1   **Increased Accumulation of Sulfur in Lake Sediments of the High Arctic**

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25

26 **Abstract**

27   We report a synchronous increase in accumulation of reduced inorganic sulfur since *c.* 1980 in

28   sediment cores from eight of nine lakes studied in the Canadian Arctic and Svalbard (Norway).

29   Sediment incubations and detailed analyses of sediment profiles from two of the lakes indicate

30   that increases in sulfur accumulation may be due ultimately to a changing climate. Warming-

31   induced lengthening of the ice-free season is resulting in well-documented increases in algal

32   production and sedimentation of the resulting detrital matter. Algal detritus is a rich source of

33   labile carbon, which in these sediments stimulates dissimilatory sulfate reduction. The sulfide

34   produced is stored in sediment (as acid volatile sulfide), converted to other forms of sulfur, or

35   reoxidized to sulfate and lost to the water column. An acceleration of the sulfur cycle in Arctic

36   lakes could have profound effects on important biogeochemical processes, such as carbon burial

37   and mercury methylation.

Introduction

Unprecedented warming of the Arctic is resulting in a cascade of events to push lake biogeochemistry beyond its Holocene limits (*1*). Surface air temperatures across the Arctic increased, on average, by 1.5°C during *c.* 1840-1950, decreased slightly during *c.* 1950-1970, and since then are increasing again, but at an accelerated rate (*2, 3*). From *c.* 1980 to the present, weather stations in the Canadian Arctic archipelago and Svalbard (Norway), for example, have commonly recorded upwards of 2°C increases in annual mean temperature (*4, 5*). The effect on lake physics thus far has been to delay the formation of ice cover and to accelerate its breakup (*6*). Quantitative records are rare, but a recent analysis of satellite images of "perennially ice-capped lakes" on northern Ellesmere Island, for example, revealed that the lakes now lose a substantial portion (sometimes 100%) of ice cover during summer (*7*). Ice cover limits the sunlight available to photosynthetic autotrophs underneath in the unfrozen water, and lengthening of the ice-free season has, in effect, resulted in a longer growing season (*8*). Algae have responded with dramatic increases in abundance and diversity (*9*), which, in turn, is resulting in a greater flux of algal detritus to sediments. The latter is evidenced by pigment records (*10, 11*), Rock Eval pyrolysis of bulk organic matter (*12*), and up-core increases in both the accumulation of organic carbon (beyond what is expected from progressive diagenetic consumption of a constant supply of organic carbon) and the ratio of ^{13}C to ^{12}C (*13*).

Our objective was to determine if this cascade extends to sedimentary sulfur cycling. Sulfur is a major nutrient for all organisms and also plays an important role in the cycling of other nutrients, trace metals, and radioisotopes, largely via dissimilatory sulfate reduction and the sulfide that is produced (*14*). Sediments of ultraoligotrophic Arctic lakes have been compared (*15*) to deep-sea sediments, where low rates of organic carbon flux limit sulfate reduction (*16*).

61   It is an imperfect comparison, however, because sulfate reduction in freshwater systems is also

62   generally limited by low sulfate concentrations. Still, in sediments of Toolik Lake (68° N; *15*)

63   and Lake DV-09 (75° N; *17*) sulfide formation was thought to be at least co-limited by low

64   organic carbon content. As aptly pointed out by Chételat and Amyot (*18*), though, drastic effects

65   can occur with even slight increases in algal production in these resource-poor lakes. Increases

66   in the sedimentation of algal detritus rich in organic carbon may act, as is the case for sediments

67   in deep basins of the Arctic Ocean (*19*), to stimulate sulfate reduction. We tested this hypothesis

68   with sediment archives, incubation experiments, and newly-collected sediment cores processed

69   to preserve sulfur redox chemistry.

70

71   **Experimental Section**

72   Archived sediment cores from five lakes in the Canadian Arctic archipelago (*20*) and four lakes

73   in Svalbard (*21*) were analyzed for total reduced inorganic sulfur. Information about the lakes is

74   given in Table 1. Details of the collection, processing, and dating of cores can be found in the

75   supporting information. Sulfur analysis followed the chromium reduction method of Canfield et

76   al. (*22*). We selected this method because although the handling of the archived cores very likely

77   resulted in oxidation of some forms of reduced inorganic sulfur (e.g., FeS), the oxidation

78   products are still obtainable by chromium reduction. One out of every ten samples was analyzed

79   in duplicate, and the mean percent relative standard deviation (%RSD) of duplicates was 8.6%.

