

Lake-specific responses in sedimentary sulphur, after additions of copper sulphate to lakes in Michigan, USA

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Abstract

Copper sulphate (CuSO₄) is commonly added to lakes and reservoirs to manage nuisance and exotic species. Several studies have previously reported that CuSO₄ is very useful for this purpose, and that the copper is ultimately stored in lake sediments. In contrast, there has been little study on the fate of the sulphate from CuSO₄ additions. The purpose of this study was to elucidate the effects of CuSO₄ additions on sedimentary sulphur. Concentrations, isotopes, and fluxes of total and reduced sulphur in sediment cores from four Michigan lakes were compared, including two reference lakes that have never received CuSO₄ additions, and two treatment lakes that have received CuSO₄ additions by lake managers totalling 1–3 kg sulphate ha⁻¹ year⁻¹ since 1940. The results of this study confirm that sediments do not consistently provide records of sulphate loading across lakes. Isotopic evidence indicates this inconsistency is caused, in part, by lakes with well-mixed sediments, in which sulphate is reduced to sulphide, but then subsequently reoxidized to sulphate and remobilized to the overlying water column. One of the treatment lakes, however, exhibited a clear correlation between CuSO₄ additions and an increased sulphur flux to the sediment. During any given year, however, the sulphate added from CuSO₄ additions amounted to no more than 10% of the sulphate added from wet deposition. Based on this seemingly insignificant quantity of sulphate, ascribing any effect of CuSO₄ additions on sedimentary sulphur is tenuous at best. One possibility is that the addition of CuSO₄ at rates that do not overwhelm the natural sulphur cycle of a lake or reservoir is a reasonable management tool for nuisance and exotic species.

Key words

copper sulphate, lake, sediment, sulphur.

INTRODUCTION

Copper sulphate (CuSO₄) is commonly added to lakes and reservoirs to control nuisance and exotic species. The state of Michigan (USA), for example, began a CuSO₄ programme in 1940 to control snails that are the intermediate hosts of trematodes that cause 'swimmer's itch' (Blankenspoor *et al.* 1985). The programme, which continues to this day, is now also intended to control nuisance algal and plant growths (e.g. cyanobacteria; Eurasian water milfoil). It consists of adding as much as 100 metric tons of CuSO₄ to lakes and reservoirs throughout

the state each year (Preisser M, written comm., 2008). Michigan is not alone in this management approach, with CuSO₄ additions to lakes and reservoirs having become common throughout North America and Europe over the past century (Moore & Kellerman 1905; Sawyer 1962).

Several studies have reported that CuSO₄ is very useful for controlling unwanted algal and plant species, and that the copper is ultimately stored in lake sediments. Horne and Goldman (1974), for example, found that 5 µg CuSO₄ L⁻¹ was sufficient to disrupt nitrogen fixation of nuisance cyanobacteria. For lake management purposes, however, additions of CuSO₄ in concentrations ranging between 100 and 1000 µg L⁻¹ are more typical. Once in solution, CuSO₄ dissociates into copper and sul-

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phate ions. The copper might interact with target organisms and result in the desired toxicity. It may, however, also directly or indirectly kill fish or other desired species (Hanson & Stefan 1984). The copper eventually forms insoluble compounds, precipitates out of the water column and accumulates in lake bottom sediments (Sanchez & Lee 1978; Haughey *et al.* 2000). Lakes and reservoirs that have received repeated CuSO_4 treatments can have very high sedimentary copper concentrations (e.g. 0.6% by dry weight; Hanson & Stefan 1984), and potentially be toxic to benthic organisms.

In contrast to copper, there has been little study on the fate of sulphate from CuSO_4 additions. Low sulphate concentrations typical of lakes and reservoirs generally limit dissimilatory sulphate reduction (Cook & Kelly 1992). Increases in sulphate concentrations can significantly stimulate dissimilatory sulphate reduction which, as illustrated with the whole-ecosystem manipulation of Little Rock Lake, Wisconsin, can trigger a complex cascade of biogeochemical changes. These changes can result in more alkalinity generation, mercury methylation and decreased immobilization of phosphorus in lake bottom sediments (Frost *et al.* 1999). The single published study we found that investigated the fate of sulphate from CuSO_4 additions, however, reported the opposite effect (Manning *et al.* 1988). Although CuSO_4 additions more than doubled the concentration of sulphate in Figure Eight Lake, Alberta, Manning *et al.* (1988) reported an inhibition of sedimentary pyrite (FeS_2) formation and, by speculation, dissimilatory sulphate reduction. The researchers suggested this inhibition might have been a consequence of copper toxicity to sulphate-reducing bacteria. The copper concentrations in the sediment ($<60 \mu\text{g g}^{-1}$ dry weight), however, were far below values known to be toxic to these robust organisms (Lane 2006).

