Supporting information (SI)

Mercury Export from the Yukon River Basin and Potential Response to a Changing Climate

PAUL F. SCHUSTER

ROBERT G. STRIEGL

GEORGE R. AIKEN

DAVID P. KRABBENHOFT

JOHN F. DEWILD

KENNA BUTLER

BEN KAMARK

MARK DORNBLASER

18 Pages

6 Figures

The Yukon River Basin Study

During the water years (WY) 2001 through 2005 (WY is October 1 through September 30), the U.S. Geological Survey conducted an extensive five-year water-quality study of the Yukon River from its headwaters in Canada to Pilot Station, Alaska near its mouth (Figure S1) (*1-7*). The overall study included five major sub basin baseline monitoring stations and extensive sampling campaigns for the outlets of 43 tributaries to the Yukon River within the YRB. In Situ measurements included pH, temperature, dissolved oxygen, specific conductance, and greenhouse gases (carbon dioxide and methane). Samples were collected and processed for analysis of carbon and mercury (Hg) species, major ions, trace metals, water isotopes, and nutrients. Two main objectives of the study were to establish a water-quality baseline to assess possible future changes from a warming climate and to investigate the process-based hydrogeochemical evolution of water quality in the basin.

YRB Characteristics

Details of YRB characteristics are given in Brabets et al., 2000 (*8*), and briefly described here. The YRB is comprised of six physiographic regions ranging from plains and lowlands to high rugged mountains resulting in a highly variable continental climate which, in the last 50 years, has generally experienced continuous air temperature warming (*9*). The geology of the YRB is complex; essentially, half of the basin is underlain by sedimentary rocks and the remaining half is composed of intrusive, volcanic, metamorphic, sedimentary/volcanic, and unconsolidated rocks at about 10 percent each. More than half the land cover is needle leaf forest dominated by white spruce in the uplands and black spruce in the lowlands. The dominant soil type is Cryosol (Gelisol) and 75 percent of the YRB is underlain by continuous to discontinuous permafrost. Approximately 30 percent of the YRB is classified as wetland. The complexity of YRB terrain is reflected by its 20 diverse ecoregions.

Carbon and Mercury Sample and Data Collection

The Yukon River at Pilot Station (YRP) was sampled 7 times a year; once in March or April (under ice base flow) and then every 2-3 weeks during open water for WY 2001 through 2005. During this time, filtered total mercury (FHg) and particulate total mercury (PHg) were measured in 37 samples. The most accurate estimation of average exports and yields required measurements of Hg and organic carbon (OC) over a range of hydrologic regimes at a greater than annual scale. During the 5 years of study, minimum, maximum and average discharges were measured and compared closely with those measured over the 33 year long-term record from Pilot Station (YRP) (Figure S2). YRP is defined in this study as the operation outlet of the YRB. It is the furthest downstream location where discharge (Q) can be measured accurately in a confined channel and far enough above the Yukon Delta where there is no tidal influence. Samples collected at YRP represent an integration of surface and groundwater from the YRB. The 2001-05 dataset captured a robust representation of end member or extreme flow events and also included four years in which average flow conditions closely matched the 33-year average (Figure S3).

Extrapolation of the THg record

Measurements of OC and Hg concentrations are limited to 5 consecutive years (2001-2005) at YRP. There is, however, at long-term data base of continuous Q. Based on the weak but significant relation between OC and Q and the strong relation between FHg and DOC and PHg and POC, a multi-linear regression was developed to reconstruct the Hg export record based on Q. First, DOC and POC concentrations were calculated from their weak but significant correlation with Q (Figure S4).

Calculated DOC (mg/L) = 1E-05[Q (cfs)]+2.5064 (equation 1)

Calculated POC (mg/L) = 7E-06[Q (cfs)]+0.7053 (equation 2)

Second, FHg and PHg concentrations were calculated from their correlation with DOC and POC (See Figure 2 in paper), respectively, as determined from empirical data but using the calculated DOC and POC values from equations 1 and 2.