80   Concentrations were multiplied by sedimentation rates to calculate accumulation (or flux) rates

81   of total reduced inorganic sulfur.

82   Inferential statistics were used to relate accumulation rates of total reduced inorganic

83   sulfur to variables that may explain trends both within and among cores. Variables included

84   other elements analyzed in the cores (Canada: Al, Zn, reactive Fe, reactive Mn, Pb, Hg, organic

85   C, organic N; Svalbard: Si, Ti, Ca, K, Fe, Mn, Cu, Pb, Zn, loss-on-ignition (LOI) as a proxy for

86   organic matter) and records of sulfate deposition and temperature. Elemental data are from Muir

87   et al. (*20*) and Boyle et al. (*23*). Sulfate deposition records are from ice cores (*24, 25*).

88   Temperature records (mean surface air temperature during June, July, and August) are from

89   Overpeck et al. (*2*) and were extended to the year 2000 with data from Environment Canada (*4*)

90   and the Norwegian Meteorological Institute (*5*). Within lakes, accumulation of total reduced

91   inorganic sulfur was related to each variable with simple linear regression. Among lakes,

92   relationships of possible predictors and accumulation of total reduced inorganic sulfur were

93   evaluated with a random-effects analysis-of-variance (ANOVA) approach.

94   Two lakes in the Canadian Arctic archipelago, Amituk Lake and Char Lake, were cored

95   again to better elucidate the factors controlling the sedimentary accumulation of inorganic sulfur.

96   These lakes were chosen because they are relatively easy to access from the Polar Continental

97   Shelf Program base and, for High Arctic lakes, they are well studied. Importantly, both lakes

98   have recently documented climate-induced increases in algal production (*17, 26, 27*). Details of

99   core collection and processing, which was performed to minimize exposure to air and thus

100   preserve sulfur redox chemistry, can be found in the supporting information. For each lake, one

101   core was used for incubation experiments and two cores were used for analysis of sulfur forms

102   and their isotopic compositions.

103   Incubation experiments with the sediment slurries from Amituk Lake and Char Lake

104   were conducted to determine the effects of sulfate and labile carbon supplies on sulfide

105   formation. The experiment consisted of nine treatments (each consisting of three replicates): (1)

106   time-zero control (frozen at beginning of incubation), (2) control, (3) 200 μM molybdate

107   (metabolic inhibitor of sulfate-reducing bacteria), (4) 200 µM sulfate, (5) 200 µM acetate (labile

108   carbon), (6) 200 µM molybdate and 200 µM sulfate, (7) 200 µM molybdate and 200 µM acetate,

109   (8) 200 µM sulfate and 200 µM acetate, and (9) 200 µM molybdate, 200 µM sulfate, and 200

110   µM acetate. Details of incubation set up, which was (again) performed to minimize exposure to

111   air, can be found in the supporting information. Incubations were run for 16 d and 18 d for

112   sediments from Amituk Lake and Char Lake, respectively, and then terminated by freezing at -

113   20°C. The incubated sediment slurries were then freeze-dried, and the dried sediment was

114   analyzed for acid volatile sulfide (AVS) according to Canfield et al. (28). We were specifically

115   interested in AVS because it represents the short-term end products of sulfate reduction. By

116   excluding other forms of reduced inorganic sulfur, which can constitute a majority of the total,

117   the likelihood of observing significant effects in these brief experiments was increased. To test

118   for differences in AVS among treatments, a one-way ANOVA and Tukey-Kramer posthoc tests

119   were performed for each lake. It should be noted that the incubations were likely not anoxic, at

120   least at the beginning, but the results indicate that sulfate reduction occurred.

