

Response to Comment on Climate Change and Mercury Accumulation in Canadian High and Subarctic Lakes

We appreciate the comments made by Outridge et al. on our recent paper¹, and we agree that this interesting hypothesis requires rigorous evaluation, to which we hoped our study had contributed. We are thus surprised by many of the criticisms, particularly since our approach was based closely on their work.^{2–4} Furthermore, we attempted to provide greater data transparency and improved graphical presentation relative to previous studies by, for example, plotting Hg versus S2 so that readers could evaluate the linearity of the relationships, and by providing data in numerous graphics in the Supporting Information. Our major goal was to address the issue of using sediment cores to infer anthropogenic Hg deposition in the Arctic because the above authors have, in previous studies, suggested that anthropogenic Hg inputs inferred from Arctic lake sediments “...are overestimated by approximately 4-fold”³ and are “...responsible for no more than 22% of the 20th Century [Hg] increase in...study lakes...”² These conclusions, if correct, have major implications for international action on Hg, and for policies related to the health of Arctic wildlife and indigenous people. Our point-by-point response thus follows.

First, Outridge et al. suggest that our conclusions regarding the lack of correlation between Hg and S2 are “without corroborating evidence”. We are unclear as to why they have ignored the algal data presented in our study. These data provide ample corroboration of our conclusions and we fail to see where previous work has been misrepresented.

Outridge et al. then state “...S2 compounds are not uniquely algal as stated by Kirk et al...” yet our definition of S2 was similar to their own.^{2–4} We stated that “S2...represents high molecular weight, kerogen-derived aliphatic hydrocarbons, which correspond to the biomacromolecular structure of algal cell walls. S2 has therefore been referred to as algal-derived OC” and cited appropriate references.^{2–6} Similarly, Outridge et al.² defined S2 as “...representing higher molecular weight, kerogen-derived aliphatic hydrocarbons released from algal cell walls by the thermal cracking of organic matter...” and Stern et al.³ as “...released mainly from the algal-derived organic content of the sample...”.

Outridge et al. state that S2 “...may be significantly influenced by inputs from other plant types”, particularly in subarctic lakes. They thus suggest corroboration of S2 with other proxies and emphasize petrology “to distinguish plant sources”. First, our study included another proxy of algal productivity: algal microfossils. Furthermore, five of the six lakes with no positive Hg:S2 relationship were high Arctic lakes with catchment vegetation similar to that of Amituk, DV-09, and H2, where Outridge et al. suggested that “S2 is effectively equivalent to algal OM because other plant sources are negligible.” In fact, petrology has only been used in four subarctic lakes,^{3,4,7} all having catchments with vascular plants or partial forest and likely complex OC depositional environments.

Regarding the determination of residual carbon (RC), our formula yielded a rough approximation and we have recalculated RC using the approach of ref 5. In most lakes, RC values were

comparable, with new values being consistently lower. Most importantly, in 11 of 14 lakes, down-core RC and S2:RC patterns were nearly identical and thus our interpretation is not affected. In Fisherman Lake, for example, the down-core decrease in the S2:RC ratio, which is indicative of S2 decomposition, was unchanged. Readers interested in the recalculated RC data are welcome to contact us directly. We are surprised by Outridge et al.’s comment that “...S2/RC profiles were used simplistically as an OM decomposition indicator” since we used the approach of Outridge et al.,² where it is stated that “If diagenesis explained the S2 patterns, S2/RC should decline consistently down-core...”.

Outridge et al. also seem to imply that our characterization of kerogen type was incorrect. We did not overstate our conclusions and merely remarked that the hydrogen index (HI) and oxygen index (OI) values observed in our cores were “characteristic of type III and type II/type III kerogen mixtures”. In addition, our values were similar to those of ref 8 for the Mackenzie River Basin (MRB) who concluded that “The organic matter in the MRB sediments is predominantly type III kerogen as characterized by their low hydrogen indices in the van Krevelen diagram...”.

Outridge et al. also discuss the use of total diatom abundance versus relative algal abundance as a proxy of algal productivity. There are well-understood problems with using the concentration data of microfossils, such as diatoms, as a proxy for past diatom production (e.g., ref 9, pp. 71–72). In fact, Outridge et al. have themselves recognized that “valve counts do not always relate linearly to living autochthonous primary productivity”.² These limitations have led to the almost universal use of relative algal abundance in paleolimnological studies inferring past conditions, including indirect inferences of ice cover and climate-mediated limnological changes that are intimately linked to productivity (e.g., refs 10–19). Furthermore, many surface sediment training sets exist that establish quantitative relationships between present-day limnological properties and diatom relative abundances using multivariate gradient analysis (e.g., refs 20–27). These “calibration sets” are exclusively based on percentage data, while no such “calibration” has been successful for diatom absolute abundances. Absolute diatom abundances were actually calculated in eight of our study lakes: of these, three (Fisherman, Cli, and Amituk) showed significant ($p < 0.05$) relationships between diatom and Hg concentrations, and only one (Amituk) had a significant S2:diatom relationship. Our central conclusions are therefore substantiated using *both* relative and absolute abundance measures. Most importantly, since decreased ice cover (i.e., increased light availability) is a prerequisite for increases in open-water primary production in the high Arctic, on what grounds should we question the indirect links made between increased productivity to changes in diatom assemblages?

