active layer water from base flow that enters the lake via net river input); and the only losses are due to decay and atmospheric evasion. Using an iterative approach and accounting for decay (known) and the measured

atmospheric losses (based on wind speed and temperature data), the total ^{222}Rn input flux is estimated (38).

Radium Activity. Large volumes (300–500 L per sample) of lake water and river water were collected using either submersible pumps or buckets. Active layer water samples (volume 8–500 L per sample) were collected using submersible pumps, and thaw bulb water was collected from the camp water supply well. Active layer water samples were also collected in a few other lakes (e.g., a lake at the Barrow Environmental Observatory, 71.278425°N, 156.633399°W; Imikpuk Lake at Barrow, 71.331791°N, 156.661251°W; and in several small lakes near Toolik N1, NE2, S3, E1, and E5) and gave similar results (high Ra and high methane in active layer water; see *SI Text*); however, due to the limited data, water and methane fluxes were not calculated. Ra from the water samples was collected on MnO_2-impregnated acrylic fiber [flow rate <2 L·min^{-1} (35)]. Samples were shipped to the University of California, Santa Cruz, for analysis on a Radium Delayed Coincidence Counter (RaDeCC) for measurement of ^{224}Ra activities within 5 d (Alaska Air Cargo's GoldStreak Package Express). The fibers were analyzed on the RaDeCC again 3–5 wk after collection for correction of the ^{228}Th supported Ra. Standards were run on a monthly basis as part of the quality control for maintenance of the instrument. Analytical error was calculated using established procedures (36) and was typically <10%.

Active layer water fluxes were also determined from ^{224}Ra mass balance. (See *SI Text* for comparison with Rn-derived fluxes and reported methane fluxes to the atmosphere from Toolik Lake.)

Methane Concentration. Samples for methane analysis were collected and prepared as described previously (40, 41).

ACKNOWLEDGMENTS. This work was supported by the National Science Foundation through Grants ARC-1114485 (to A.P.) and OCE-1139203 (to S. A. Yvon-Lewis and J.D.K.).