121   To analyze sulfur forms and their isotopic compositions in the sediment cores from

122   Amituk Lake and Char Lake, we used a sequential extraction method similar to that of Canfield

123   et al. (28). The reduced inorganic forms extracted include AVS (primarily HS^- and FeS),

124   elemental sulfur (S^0), and pyrite (as Cr-reducible S; CRS). The organic forms extracted include

125   hydrolyzable S (HyS) and non-CRS, both of which likely are derived from biosynthesis, but the

126   latter being more refractory than the former. One out of every ten samples was analyzed in

127   duplicate, and the mean %RSD of duplicates was 8.8%. Further details of the extractions can be

128   found in the supporting information. Stable sulfur isotopic compositions ($\delta^{34}S$) were analyzed in

129   AVS, S^0, and pyrite by isotope-ratio mass spectrometry (29), with a precision of at least ± 0.5‰.

130   Concentrations of total sulfur were directly measured on a separate subsample of sediment and

131   also calculated as the sum of inorganic and organic forms. There is close agreement between the

132   measured and calculated values (see supporting information), indicating consistent recovery of

133   the different forms of sulfur. In addition to sulfur analyses, sediments were also analyzed for

134   concentrations and isotopic compositions (δ^{13}C) of total organic carbon (*30*).

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Results and Discussion

137   Sediment archives from the Canadian Arctic archipelago and Svalbard show variable trends in

138   accumulation rates of total reduced inorganic sulfur, except at the top of the cores, corresponding

139   to the period 1980-present, where there is a synchronous increase among lakes (Figure 1). The

140   only exception to this recent increase is in Romulus Lake, which shows a decreasing trend of

141   total reduced inorganic sulfur towards the sediment surface (see supporting information, Figure

142   S1). Unlike all the other lakes in the study, Romulus Lake is meromictic and is anoxic below the

143   chemocline because of hypersaline groundwater inflow (*31*). Meromictic lakes are not

144   uncommon in coastal areas of the High Arctic and exhibit a dynamic sulfur cycle. At the

145   chemocline, sulfate-reducing bacteria create a sulfidic environment in which photosynthetic

146   sulfur bacteria thrive by using sulfide and other forms of reduced sulfur to fix carbon dioxide.

147   We do not know specifically the reason the surface sediment of Romulus Lake is low in total

148   reduced inorganic sulfur, but it likely relates to the biologically-active nature of sulfur in these

149   systems. In our within-lake regression modeling (see supporting information, Table S1) we

150   found no suitable predictors for total reduced inorganic sulfur in Romulus Lake. In contrast, the

151   other eight lakes in this study exhibit limnological characteristics considered more typical of the

152   Arctic – holomictic and fully oxygenated. In these lakes, sulfate reduction is limited to anoxic

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153 sediments, and the sulfide produced is either reoxidized to sulfate and lost to the water column or

154 is bound to Fe or organic matter and retained in the sediment. Accordingly, Fe and organic

155 matter (organic C, organic N, or LOI) were generally good predictors, in the within-lake

156 regression models, of total reduced inorganic sulfur. Manganese was also a good predictor in the

157 models, likely because, as for sulfur (and N and Fe), it is involved in the mineralization of

158 organic carbon.

159   Sulfate deposition, from ice core records, was a suitable predictor of total reduced

160 inorganic sulfur in only Char Lake, and this correlation may be a function of local disturbance

161 that coincided with peaks in the ice core record. In 1949, an air base was built near Char Lake

162 that may have caused local atmospheric pollution (*32*). Also, during 1969-1972 gravel was taken

163 from the lake's watershed to construct a new airstrip and this action caused a "great increase" in

164 sulfate concentration in one inflow stream (*33*), although the effect was temporary (*26*).

165 Tendammen in Svalbard may also be affected by local pollution, as this lake is located near a

166 coal-fired power plant and coal mining operations. Modern accumulation of reduced inorganic

167 sulfur in the sediments of Tendammen is an order of magnitude greater than the other Svalbard

168 lakes. In the other study lakes, however, local disturbance is slight or nonexistent, and geology

169 (sedimentary rock) and proximity to the ocean (i.e., exposure to marine aerosols) indicate that

170 natural sources of sulfate should dominate input (*34*), even with the human-caused circum-arctic

171 increase in sulfate deposition during the past century (*24*). It thus seems unlikely that the surface

172 enrichment of sulfur as observed in these sediments results from increased anthropogenic sulfur

173 sources, as is true of lakes nearer industrial centers and underlain by crystalline bedrock (*35, 36*).