Calculated FHg (ng/L) = 0.2172[DOC (mg/L)]+0.0352 (equation 3)

Calculated PHg (ng/L) = 3.2825[POC (mg/L)]+3.7833 (equation 4)

Third, FHg and PHg concentrations were summed up and calculated into total annual THg exports. Finally, annual averages of export were calculated to remove seasonal variability and 3- and 5-year running averages were calculated to identify any trends on a decadal scale (See Figure 4 in paper). The USGS gage was decommissioned from 1997 to 2000, resulting in a 4.5 year hiatus in the 34-year record of Q data collection (2001 has a partial year of Q). Annual Hg export averages calculated from the multi-linear regression were also plotted with annual Hg exports calculated by LOADEST for the WY's 2002-05. Both approaches were in good agreement during the highly variable measured annual exports from 2002 through 2005 indicating their reliability as predictive tools.

Additional Methylmercury Research

As part of the larger YRB study, MeHg concentrations were measured intensely at 5 major sub basin scales and discretely at the outlets of 43 major tributaries to the Yukon River during early and late summer (Hg methylation potential should be at its annual maximum in late summer). Based on measurable TMeHg concentrations, there is evidence of Hg methylation. However, TMeHg/THg ratios are much lower relative to those measured in other studies and there is no relation between the percent of wetland cover in a sub basin to measured TMeHg concentrations, exports, or yields (Figure S6).

<u>Resources for Table 2</u>

An extensive literature review was conducted to develop Table 2. Because the citations are numerous they are given in the narrative that follows. Specific details of Table 2 are also given.

Churchill and Nelson Rivers

Mercury (Hg) concentrations and export are from Hare et al. (*22*) who sampled in high flow conditions for the Nelson River, and during high and low flow for the Churchill River during 2003-2005. The number of sites and total number of Hg samples were not reported by Hare et al. (*22*). TSS exports are from Hare et al. (*22*) and are reported in previous studies. Kirk et al. (*10*) also reported Hg concentrations and Hg export (not shown in Table 2) that were lower, but of the same magnitude as Hare et al. (*22*) from a 2003-2007 sampling effort. Average water export, total methylmercury (TMeHg) concentration, and TOC export are from Kirk et al. (*10*), but as noted with an asterisk in Table 2, the TOC values reported are filtered, or dissolved organic carbon (DOC) (*10*). The total number Hg samples from the 3 sampling sites were not reported by Kirk et al. (*10*). Watershed areas, including the Churchill River diversion watershed area, are from the National Atlas of Canada (*11*). In this study, the diverted area of the Churchill

River was added to the Nelson River watershed area to include the total area that contributes to the Nelson River's water export. Percent permafrost cover was estimated in this study with GIS software using permafrost geospatial data from Brown et al. (*23*) and watershed boundary geospatial data from the Department of Natural Resources Canada (*24*). The Churchill River watershed area and the Churchill River diversion watershed areas were extracted from a larger regional watershed boundary in this study, and as such, estimates of percent permafrost cover for both the Churchill and Nelson River watersheds have additional uncertainty when compared with other watersheds in Table 2.

Mackenzie River

Hg and TMeHg concentrations and exports, and average water export are from Leitch et al. (*13*) who sampled the lower Mackenzie at 79 sites during the 2003-2005 summers and 2004-2005 freshets. The total number of Hg samples was not reported by Leitch et al. (*13*). As noted with an asterisk in Table 2, TMeHg concentration and export is reported as filtered or dissolved methylmercury (DMeHg) (*13*), and is likely an underestimate of TMeHg. TOC export is from PARTNERS (*14*). TSS export is from Hare et al. (*22*) and is reported from previous studies. Percent permafrost cover is from Dyke et al. (*26*). Watershed area is from Vörösmartya et al. (*12*).

Mississippi River

Hg and TSS concentrations are from the Louisiana Department of Environmental Quality, sampled 62 times during 2001-2004 (Parsons et al. (*15*)). Particulate mercury (PHg) and total mercury (THg) concentrations were not tabulated in Parsons et al. (15), but can be found in calculations there. The average TSS concentration was multiplied by average water export to estimate TSS export in this study. Watershed area is reported in Vörösmartya et al.

(*12*), and average water export is from Mead et al. (*17*), which agrees with Parsons et al. (15). TOC export was estimated in this study as the average of values from Guo (*16*).