We agree that “...TOC or S2 loss alone cannot disprove the scavenging hypothesis” and hope our study has not been

Published: July 08, 2011

misinterpreted. Our major findings¹ were 1. Hg and S2 were uncorrelated in 6 of 14 lakes, 2. In many lakes where Hg and S2 increased through time, algal assemblages either were unchanged or the timing of shifts did not correspond to changes in Hg deposition, and 3. catchment-derived Hg deposition appears to be increasing in many Arctic lakes, possibly due to climate-induced erosion. Finally, we feel that for this field to move forward, future work should: 1. calibrate sediment S2 as an indicator of primary productivity where long-term records of primary production are available, and 2. identify S2 and other compounds that bind Hg in lake water, determine their Hg binding coefficients, and quantitatively determine relationships between changing primary productivity and sediment Hg flux using a combination of laboratory and field-based, particularly whole-ecosystem, experiments.

Jane L. Kirk,^{*,†} Derek C. G. Muir,[†] Dermot Antoniades,[‡] Marianne S. V. Douglas,[§] Marlene S. Evans,^{||} Togwell A. Jackson,[†] Hedy Kling,[⊥] Scott Lamoureux,[#] Darlene S. S. Lim,[▽] Reinhard Pienitz,[‡] John P. Smol,[○] Kailey Stewart,[#] Xiaowa Wang,[†] and Fan Yang[†]

[†]Aquatic Ecosystem Protection Research Division, Environment Canada, Burlington, ON, Canada L7R 4A6

[‡]Centre d'études nordiques, Université Laval, Quebec, QC, Canada G1V 0A6

[§]Canadian Circumpolar Institute, University of Alberta, Edmonton, AB, Canada T6G 1K8

^{||}Aquatic Ecosystem Protection Research Division, Environment Canada, Saskatoon, SK, Canada S7N 3H5

[⊥]Algal Taxonomy and Ecology, Winnipeg, MB, Canada R3T 2 × 8

[#]Department of Geography, Queen's University, Kingston, ON, Canada K7L 3N6

[▽]SETI Institute, Mountain View, CA, United States 94043-2172

[○]Department of Biology, Queen's University, Kingston, ON, Canada K7L 3N6

AUTHOR INFORMATION

Corresponding Author

*Phone: (905) 336-4712; fax: (905) 336-6430; e-mail: Jane.Kirk@ec.gc.ca.