174   From our statistical analyses, temperature is the most important predictor of sedimentary

175 accumulation of total reduced inorganic sulfur, and we hypothesize this relationship is not direct

176   but rather mediated through a warming-induced biogeochemical cascade. In the within-lake

177   regression modeling, temperature was the variable most consistently associated with total

178   reduced inorganic sulfur. Further, temperature was the only significant covariate in the among-

179   lakes random-effects ANOVA modeling (Canada: $r^2 = 0.74$, $p = 0.011$; Svalbard: $r^2 = 0.68$, $p =$

180   0.032). Rates of sulfate reduction do increase with temperature as an Arrhenius function (e.g.,

181   *37*), but there is no data to suggest that temperatures in profundal sediments of these lakes have

182   followed trends in air temperature. Instead, there is overwhelming evidence from the study lakes

183   that warming-induced lengthening of the ice-free season is resulting in increases in algal

184   production (*17, 26, 27, 38*). In the Svalbard lakes, there is additional evidence that the increases

185   in algal production are causing greater fluxes of organic matter to sediments (*23*). A link to

186   organic matter flux is also being made for the study lakes in the Canadian Arctic. For Amituk,

187   Char, and Romulus lakes, Muir et al (*20*) found that concentrations of organic carbon were >10%

188   higher in surface sediments compared to pre-1900 horizons. This trend is likely, in part, due to

189   the progressive diagenetic consumption of carbon following sedimentation. Outridge et al. (*12*),

190   however, used Rock Eval pyrolysis to show an increase in the sedimentary flux of "S2" carbon

191   in Amituk Lake. S2 is an operationally-defined term (it is measured during step 2 of the Rock

192   Eval method) and is thought to be of algal origin and resistant to diagenesis. More recently, Kirk

193   et al. (*27*) determined sedimentary fluxes of S2 in Amituk Lake, Char Lake, and Lake Hazen and

194   found increasing S2 in all three lakes, along with shifts in the algal community. Also, we found

195   modest up-core increases in $\delta^{13}C$ in sediments from Amituk Lake (-27.2‰ to -26.5‰) and Char

196   Lake (-25.8‰ to -24.7‰) (see supporting information, Figure S2) that could suggest that the

197   sedimentation of autochthonous carbon has increased recently (*39*).

198   Urban (*14*) predicted that increases in autochthonous carbon flux will stimulate sulfate

199   reduction in surface sediments of ultraoligotrophic lakes with low rates of carbon sedimentation

200   and oxic hypolimnia, a fitting description of our study lakes. Sulfate-reducing bacteria derive

201   energy by transferring electrons from organic carbon compounds or H_2 to sulfate (*40*).

202   Laboratory experiments have shown that the amendment of lake sediments with labile carbon

203   stimulates sulfate reduction (e.g., *41*), which may lead to increases in storage of reduced sulfur in

204   sediments. There is a well-established relationship among algal productivity, organic carbon

205   sedimentation, and sulfur content of sediment in temperate lakes that exhibit seasonal water-

206   column anoxia (e.g., *42*), but not for Arctic lakes with oxic hypolimnia. Recently, however,

207   Korhola et al. (*10*) and Klug et al. (*43*) reported concomitant increases in concentrations of

208   organic carbon and total sulfur in sediment cores from lakes in Finnish Lapland (Lake

209   Saanajärvi, 69° N) and northeast Greenland (Melles Lake, 76° N), respectively. In both cases,

210   the increases in sedimentary sulfur were thought to ultimately relate to climate.

211   Variation among lakes in pre-1980 accumulation rates of total reduced inorganic sulfur

212   may reflect the non-conservative nature of this element. The records from Amituk and Daltjørna

213   seem to follow trends in air temperature since the 19th century. Char and Tendammen have large

214   peaks that could be due to local pollution. BI-02 and Yterjørna have no discernable trends. For

215   all of these lakes, however, subsurface peaks could be associated with redox gradients. Sulfur,

216   depending upon speciation, is subject to steep diffusion gradients and biological and chemical

217   redox reactions. Consequently, sulfur profiles in sediments can reflect both historical records

218   and contemporary processes. The latter can prevent interpretation of the former (*36*), which may

219   be the case for the pre-1980 sediments in our study lakes. The recent (post-1980) record of

220   increased accumulation rates may be evident because, as we hypothesize, it is process driven.

221   Results from our incubation experiments provide clear evidence that increased supply of

222   labile carbon to Arctic lake sediments can result in increased storage of reduced sulfur (Figure

223   2). There were statistically significant differences in AVS among treatments in the incubations

224   from both Amituk Lake ($F_{7,14} = 26.4$, $p < 0.001$) and Char Lake ($F_{7,16} = 75.2$, $p < 0.001$). The

225   control treatments had AVS concentrations greater than initial test conditions (time-zero).