St. Lawrence River

FHg concentration, watershed area, and Hg export are from Quémerais et al. (*18*) who sampled the St. Lawrence River at Québec City 79 times during 1995-1996. The PHg concentration was estimated in this study from PHg export reported in Quémerais et al. (*18*) and the average water export reported in Benke et al. (*19*). The THg concentration is estimated in this study as the sum of FHg and PHg concentrations. TOC export is from Pocklington et al. (*20*) and TSS export is from Rondeau et al. (*27*). The percent permafrost area was estimated in this study with GIS software using permafrost geospatial data from Brown et al. (*23*) and watershed boundary geospatial data from the Department of Natural Resources Canada (*24*).

Lena, Ob, and Yenisei Rivers

FHg concentrations, Hg exports and average water exports are from Coquery et al. (*21*) who very minimally sampled the Lena in 1991 and the Ob and Yenisei in 1993. Coquery et al. (21) acknowledge the uncertainties associated with Hg exports based on their limited data set and despite using methods to extrapolate yearly concentrations conclude that their published values are likely to be underestimates. Table 2 includes data from Coquery et al. (21) with the understanding that the data are limited temporally yet may provide meaningful comparisons with the Yukon River Basin. PHg concentrations are averages that were estimated in this study from paired data of Hg concentrations in suspended sediments and suspended sediment concentrations found in in Coquery et al. (*12*). THg concentrations are estimated in this study as the sums of FHg and PHg concentrations. TSS exports are from Hare et al. (*22*), and watershed areas are from Vörösmartya et al. (*12*). TOC exports are from PARTNERS (*14*) and percent permafrost covers were estimated in this study using tabulated data in McClelland et al. (*25*). It should be noted that permafrost cover data were listed with sporadic and intermittent (isolated) data combined in one column and calculations were performed by combining the percent permafrost associated with each category, 10-50% and 0-10%, respectively, into one range of 0-50%, because McClelland et al. only published data with those categories combined.

Literature Cited

1) Schuster, P.F. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2001. *Open-File Report 2003-03427; U.S. Geological Survey*, **2003**. Available at http://water.usgs.gov/pubs/of/2003/ofr03427/ (accessed Aug. 2010).

2) Schuster, P.F. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2002. *Open-File Report 2005-1199; U.S. Geological Survey*, **2005**. Available at http://pubs.usgs.gov/of/2005/1199/ (accessed Aug. 2010).

3) Schuster, P.F. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2003; *Open-File Report 2005-1397. U.S. Geological Survey*, **2005**. Available at http://pubs.usgs.gov/of/2005/1397/ (accessed Aug. 2010).

4) Schuster, P.F. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2004. *Open-File Report 2006-1258; U.S. Geological Survey*, **2006**. Available at http://pubs.usgs.gov/of/2006/1258/ (accessed Aug. 2010).

5) Dornblaser, M.; Halm, D.R. Water and sediment quality of the Yukon River and its tributaries, from Eagle to St. Mary's, Alaska, 2002-2003. *Open-File Report 2006-1228; U.S. Geological Survey*, **2006**. Available at http://pubs.usgs.gov/of/2006/1228/ (accessed Sept. 2010).

6) Halm, D.R.; Dornblaser, M.M. Water and sediment quality in the Yukon River and its tributaries between Atlin, British Columbia, Canada, and Eagle, Alaska, USA, 2004. *Open-File Report 2007-1197; U.S. Geological Survey*, **2007**. Available at http://pubs.usgs.gov/of/2007/1197/ (accessed July 2010).

7) Schuster, P.F. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2005. *Open-File Report 2007-1037; U.S. Geological Survey*, **2007**. Available at http://pubs.usgs.gov/of/2007/1037/ (accessed Aug. 2010).

8) Brabets, T.P.; Wang, B.; Meade, R.H. Environmental and hydrologic overview of the Yukon River Basin, Alaska and Canada. *Water-Resources Investigations Report 99-4204; U.S. Geological Survey*, **2000**. Available at http://pubs.usgs.gov/wri/wri994204/ (accessed July 2010).

9) Chapman, W.L. and Walsh, J.E. Recent variations of sea ice and air temperature in high latitudes. *Bulletin of American Meteorology Society*, **1993**, *74*, 33-47.

10) Kirk, J.; St Louis, V.L. Multiyear total and methyl mercury exports from two major sub-arctic rivers draining into the Hudson Bay, Canada. *Environ. Sci. Technol.*, **2009**, *43*, 2254-2261.

11) National Atlas of Canada, http://atlas.nrcan.gc.ca/site/english/maps/archives/5thedition/environment/water/mcr405.

