

1 **Legacy mercury and stoichiometry with C, N, & S in soil, pore water, and stream water**
2 **across the upland-wetland interface: the influence of hydrogeologic setting.**

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12 **Online Supporting Information**

13 *Quality Control for Analytical Procedures*

14 *Stream Water and Pore Water Analyses*

15 Dissolved organic carbon (DOC) concentrations in stream water and pore water were
16 determined for filtered samples (0.7 µm glass fiber filter, pre-baked at 450°C) with a Dohrmann
17 Phoenix 8000 Analyzer using the persulfate-ultraviolet oxidation method (APHA 1998). The
18 concentration of total mercury was determined for filtered samples (THg_d); prior to analysis for
19 THg_d, samples were subjected to UV light treatment to remove measurement interferences (i.e.,
20 high concentrations of DOC). Mercury concentrations were quantified according to EPA
21 Method 1631 using automated CVAFS (Tekran, Toronto, Ontario, Canada, USEPA 1998).
22 Here, we provide a summary of the QAQC results for each analyte.

23 *Dissolved Organic Carbon* – Linear standard curves (0 – 100 mg/L DOC) had a
24 coefficient of variation (r) > 0.9998. Percent recovery of the expected value for the lowest
25 standard (1 mg/L DOC) was 121.2% (SE = 3.8%, n = 3); all remaining standards recovered
26 within 95.1 – 106.4% across all analyses. The method detection limit (MDL) estimated from
27 standards run with analytical sessions was 0.4 mg/L DOC. Second source calibration

28 verification standards analyzed at 10 mg/L, 30 mg/L, and 50 mg/L recovered at 100.2% (SE =
29 1.1, n = 11). Every set of 10 samples (3 sets per analytical session) was bracketed by a
30 continuing calibration verification standard (from the midpoint of the standard curve) and
31 continuing calibration blanks (filtered de-ionized water). Continuing calibration verification
32 standards (50 mg/L DOC) recovered at 102.2% (SE = 1.5, n = 20). Nearly all initial and
33 subsequent continuing calibration blanks were below the reporting limit (< 1 mg/L DOC, n =
34 18), two continuing calibration blanks were measured at 1.3 mg/L DOC. Because of sample
35 volume limitations, only a small number of samples were analyzed with matrix spikes or in
36 duplicate. Matrix spikes (10 mg/L or 50 mg/L DOC) were recovered at 102.4% (SE = 1.9, n =
37 4). Relative Percent Difference (RPD) among duplicate sample analyses was 3.5% (SE = 0.7, n
38 =7).

39 *Total Mercury* -The percent relative standard deviation (%RSD) of the mean calibration
40 factor (CF_m) for standards (0.5 – 100 ng/L Hg) averaged 3.5% (SE = 0.6%, n = 9) across all
41 analyses. Percent recovery of the expected value for the lowest standard was 104.3% (SE =
42 2.9%, n = 9). Initial calibration verification standards run after each standard curve using a
43 certified second source had a percent recovery of 102.1% (SE = 0.9%, n = 11). The method
44 detection limit (MDL) estimated from standards run within analytical sessions was 0.31 ng/L Hg
45 (APHA 1998). Samples were analyzed in batches with quality control, and batches did not
46 exceed 20 samples. All initial calibration blanks and subsequent continuing calibration blanks
47 were below the MDL (<0.31 ng/L, n = 76). Initial and ongoing instrument precision and
48 recovery checks utilizing either a 3ng/L or 5 ng/L standard solution recovered at 96.6% (SE =
49 0.6%, n = 53). Continuing calibration verification standard recovery was 95.9% (SE = 0.8%, n =
50 65). To assess analytical accuracy and precision, matrix spike (25 ng/L) samples were analyzed,
51 and average recovery was 97.4% (SE = 1.0%, n = 33). Relative percent difference among
52 duplicate sample analyses was 2.0% (SE = 0.4%, n = 32). Certified reference materials were
53 successfully recovered throughout all analytical sessions; after dilution, the recovery of NIST
54 1641d (mercury in water) was 103.1% (SE = 1.6%, n = 14).

55 *Soil and Wetland Peat Analyses*

56 We analyzed soil and wetland peat samples for total mercury (THg) using a hot refluxing
57 nitric:sulfuric (3:7) acid digestion, followed by analysis with a Tekran 2600 Cold Vapor Atomic
58 Fluorescence Spectrophotometer (EPA Method 1631)(USEPA 1998). We analyzed soil and
59 wetland peat samples for carbon, nitrogen, and sulfur using an Elemental Combustion System,
60 Model ECS 4010, manufactured by Costech Analytical Technologies. Here, we provide a
61 summary of the quality control results for each analyte.