226   Conversely, all treatments involving molybdate, a metabolic inhibitor of sulfate-reducing

227   bacteria, had AVS concentrations equivalent to that of time-zero. Collectively, the results from

228   the control and molybdate treatments indicate that AVS formation is a normal process in these

229   sediments and is due to the activities of sulfate-reducing bacteria. The sulfate treatments and the

230   acetate (labile carbon) treatments had AVS concentrations greater than controls, although this

231   was only significant in the sediment from Char Lake. (A missing replicate in the control for

232   Amituk Lake caused the control to not be statistically different from several of the other

233   treatments.) Sulfate and acetate in combination resulted in even greater AVS concentrations in

234   Amituk Lake. We do not completely understand the responses to sulfate, acetate, and the two in

235   combination (i.e., how is it that sulfate alone and acetate alone caused the same relative increase

236   in AVS?). However, it is clear that both sulfate (electron acceptor) and acetate (electron donor)

237   limit sulfate reduction in the sediments of these lakes. Logic dictates, though, that if sulfate

238   concentrations in the lakes are not changing (*26*) but organic carbon flux to sediments is

239   increasing, it is more likely that organic carbon is driving the increases in accumulation rates of

240   total reduced inorganic sulfur observed in the sediment archives.

241   In the cores from Amituk Lake and Char Lake that were processed to preserve redox

242   chemistry, examination of the sulfur forms that comprise total reduced inorganic sulfur (AVS,

243   S^0, pyrite) indicates that AVS is likely oxidized to S^0, which is then stored in sediment (Figure

244 3). Concentrations of AVS are low at the sediment surface (0-2 cm), but increase with depth.

245 These AVS profiles are typical for lakes in which, at least seasonally, oxygen penetrates into

246 surficial sediments (44). Oxygen both inhibits sulfate reduction and oxidizes reduced sulfur.

247 These cores were collected in the winter season through thick ice cover – a time when, because

248 of limited algal production and sedimentation of organic matter, there is little oxygen demand in

249 the sediments and thus oxygen penetrates relatively deeply. Gobeil et al. (19) described that

250 during the open water season, however, greater algal production results in a pulse of organic

251 matter that consumes oxygen in the sediments. The oxic-anoxic boundary moves near the

252 sediment surface, below which sulfate reduction produces AVS. It is this seasonal pattern that

253 can explain the spike in concentration at the top of the S^0 profiles. There is likely an increase in

254 AVS formation during the open water season, but it is oxidized to S^0 during winter. This

255 explanation is supported by a simple mass balance, as the decrease in AVS concentration is

256 roughly equal to the increase in S^0 concentration. It is also supported by the nearly identical $\delta^{34}S$

257 values of AVS and S^0, thus indicating a common source (i.e., sulfate reduction) (45). In contrast,

258 pyrite is considerably enriched in ^{34}S compared to AVS and S^0. Sedimentary pyrite formation is

259 traditionally thought to occur from the reaction of iron monosulfide (a major component of AVS)

260 and S^0 (46), and results in negligible sulfur isotope fractionation (47). The pyrite in these

261 sediments, therefore, may not be formed *in situ* (48) but instead derive from a different source,

262 such as from weathering of sedimentary rocks in the lakes' watersheds. Values of $\delta^{34}S$ in

263 sulfides, including pyrite, from rocks on Cornwallis Island and nearby islands (typically +10‰

264 (49), but reported as low as -9‰ (50)) overlap with the values we find for pyrite in sediment.

265 The delivery of substances from watershed to lake has generally not yet been significantly

266 altered by climate change in the High Arctic (1, 20, 26), and fittingly, the concentration profiles

267 for pyrite are relatively stable, except at the bottom of the profiles from Char Lake. The

268 concentrations profiles for AVS and S^0, as well as the $\delta^{34}S$ values of all three sulfur forms are

269 similarly affected at this depth, and we think the change is due to a marine origin of the sediment

270 below 8-cm depth (Char Lake was created with post-glacial rebound approximately 6000 years

271 ago (*33*) and did not clear of seawater for some time (*51*, see figure 3 therein)).