12) Vörösmartya, C.J.; Feketea, B.M.; Meybeckc, M.; Lammersa, R.B. Geomorphometric attributes of the global system of rivers at 30-minute spatial resolution. *Journ. Hydro.* ***2000***, *237*, 17-39.

13) Leitch, D.R.; Carrie, J.; Lean, D.; Macdonald, R.W.; Stearn, G.A.; Wang, F. The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. *Sci. Tot. Environ*. **2007**, *373*, 178-195.

14) PARTNERS, Arctic Great Rivers Observatory, **2007**. LOADEST results from data at: http://ecosystems.mbl.edu/partners/data.html. Accessed 1/2011

15) Mississippi River Water Quality and the Clean Water Act: Progress, Challenges, and Opportunities Committee on the Mississippi River and the Clean Water Act. National Research Council ISBN: 0-309-11410-1, 2008, 252 p.

16) Guo, L. Isotopic composition and export fluxes of organic carbon species from the lower Mississippi River. American Geophysical Union, Fall Meeting, 2010, abstract OS22A-01, http://adsabs.harvard.edu/abs/2010AGUFMOS22A..01G accessed 5/11

17) Meade, R.H., Ed. Contaminants in the Mississippi River. *U.S. Geological Survey Circular 1133*, Reston, Virginia, **1995**. http://pubs.usgs.gov/circ/circ1133/

18) Quémerais, B.; Cossa, D.; Rondeau, B.; Thanh, T.P.; Gagnon, P.; Benoít, F. Sources and fluxes of mercury in the St Lawrence River. *Environ. Sci. Technol*. **1999**, *33* (6), 840-849.

19) Benke, A.C.; Cushing, C.E. Rivers of North America. *Academic Press, ISBN 9780120882533*, **2005**, p.990.

20) Pocklington, R.; Tan, F.C. Seasonal and annual variations in the organic matter contributed by the St Lawrence River to the Gulf of St. Lawrence. *Geochim. Cosmochim. Acta.* **1987**, *51,* 2579-2586..

21) Coquery, M.; Cossa, D.; Martin, J.M. The distribution of dissolved and particulate mercury in three Siberian estuaries and adjacent arctic coastal waters. *Water, Air, and Soil Pollut.* **1995**, *80*, 653-664.

22) Hare, A.; Stern, G.A.; Macdonald, R.W.; Kuzyk, Z.Z.; Wang, F. Contemporary and preindustrial mass budgets of mercury in the Hudson Bay marine system: The role of sediment recycling. *Sci. Tot. Environ*. **2008**, *406*, 190-204.

23) Brown, J.; Ferrians,; O.J. Jr.; Heginbottom, J.A.; Melnikov, E.S. Circum-arctic map of permafrost and ground ice conditions. *National Snow and Ice data Center/World Data Center for Glaciology. Digital Media, Boulder, Colorado*, **1998**. Revised February 2001.

24) Department of Natural Resources Canada, *GeoGratis*, **2011**, http://geogratis.gc.ca. Accessed 6/2011.

25) McClelland, J.W.; Holmes, R.M.; Peterson, B.J.; Stieglitz, M. Increasing river discharge in the Eurasian Arctic; Consideration of dams, permafrost thaw, and fires as potential agents of change. *J. Geophys. Res*. **2004**, *109*, D18102, doi:10.1029/2004JD004583.

26) Dyke, L.D.; Aylsworth, J.M.; Burgess, M.M.; Nixon, F.M.; Wright, F. Permafrost in the Mackenzie Basin, its influence on land-altering processes, and its relationship to climate change. Mackenzie Basin Impact Study: Final Report. **1997,** 111-116.

27) Rondeau, B.; Cossa, D.; Gagnon, P.; Bilodeau, L. Budget and sources of suspended sediment transported in the St. Lawrence River, Canada. *Hydrol. Process.* **2000**, *14*, *21-36.*