The objective of this study was to elucidate the effects of CuSO_4 additions on sedimentary sulphur. The concentrations, isotopes and fluxes of total and reduced sulphur in two 'reference' lakes that have never received CuSO_4 additions were compared with two 'treatment' lakes that have received CuSO_4 additions since 1940. The results of this study confirm that, across lakes, sediments do not consistently provide records of sulphate loading (Bindler *et al.* 2008). One of the treatment lakes, however, exhibited a clear correlation between CuSO_4 additions and increased accumulation of sulphur in the sediment. During any given year, the sulphate added from CuSO_4 additions amounted to no more than 10% of the sulphate added from wet deposition. With this seemingly insignificant quantity of sulphate, ascribing any effect of CuSO_4 additions on sedimentary sulphur is tenuous at best.

METHODS

Setting

The reference lakes, Lake Richie (lat. $48^\circ 2' \text{N}$, long. $88^\circ 42' \text{W}$) and Sargent Lake (lat. $48^\circ 5' \text{N}$, long. $88^\circ 39' \text{W}$), are located in Isle Royale National Park, Michigan. The park, an island archipelago in Lake Superior, was established in 1940, having since been managed as a wilderness area. Accordingly, the lakes are little influenced by human activities, and have never received CuSO_4 additions. Isle Royale is naturally enriched in copper, however, and there was some mining in prehistory by aboriginal peoples, and again in the 19th century by European settlers, albeit outside the watersheds of our study lakes (Rakestraw 1965). The lakes are typical small (Richie, 216 ha; Sargent, 143 ha), dimictic, temperate lakes. Further details on the lakes are available from other studies (Kallemeyn 2000; Gorski *et al.* 2003; Drevnick *et al.* 2007).

The treatment lakes, Lake Cadillac (lat. $44^\circ 14' \text{N}$, long. $85^\circ 25' \text{W}$) and Houghton Lake (lat. $44^\circ 20' \text{N}$, long. $84^\circ 43' \text{W}$), are located in the northern portion of the lower peninsula of Michigan. The watersheds of the treatment lakes have been continuously disturbed (e.g. forestry; agriculture; cottage and urban development) since its European settlement. Both lakes were a part of Michigan's original CuSO_4 programme, with the quantities added to each lake annually being listed in Appendix I. Houghton Lake (8112 ha) is the largest inland lake in Michigan, often receiving half or more of the CuSO_4 annually added to all the lakes in the state. Lake Cadillac is smaller in size (465 ha), being connected to adjacent Lake Mitchell (1044 ha) by a canal. Records of annual CuSO_4 additions generally indicate a single quantity for Cadillac/Mitchell, which is much less in mass (kg) than for Houghton Lake, but being added at a greater rate (kg ha^{-1}). The lakes are rather shallow, and do not exhibit consistent thermal or chemical stratification. The treatment lakes differ from the reference lakes in this regard, with the latter developing anoxic hypolimnia during stratification (although little characterized, anoxic hypolimnia was observed in August 1998 and 1999 in both Lake Richie and Sargent Lake; Gorski P, unpubl. data). Eimers *et al.* (2006), however, found no significant difference in the storage of sulphur in the sediments across six lakes in nearby Ontario, whose duration of anoxic bottom waters ranged from a few days per year to >3 months per year. Thus, it was considered unlikely that this difference between reference and treatment lakes would confound the interpretation of the results of this study. Further details about the treatment lakes are published elsewhere (Yohn *et al.* 2003, 2004).

Sediment coring

Sediment cores were collected from preliminary sampling sites in the middle of Lake Richie and Sargent Lake on 13 February 1999. The sites were located as far away from each shoreline as possible to reflect an average depth. One hole was drilled through the ice for each lake, and four additional holes (≈ 30 m directly N, S, E and W of the initial hole) were then drilled. Depth measurements were taken at each hole to ensure less than a 10% grade between the central hole and each subsequent hole, to avoid taking a core sample on a steep grade. A single core sample was then taken from each lake at the central hole with a Peterson piston corer. Sediment cores were extruded and sectioned on site (every cm) and frozen.

Sediment cores were collected from Lake Cadillac and Houghton Lake during the summer of 2001 and 2002 respectively. From the deepest portion of each lake, an MC-400 Lake/Shelf Multicorer (Ocean Instruments, San Diego, CA, USA), which takes four replicate cores, was deployed from the vessel *M/V Nibi*. Taken to the shore, the cores were then extruded, sectioned (every half cm for the top 5–8 cm of the core; every cm for the remainder), and frozen.

Laboratory sediment analysis

The collected sediments were freeze-dried and then analysed for lead (²¹⁰Pb), copper and sulphur. Analysis of ²¹⁰Pb was performed to determine the core age and the sedimentation rate (Appleby & Oldfield 1983). Sedimentation rates were multiplied by a correction factor (calculated as the atmospheric ²¹⁰Pb flux divided by the core-specific ²¹⁰Pb flux) to adjust for focusing. Details on ²¹⁰Pb analysis and modelling for these cores are available elsewhere (Drevnick *et al.* 2007; Parsons *et al.* 2007a). Copper was analysed in nitric acid-digested sediment by inductively-coupled plasma-mass spectrometry (Yohn *et al.* 2002). Total sulphur (TS), chromium-reducible sulphur (CRS; reduced forms of sulphur that are decomposed in hot, acidic CrCl₂ to H₂S) and stable sulphur isotopic compositions ($\delta^{34}\text{S}$) were analysed with the methods of Canfield *et al.* (1998). Sediment fluxes of TS were calculated by multiplying ²¹⁰Pb-based sedimentation rates by TS concentrations. The reliability and validity of the data were ensured by strict adherence to quality assurance/quality control procedures (e.g. calibration with standards; analysis of externally supplied standards, reagent blanks and duplicates; recovery of known additions).