REFERENCES

- (1) Kirk, J. L.; Muir, D.; Antoniades, D.; Douglas, M.; Evans, M.; Jackson, T.; Kling, H.; Lamoureux, S.; Stewart, K.; Lim, D. S.; Pienitz, R.; Smol, J.; Wang, X.; Yang, F. Climate change and mercury accumulation in Canadian high and subarctic lakes. *Environ. Sci. Technol.* **2011**, *45*, 964–970.
- (2) Outridge, P. M.; Sanei, H.; Stern, G. A.; Hamilton, P. B.; Goodarzi, F. Evidence for control of mercury accumulation rates in Canadian high Arctic lake sediments by variations of aquatic primary productivity. *Environ. Sci. Technol.* **2007**, *41*, S259–S265.
- (3) Stern, G. A.; Sanei, H.; Roach, P.; De La Ronde, J.; Outridge, P. M. Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a subarctic lake in Yukon, Canada: Further evidence toward the algal-mercury scavenging hypothesis. *Environ. Sci. Technol.* **2009**, *43*, 7684–7690.
- (4) Carrie, J.; Wang, F.; Sanei, H.; Macdonald, R. W.; Outridge, P. M.; Stern, G. A. Increasing contaminant burdens in an arctic fish, burbot (*Lota lota*), in a warming climate. *Environ. Sci. Technol.* **2010**, *44*, 316–322.
- (5) Lafargue, E.; Espitalité, J.; Marquis, F.; Pillot, D. Rock-Eval 6 applications in hydrocarbon exploration, production and soil contamination studies. *Rev. Inst. Fr. Pet.* **1998**, *53*, 421–437.
- (6) Sanei, H.; Stasiuk, L. D.; Goodarzi, F. Petrological changes occurring in organic matter from recent lacustrine sediments during thermal alteration by Rock-Eval pyrolysis. *Org. Geochem.* **2005**, *36*, 1190–1203.
- (7) Sanei, H.; Outridge, P. M.; Dallimore, A.; Hamilton, P. B. Mercury-organic matter relationships in pre-pollution sediments of thermokarst lakes from the Mackenzie River Delta, Canada: the role of depositional environment. *Biogeochem.* **2010**, DOI: 10.1007/s10533-010-9543-1.
- (8) Carrie, J.; Sanei, H.; Goodarzi, F.; Stern, G.; Feiyue, W. Characterization of organic matter in surface sediments of the Mackenzie River Basin, Canada. *Int. J. Coal Geol.* **2009**, *77*, 416–423.
- (9) Smol, J. P. *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective*. 2nd ed.; Wiley-Blackwell Publishing: Oxford, UK, 2008.
- (10) Douglas, M.; Smol, J.; Blake, W. Marked post-18th century environmental change in high arctic ecosystems. *Science* **1994**, *266*, 416–419.
- (11) Sorvari, S.; Korhola, A. Recent diatom assemblage changes in subarctic Lake Saanaajärvi, NW Finnish Lapland, and their paleoenvironmental implications. *J. Paleolimnol.* **1998**, *20*, 205–215.
- (12) Schmidt, R.; Psenner, R.; Müller, J.; Indinger, P.; Kamenik, C. Impact of late glacial climate variations on stratification and trophic state of the meromictic lake Längsee (Austria): validation of a conceptual model by multi proxy studies. *J. Limnol.* **2002**, *61*, 49–60.
- (13) Rühland, K.; Priesnitz, A.; Smol, J. P. Paleolimnological evidence from diatoms for recent environmental changes in 50 lakes across Canadian arctic treeline. *Arct. Antarct. Alpine Res.* **2003**, *35*, 110–123.
- (14) Bradsahw, E. G.; Rasmussen, P.; Nielsen, H. and lake development at Dallund Sø, Denmark: trends in lake primary production as reflected by algal and macrophyte remains. *Holocene* **2005**, *15*, 1130–1142.
- (15) Smol, J. P.; Wolfe, A. P.; Birks, H. J. B.; Douglas, M. S. V.; Jones, V. J.; Korhola, A.; Pienitz, R.; Rühland, K.; Sorvari, S.; Antoniades, D.; et al. Climate-driven regime shifts in the biological communities of arctic lakes. *Proc. Nat. Acad. Sci.* **2005**, *102*, 4397–4402.
- (16) Michelutti, N.; Wolfe, A. P.; Briner, J. P.; Miller, G. H. Climatically controlled chemical and biological development in arctic lakes. *J. Geophys. Res., [Biogeosci.]* **2007**, *112*, G03002.
- (17) Smol, J. P.; Douglas, M. S. V. From controversy to consensus: making the case for recent climatic change in the Arctic using lake sediments. *Front. Ecol. Environ.* **2007**, *5*, 466–474.
- (18) Lim, D. S. S.; Smol, J. P.; Douglas, M. S. V. Recent environmental changes on Banks Island (N.W.T., Canadian Arctic) quantified using fossil diatom assemblages. *J. Paleolimnol.* **2008**, *40*, 385–398.
- (19) Axford, Y.; Brinder, J. P.; Cooke, C. A.; Francis, D. R.; Michelutti, N.; Miller, G. H.; Smol, J. P.; Thomas, E. K.; Wilson, C. R.; Wolfe, A. P. Recent changes in a remote Arctic Lake are unique within the past 200,000 years. *Proc. Nat. Acad. Sci.* **2009**, *44*, 18443–18446.
- (20) Pienitz, R.; Smol, J. P.; Birks, H. J. B. Assessment of freshwater diatoms as quantitative indicators of past climate changes in Yukon and Northwest Territories, Canada. *J. Paleolimnol.* **1995**, *13*, 21–49.
- (21) Weckstrom, A.; Korhola, A.; Blom, T. The relationship between diatoms and water temperature in thirty subarctic Fennoscandian lakes. *Arctic Alpine Res.* **1997**, *29*, 75–92.
- (22) Korhola, A.; Weckstrom, J.; Nyman, M. Predicting the long-term acidification trends in small subarctic lakes using diatoms. *J. Appl. Ecol.* **1999**, *36*, 1021–1034.
- (23) Laing, T. E.; Smol, J. P. Factors influencing diatom distribution in circumpolar treeline lakes of northern Russia. *J. Phycol.* **2000**, *36*, 1035–1048.
- (24) Lim, D. S. S.; Douglas, M. S. V.; Smol, J. P. Diatoms and their relationship to environmental variables from lakes and ponds of Bathurst Island, Nunavut, Canadian High Arctic. *Hydrobiologia* **2001**, *450*, 215–230.
- (25) Joynt, E. H.; Wolfe, A. P. Paleoenvironmental inference models from sediment diatom assemblages in Baffin Island lakes (Nunavut, Canada) and reconstruction of summer water temperature. *Can. J. Fish. Aquat. Sci.* **2001**, *58*, 1222–1243.
- (26) Ryves, D. B.; McGowan, S.; Anderson, N. J. Development and evaluation of a diatom-conductivity model from lakes in West Greenland. *Freshwater Biol.* **2002**, *47*, 995–1014.
- (27) Antoniades, D.; Douglas, M. S. V.; Smol, J. P. Diatom species-environment relationships and inference models from Isachsen, Ellef Ringnes Island, Canadian High Arctic. *Hydrobiologia* **2004**, *529*, 1–18.