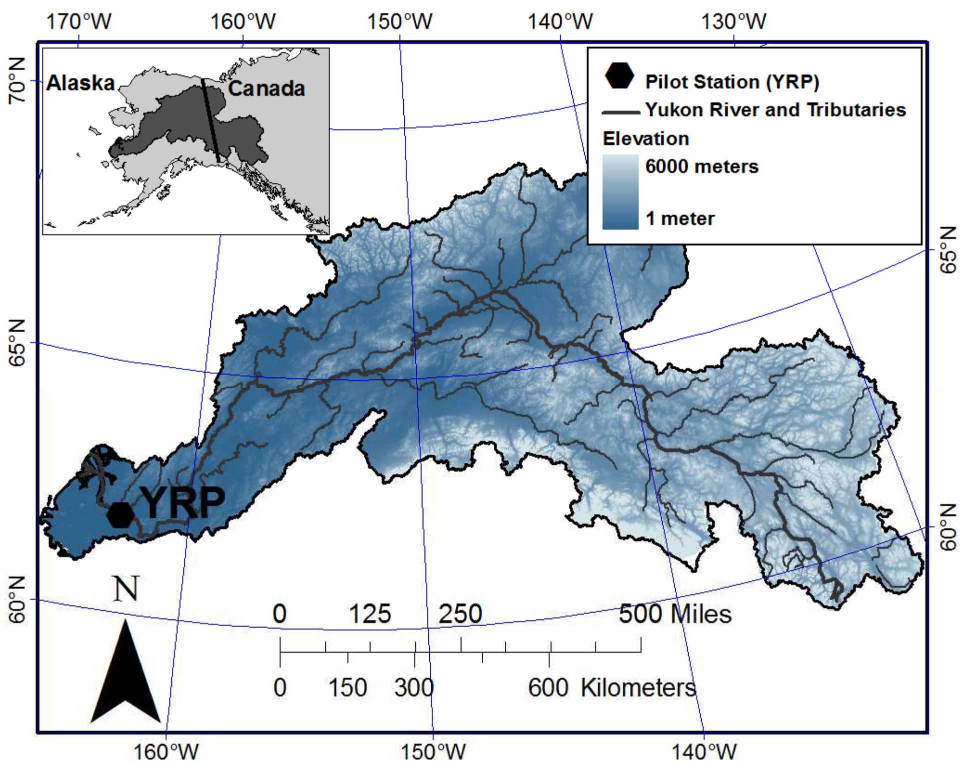

Figure S1. The Yukon River Basin (YRB) watershed showing the location of water sampling and continuous discharge measurements at Pilot Station (YRP); YRP is defined as the operational outlet of the YRB.

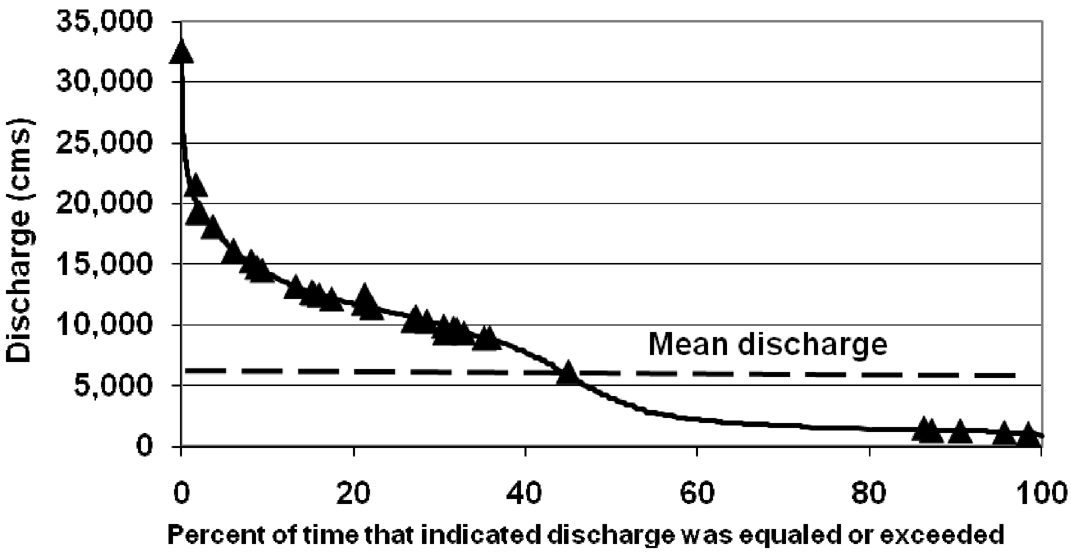

Figure S2. Flow duration curve for the Yukon River at Pilot Station (YRP) compiled from continuous discharge data from 1976 to 2009. The number of samples collected from 2001 through 2005 are plotted on the curve. Samples collected at >80% were during winter and early spring under ice at base flow.