62 *Total Mercury* - Standard curves ranged from 0.5 – 100 ng/L Hg and all had a coefficient
63 of variation (r) > 0.9998. Percent recovery of the expected value for the lowest standard was
64 92.9% (SE = 5.0%, $n = 14$), and the average percent recovery of expected values for all standards
65 was 98.3% (SE = 1.0%, $n=14$ sets of standards). Initial calibration verification standards (50
66 ng/L) run after each standard curve using a certified second source had a percent recovery of
67 101.0% (SE = 2.8%, $n = 14$). The method detection limit (MDL) estimated from standards run
68 within analytical sessions was 0.25 ng/L Hg (APHA 1998). Samples were analyzed in batches
69 with quality control, and batches did not exceed 20 samples. Nearly all initial calibration blanks
70 and subsequent continuing calibration blanks were below the MDL (<0.25 ng/L, $n = 66$), eight
71 blanks ranged between the MDL and the reporting limit (0.25 – 0.50 ng/L, $n=8$). One batch
72 included several blanks that ranged from 0.63 – 0.99 ng/L ($n = 4$); however all of the acid
73 digestion blanks were still below the reporting limit (< 0.50 ng/L), and acid digested sample
74 solutions were all > 7.2 ng/L (mean = 30.3 ng/L). Across all analytical batches, acid digestion
75 blanks were below the MDL (< 0.25 ng/L, $n = 63$), two were between the MDL and the reporting
76 limit (0.25 – 0.50 ng/L, $n=2$). Initial and ongoing instrument precision and recovery checks
77 utilizing a 5 ng/L standard solution recovered at 100.9% (SE = 0.9%, $n = 26$). Continuing
78 calibration verification standard (50 ng/L) recovery was 102.3% (SE = 0.3%, $n = 64$). To assess
79 analytical accuracy and precision, matrix spike (25 ng/L) and matrix spike duplicates were
80 analyzed, and average recovery was 99.8% (SE = 0.81, $n = 49$ pairs); the relative percent
81 difference (RPD) between matrix spike duplicates was 2.8% (SE = 0.6%, $n = 49$). Relative

82 standard deviation (RSD) among triplicate sample analyses was 6.8% (SE = 1.3%, n = 25).
83 Certified reference materials were successfully recovered throughout all analytical sessions; the
84 average concentration of NRCC Mess3 marine sediments (91 ± 9 ng/g) was determined to be
85 94.4 (SE = 0.7, n = 27), a recovery of 103.7% (SE = 0.8, n = 27); the average concentration of
86 NIST #1515 Apple Leaves (44 ± 4.0 ng/g) was determined to be 43.7 ng/g (SE = 0.4, n = 27), a
87 recovery of 99.4% (SE = 0.8, n = 27).

88 *Carbon and Nitrogen* - Standard curves were run using variable weights of atropine (70.56%
89 C, 4.84% N) ranging from 0.34 - 12.66 mg C and 0.040 - 0.809 mg N; all standard curves had a
90 coefficient of variation (r) > 0.9998. Percent recovery of the expected value for the lowest
91 standard was 99.9% (SE = 1.5%, n = 6) for carbon, and 100.7% (SE = 2.0%, n = 6) for nitrogen.
92 Average percent recovery of expected values for all standards was 100.5% (SE = 0.1%, n=6) for
93 carbon, and 100.0% (SE = 0.2%, n=6) for nitrogen. Initial calibration verification standards run
94 after each standard curve using acetanalide as a second source (71.07% C, 10.37% N) had a
95 percent recovery of 99.9% (SE = 0.8%, n = 6) for carbon, and 98.0% (SE = 2.4%, n = 6) for
96 nitrogen. The method detection limit (MDL) estimated from standards run within analytical
97 sessions was 0.053 mg C and 0.005 mg N (APHA 1998). Samples were run in analytical
98 batches, with batches consisting of one, two, or three sets of 10 samples (i.e., 10-30 samples per
99 batch). Within each batch, we analyzed one aliquot of certified reference material (Apple
100 Leaves, NIST #1515, 47.6% C, 2.25% N), and one sample of soil or wetland peat in duplicate.
101 Every set of 10 samples was bracketed by a continuing calibration verification standard (from the
102 midpoint of the standard curve) and a continuing calibration blank (empty tin). The percent
103 recovery of the expected value for NIST #1515 Apple Leaves was 98.2% (SE = 0.6%, n = 16)
104 for carbon, and 94.6% (SE = 1.0%, n= 16) for nitrogen. The relative percent difference of
105 duplicate sample analyses was 1.9% (SE = 0.8%, n = 16) for carbon, and 4.5% (SE = 1.1%, n =
106 16) for nitrogen. The percent recovery of continuing calibration verification standards was
107 99.6% (SE = 0.4%, n = 50) for carbon, and 99.5% (SE = 0.4%, n = 50) for nitrogen; all initial
108 and continuing calibration blanks were below the method detection limit.

109 *Sulfur* - Standard curves were run using variable weights of 2,5 Bis (5-tert-butyl-2-
110 benzoxazolyl) thiopene (BBOT; 7.44% S) ranging from 0.040 mg S to 0.809 mg S, and had a
111 coefficient of variation (r) > 0.999. Percent recovery of the expected value for the lowest
112 standard was 97.2% (SE = 2.9%, n = 7). Average percent recovery of expected values for all
113 standards was 99.2% (SE = 0.6%, n=7). The method detection limit (MDL) estimated from
114 standards run within analytical sessions was 0.015 mg S (APHA 1998). Samples were run in
115 analytical batches, with batches consisting of one, two, or three sets of 10 samples (i.e., 10-30
116 samples per batch). Within each batch, we analyzed one or two second source calibration
117 verification standards (sulfanilamide; 18.62% S) in conjunction with an initial calibration blank,
118 and one sample of soil or wetland peat in duplicate. Every set of 10 samples was bracketed by a
119 pair of continuing calibration verification standards (from the midpoint of our curve) and
120 continuing calibration blanks (empty tin). The percent recovery of the second source was
121 100.5% (SE = 1.5%, n = 23), and the relative percent difference of duplicate sample analyses
122 was 17.1% (SE = 3.9%, n = 9). The percent recovery of the expected value for continuing
123 calibration verification standards was 105.0% (SE = 1.1%, n = 100) and all initial and continuing
124 calibration blanks were below the method detection limit.