1. Dlugokencky EJ Nisbet EG, Fisher R, Lowry D (2011) Global atmospheric methane: Budget, changes and dangers. *Philos. Trans. R. Soc. A* 369(1943):2058–2072.
2. Reeburgh WS (2003) *Global Methane Biogeochemistry. Treatise on Geochemistry*, eds Holland HD, Turekian KK (Elsevier, Boston), Vol 4, pp 65–89.
3. Olefeldt D, Turetsky MR, Crill PM, McGuire AD (2013) Environmental and physical controls on northern terrestrial methane emissions across permafrost zones. *Glob Change Biol* 19(2):589–603.
4. Zimov SA, Schuur EA, Chapin FS, 3rd (2006) Climate change. Permafrost and the global carbon budget. *Science* 312(5780):1612–1613.
5. Shakhova N, et al. (2010) Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science* 327(5970):1246–1250.
6. Walter KM, Zimov SA, Chanton JP, Verbyla D, Chapin FS, 3rd (2006) Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature* 443(7107):71–75.
7. Zimov SA, et al. (1997) North Siberian lakes: A methane source fueled by Pleistocene carbon. *Science* 277:800–802.
8. Walter KM, Smith LC, Chapin FS, III (2007) Methane bubbling from northern lakes: Present and future contributions to the global methane budget. *Philos Trans R Soc A* 365(1856):1657–1676.
9. Kling G, Kipphut GW, Miller MC (1992) The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. *Hydrobiologia* 240(1-3):23–36.
10. Romanovskey VE, Osterkamp TE (2000) Effects of unfrozen water on heat and mass transport processes in the active-layer and permafrost. *Permafrost Periglacial Processes* 11(3):219–239.
11. Bunga GC, Chanton JP, Cable JE, Burnett WC, Cable PH (1996) The importance of groundwater discharge to the methane budgets of nearshore and continental shelf waters of the northeastern Gulf of Mexico. *Geochim Cosmochim Acta* 60(23): 4735–4746.
12. Dulaiova H, Camilli R, Henderson PB, Charette MA (2010) Coupled radon, methane and nitrate sensors for large-scale assessment of groundwater discharge and non-point source pollution to coastal waters. *J Environ Radioact* 101(7):553–563.
13. Dimova NT, Burnett WC, Chanton JP, Corbett JE (2013) Application of radon-222 to investigate groundwater discharge into small shallow lakes. *J Hydrol* 486:112–122.
14. Tarnocai C, et al. (2009) Soil organic carbon pool in the northern circumpolar permafrost region. *Global Biogeochem Cycles* 23(2):GB2023.
15. Williams JR, van Everdingen RO (1973) Ground water investigations in permafrost regions of North America: A review. *Permafrost: North American Contribution to the Second International Conference*, eds Pewe TL, MacKay JR (Natl Acad Sci, Washington, DC), pp 435–446.
16. Kane DL, Slaughter CW (1973) Recharge of a central Alaska lake by subpermafrost groundwater. *Permafrost: North American Contribution to the Second International Conference*, eds Pewe TL, MacKay JR (Natl Acad Sci, Washington, DC) pp 458–462.
17. Markon CJ, Trainor SF, Chapin FS, III (2012) *The United States National Climate Assessment—Alaska Technical Regional Report* (US Geol Surv, Fairbanks AL), Circ 1379.
18. Downing JA, et al. (2006) The global abundance and size distribution of lakes, ponds, and impoundments. *Limnol Oceanogr* 51(5):2388–2397.
19. Bastviken D, Tranvik LJ, Downing JA, Crill PM, Enrich-Prast A (2011) Freshwater methane emissions offset the continental carbon sink. *Science* 331(6013):50–51.
20. Cable JE, Burnett WC, Chanton JP, Weatherly GL (1996) Estimating groundwater discharge into the northeastern Gulf of Mexico using radon-222. *Earth Planet Sci Lett* 144(3-4):591–604.
21. Moore WS (2010) The effect of submarine groundwater discharge on the ocean. *Annu Rev Mar Sci* 2:59–88.
22. Knee K, Paytan A (2011) Submarine groundwater discharge: A source of nutrients, metals, and pollutants to the coastal ocean. *Treatise on Estuarine and Coastal Science*, eds Wolanski E, McLusky DS (Academic, Waltham, MA), Vol 4, pp 205–233.
23. Whalen SC, Cornwell JC (1985) Nitrogen, phosphorous, and organic carbon cycling in an arctic lake. *Can J Fish Aquat Sci* 42(4):797–808.
24. Cornwell JC, Kipphut GW (1992) Biogeochemistry of manganese-and iron-rich sediments in Toolik Lake, Alaska. *Hydrobiologia* 240(1-3):45–59.
25. Walter KM, Chanton JP, Chapin FS, III, Schuur EAG, Zimov SA (2008) Methane production and bubble emissions from arctic lakes: Isotopic implications for source pathways and ages. *J Geophys Res* 113(G3):G00A08.
26. Walter Anthony KM, et al. (2010) Estimating methane emissions from northern lakes using ice bubble surveys. *Limnol Oceanogr Methods* 8:592–609.
27. Sepulveda-Jauregui A, Walter Anthony KM, Martinez-Cruz K, Greene S, Thalasso F (2014) Methane and carbon dioxide emissions from 40 lakes along a north–south latitudinal transect in Alaska. *Biogeosci Discuss* 11(9):13251–13307.
28. Kane DL, Hinzman LD, Zarling JP (1991) Thermal response of the active-layer to climatic warming in a permafrost environment. *Cold Reg Sci Technol* 19(2):111–122.
29. Schuur EA, Abbott B (2011) Climate change: High risk of permafrost thaw. *Nature* 480(7375):32–33.
30. Whiteman G, Hope C, Wadhams P (2013) Vast costs of Arctic change. *Nature* 499(7459): 401–403.
31. Anisimov OA (2007) Potential feedback of thawing permafrost to the global climate system through methane emission. *Environ Res Lett* 2(4):045016.
32. Gao X, et al. (2013) Permafrost degradation and methane: Low risk of biogeochemical climate-warming feedback. *Environ Res Lett* 8(3):035014.
33. Grosse G, et al. (2011) Vulnerability and feedbacks of arctic permafrost to climate change. *Eos Trans AGU* 9(1):73–74.
34. Fenner N, et al. (2007) Interactions between elevated CO_2 and warming could amplify DOC exports from peatland catchments. *Environ Sci Technol* 41(9):3146–3152.
35. Moore WS, Arnold R (1996) Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. *J Geophys Res* 101(C1):1321–1329.
36. Garcia-Solsona E, Garcia-Orellana J, Masque P, Dulaiova H (2008) Uncertainties associated with ^{223}Ra and ^{224}Ra measurements in water via delayed coincidence counter (RaDeCC). *Mar Chem* 109(3-4):198–219.
37. Dimova NT, Burnett WC (2011) Evaluation of groundwater discharge into small lakes based on the temporal distribution of radon-222. *Limnol Oceanogr* 56(2):486–494.
38. Burnett WC, Kim G, Lane-Smith D (2001) A continuous monitor for assessment of Rn-222 in the coastal ocean. *J Radioanal Nucl Chem* 249(1):167–172.
39. Dulaiova H, Peterson R, Burnett WC, Lane-Smith D (2005) A multi-detector continuous monitor for assessment of Rn-222 in the coastal ocean. *J Radioanal Nucl Chem* 263(2): 361–365.
40. Valentine DL, et al. (2010) Propane respiration jump-starts microbial response to a deep oil spill. *Science* 330(6001):208–211.
41. Yvon-Lewis SA, Hu L, Kessler J (2011) Methane flux to the atmosphere from the Deepwater Horizon oil disaster. *Geophys Res Lett* 38(1):L01602.