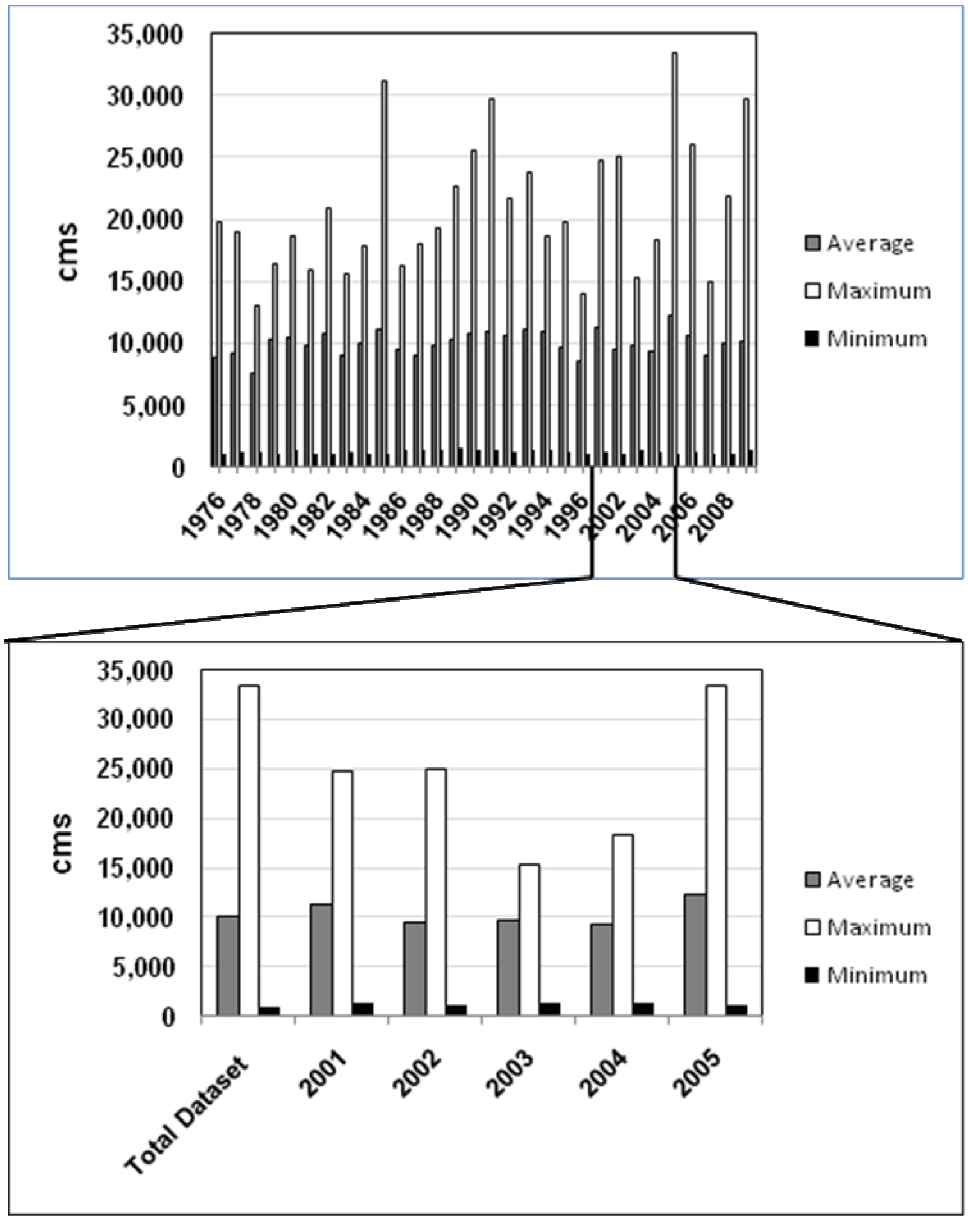

Figure S3. April-September discharge (cubic meters per second, cms) at Pilot Station for the study period compared to the 29-year record (1976-2009). USGS gage was deactivated from 1996 to 2000. Source: http://nwis.waterdata.usgs.gov