272   An alternate hypothesis to explain the presence of S^0 in the sediment cores is that it is an

273 artifact of sample processing. Acid volatile sulfide is oxygen sensitive and, even with our

274 attempts to preserve redox chemistry (sampling ports, zinc acetate), it could have been oxidized

275 to S^0 upon freeze-drying or treatment with HCl. We cannot reject this hypothesis, but regardless,

276 it does not change our finding that the accumulation of reduced inorganic sulfur is increasing in

277 sediments of High Arctic lakes, possibly due to an increasing sedimentary flux of organic carbon

278 that is stimulating sulfate reduction. The sulfide produced is being stored as AVS and/or S^0.

279   Similar to the trends in total reduced inorganic sulfur, the profiles of organic sulfur show

280 an increase at the top of the cores (see supporting information, Figure S3). In both Amituk Lake

281 and Char Lake, HyS and nonCRS (forms of organic sulfur; defined in experimental section)

282 similarly show subtle increases up core and then a big jump in concentration at the sediment

283 surface (0-2 cm). With HyS and nonCRS added together to calculate total organic sulfur, the

284 atomic C_{org}/S_{org} ratios are relatively constant throughout the profiles for each lake and average

285 193 for Amituk Lake and 103 for Char Lake. These high C_{org}/S_{org} ratios strongly suggest that the

286 source of organic sulfur is sedimenting algae, which have C_{org}/S_{org} ratios > 84 (*52*), and not from

287 the diagenetic addition of reduced sulfur to organic matter. The profiles of HyS and nonCRS

288 thus reflect the loss of sulfur from the decomposition of algae.

289   There is little other data on sedimentary sulfur in Arctic lakes to which we can compare

290   our results. Studies have documented sulfur profiles that increase towards the surface (*10*), have

291   a distinct subsurface peak associated with a redox gradient (*17, 53*), or decrease towards the

292   surface (*15*). Bindler et al. (*54*) suggested that a decrease in sulfur concentration towards the

293   surface, due to sulfide oxidation, is the steady state for lakes in the Swedish Arctic. Our results

294   indicate, however, that there is either a different steady state in lakes of the High Arctic or

295   climate warming is pushing these systems out of steady state. Perhaps, as suggested by Mueller

296   et al. (*7*), warming crossed a critical threshold in the 1980s and we are now witnessing a

297   "cascading regime shift". A 250,000-year sediment record from Lake El'gygytgyn (67° N) in

298   Siberia provides several examples of shifts in sulfur cycling in response to changes in climate

299   (*55*). The key to increased sulfur accumulation in the sediments of Lake El'gygytgyn is the

300   development of a stratified water column and, subsequently, the depletion of oxygen in the

301   bottom water. Our study lakes remain holomictic and fully oxygenated, but results from lakes

302   further south that receive intensive monitoring efforts (Lake Saanajärvi, Toolik Lake) indicate

303   that warmer air temperatures and extended ice-free periods will cause thermal stratification and

304   in some years oxygen-depleted bottom waters (*56*). Studies of Meretta Lake, located near Char

305   Lake on Cornwallis Island, but which has experienced eutrophication due to sewage inputs,

306   indicate that High Arctic lakes are indeed prone to oxygen depletion. In the early 1970s,

307   Schindler et al. (*57*) documented increased primary production in Meretta Lake, which led to

308   near anoxic conditions in bottom waters and a perturbation of sulfur cycling. Thirty percent of

309   sulfate in lake water was lost over winter. Sulfide was not measured in water or sediments, but

310   the missing sulfate was likely reduced and stored in sediment.

311   In summary, the accumulation of sulfur appears to be increasing in sediments of Arctic

312   lakes, and we argue that the cause is a climate-induced biogeochemical cascade. It is unknown if

313   the cascade extends beyond sulfur, but sulfur does play an important role in the cycling of other

314   elements. For example, sulfate reduction mineralizes organic carbon (to CO_2 that then may be

315   lost to the atmosphere) and thus works against the burial of carbon in sediments, which is an

316   important sink in the global carbon budget (*58*). As a side, increased carbon flux may stimulate

317   other anaerobic metabolisms, such as methanogenesis, which produces CO_2 and methane, both

318   greenhouse gases, and thus would constitute a positive feedback to climate warming. Sulfate

319   reduction is also the process believed to be primarily responsible for the transformation of

320   inorganic mercury to methylmercury (*59*; but see *60*), which biomagnifies in food webs and

321   results in high concentrations of this toxic metal in fish (*61-63*). A ramping up of the sulfur cycle

322   in Arctic lakes could have local to global effects on the biogeochemistry of these elements and

323   others. Further study of the flux of carbon (quality, quantity) to Arctic lake sediments and

324   effects on sulfur cycling and beyond is warranted.