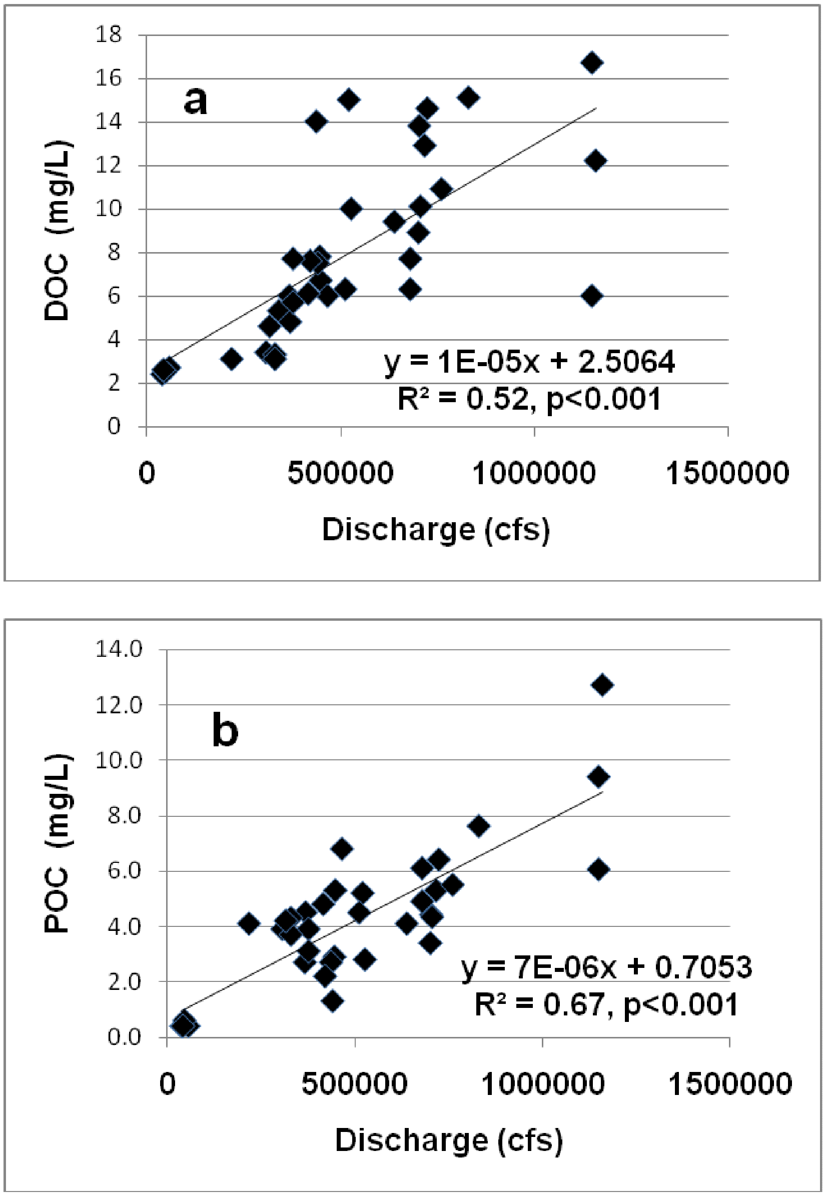

Figure S4. Relation of discharge to organic carbon concentration, a) dissolved organic carbon (DOC), b) particulate organic carbon (POC).

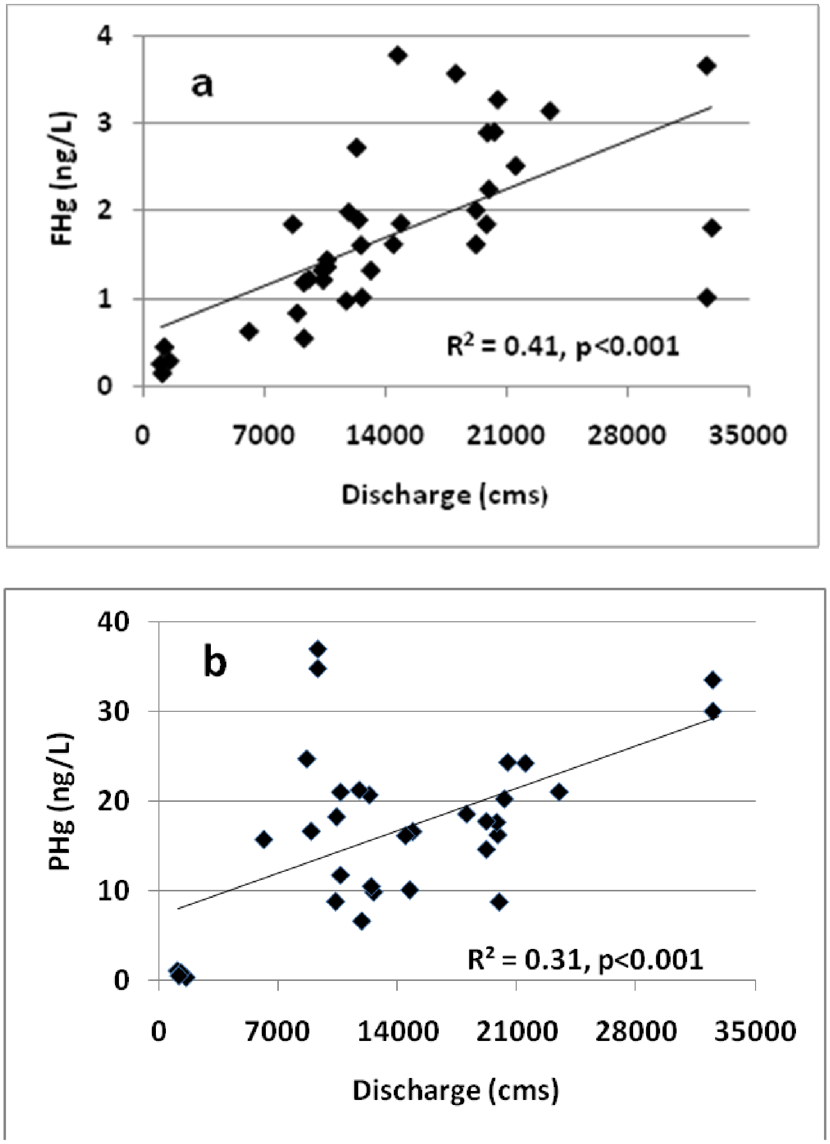

Figure S5. Relation of discharge to mercury concentration, a) filtered (dissolved) total mercury (FHg), b) particulate total mercury (PHg)

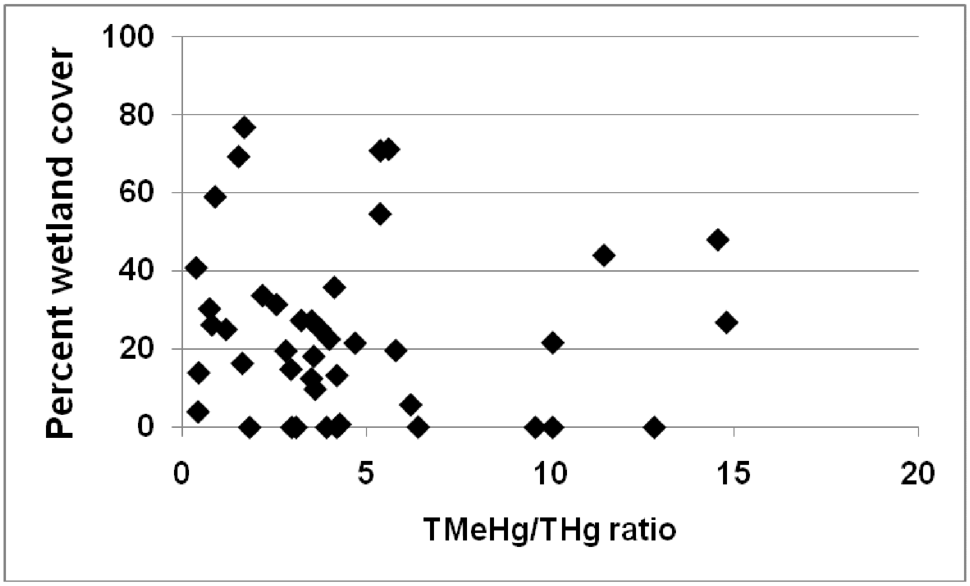

Figure S6. The ratio of Total Methylmercury (TMeHg) to total mercury (THg) concentrations discretely measured in late summer plotted against the percent of wetland cover for 43 subbasins within the YRB showing no significant correlation.