325

326 Acknowledgements

332

333 Supporting Information Available

334   Methods, acknowledgements, one table, three figures, and all original data.

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513 Table 1. Information about the study lakes, including the years archived sediment cores were collected.

Lake	Country, locality	Lat. N	Long. E/W	Area (km^2)	Max. depth (m)	Epilimnetic SO$_4$ (μM)	Sed. rate[1] (g/m^2·yr)	Sed. org. C[1,2] (%)	Yr. collected
Amituk	Canada, Cornwallis Is.	75˚02'40"	93˚48'40" W	0.38	43	16.6	260	0.89	2003
Char	Canada, Cornwallis Is.	74˚42'20"	94˚53'50" W	0.53	28	132	240	1.73	2003
BI-02	Canada, Bylot Is.	73˚02'30"	80˚05'45" W	0.033	3	4.37	200	6.04	2005
Hazen	Canada, Ellesmere Is.	81˚49'20"	70˚37'50" W	538	267	108	280	1.67	2005
Romulus	Canada, Ellesmere Is.	79˚52'15"	85˚05'10" W	4.4	60	.	820	2.16	2000
Daltjørna	Norway, Svalbard	77˚33'50"	14˚13'55" E	0.054	11	16.2	460	.	1995
Tenndammen	Norway, Svalbard	78˚06'00"	15˚02'00" E	0.15	2.5	164	540	.	1995
Yterjørna	Norway, Svalbard	78˚13'52"	12˚56'30" E	0.14	2.6	36.9	140	.	1995
Ossian Sarsfjellet	Norway, Svalbard	78˚57'04"	12˚28'38" E	0.13	26	25.4	88	.	1995

[1]Data for recent horizons (post-1990)
[2]Organic C not measured in sediments from Svalbard lakes; LOI data can be found in Boyle et al. (*23*).

514   Figure captions

515

516   Figure 1. Accumulation rates of reduced inorganic sulfur in lake sediments from the Canadian

517   Arctic archipelago (A) and Svalbard (B). Note that the scale is different for each lake. Also

518   presented for each region are records of air temperature in summer (JJA = June, July, August)

519   and sulfate concentration in ice cores. The temperature anomaly records have sigma units, which

520   are defined in Overpeck et al. (*2*). Details about the sources for the temperature and sulfate

521   records can be found in the text.

522

523   Figure 2. Concentrations of acid volatile sulfide (AVS) in sediment slurries from Amituk Lake

524   (A) and Char Lake (B) after incubation with treatments of molybdate (MoO_4; metabolic inhibitor

525   of sulfate-reducing bacteria), sulfate (SO_4; electron acceptor for sulfate-reducing bacteria),

526   and/or acetate (CH_3COO; electron donor for sulfate-reducing bacteria). Further details about the

527   treatments can be found in the text. Values represent the mean ($\pm$ 1 SE) of three replicates; units

528   are in dry weight. Lowercase letters (a, b, c, d) denote statistically significant groupings as

529   determined, for each lake, by a one-way ANOVA and Tukey-Kramer posthoc tests. The *x*-axis

530   meets the *y*-axis at the initial (time zero) concentration in sediment slurries for each lake.

531

532   Figure 3. Sediment profiles from Amituk Lake (A) and Char Lake (B) of acid volatile sulfide

533   (AVS; circles), elemental sulfur (S^0; triangles), pyrite (squares), and the stable sulfur isotopic

534   compositions ($\delta^{34}S$) of each of these forms of reduced inorganic sulfur. For profiles of AVS, S^0,

535   and pyrite, values represent the mean ($\pm$ 1 SD) of two cores; units are in dry weight. For profiles

536   of $\delta^{34}S$, materials from the two cores from each lake were pooled for analysis.

537

Brief

538 **Brief**

539 A recent increase in sedimentary accumulation of reduced sulfur in High Arctic lakes may be

540 due ultimately to a changing climate.