RESULTS AND DISCUSSION

Copper concentrations remained fairly constant throughout the profiles of sediment cores from the reference lakes, but increased greatly up the cores of treatment lakes

(Fig. 1). For the reference lakes, the copper concentrations ranged between 98–137 $\mu\text{g g}^{-1}$ dry weight in Lake Richie and 126–145 $\mu\text{g g}^{-1}$ dry weight in Sargent Lake. These are elevated concentrations, compared to most other lakes sampled in Michigan (Parsons *et al.* 2007b), likely attributable to the geological deposits of copper at Isle Royale (Rakestraw 1965). For the treatment lakes, the copper concentrations deep in the cores averaged 20 $\mu\text{g g}^{-1}$ dry weight, which is similar to most other lakes sampled in Michigan (Parsons *et al.* 2007b). Above a sediment depth of ≈ 20 cm, however, the copper concentrations greatly increased, to a maximum of 485 $\mu\text{g g}^{-1}$ dry weight in Lake Cadillac and 261 $\mu\text{g g}^{-1}$ dry weight in Houghton Lake. Undoubtedly due to the addition of CuSO₄, these copper concentrations are remarkably high, and probably toxic to benthic organisms (MacDonald *et al.* 2000). Sediments above a depth of 20 cm have been deposited since 1940 (i.e. since Michigan's CuSO₄ programme began). Copper fluxes by year have been reported previously for these two lakes (Yohn *et al.* 2003, 2004), and correspond closely to the quantities of CuSO₄ added annually (Appendix I).

Sulphur is a less conservative element than copper, as became apparent with examination of the sulphur concentration profiles in the sediment samples, which vary considerably within, and among, the study lakes (Fig. 2). Deep in the cores taken from all the study lakes, the TS and CRS concentrations are fairly constant. This trend continues up core for Lake Richie, but not for the other lakes. The TS and CRS concentrations decrease up core for Lake Cadillac, and increase up core for Sargent Lake and Houghton Lake, with a levelling off near the sediment surface. This variability appears to be primarily a function of changes in the CRS (the fraction of TS that results from microbial reduction of sulphate to sulphide), with subsequent diagenetic transformations to other forms of reduced sulphur, such as acid-volatile sulphide, pyrite, and elemental sulphur (Luther & Church 1992). The fraction of TS that is not CRS (calculated as TS minus CRS, consisting largely of organic sulphur) has not changed (data not shown). Thus, the variability in the sulphur concentration profiles is due to controls on the CRS concentration. Fry *et al.* (1995) reported these controls to be sulphate and carbon supplies (which together control dissimilatory sulphate reduction) and sulphide oxidation. Organic carbon concentrations are quite high in sediments from all of the lakes, therefore not being a limiting factor. Thus, the focus is on sulphate supply and sulphide oxidation to explain the sedimentary sulphur concentration profiles.

Although the sulphate supply to all of the lakes has changed considerably over the past 150 years, this fact is only evident in one reference lake (Sargent) and one

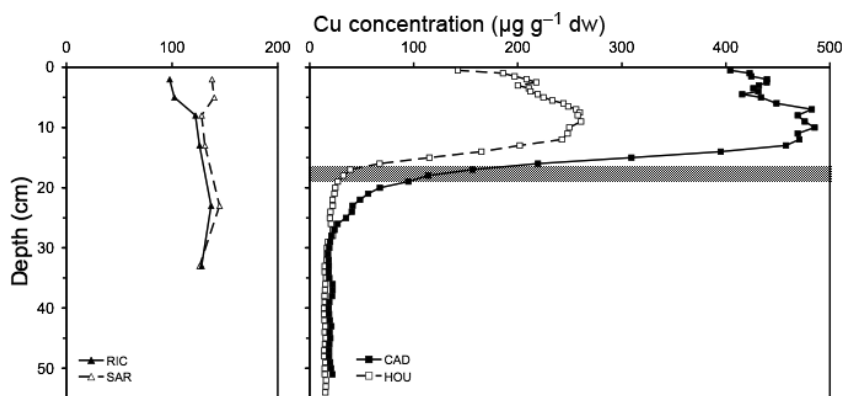


Fig. 1. Left panel: Concentrations of copper in sediment cores from Lake Richie (RIC; closed triangles, solid line) and Sargent Lake (SAR; open triangles, dashed line); Right panel: Lake Cadillac CAD; (closed squares, solid line) and Houghton Lake (HOU; open squares, dashed line) (grey, horizontal line in right panel represents beginning of copper sulphate additions to Lake Cadillac and Houghton Lake in 1940).

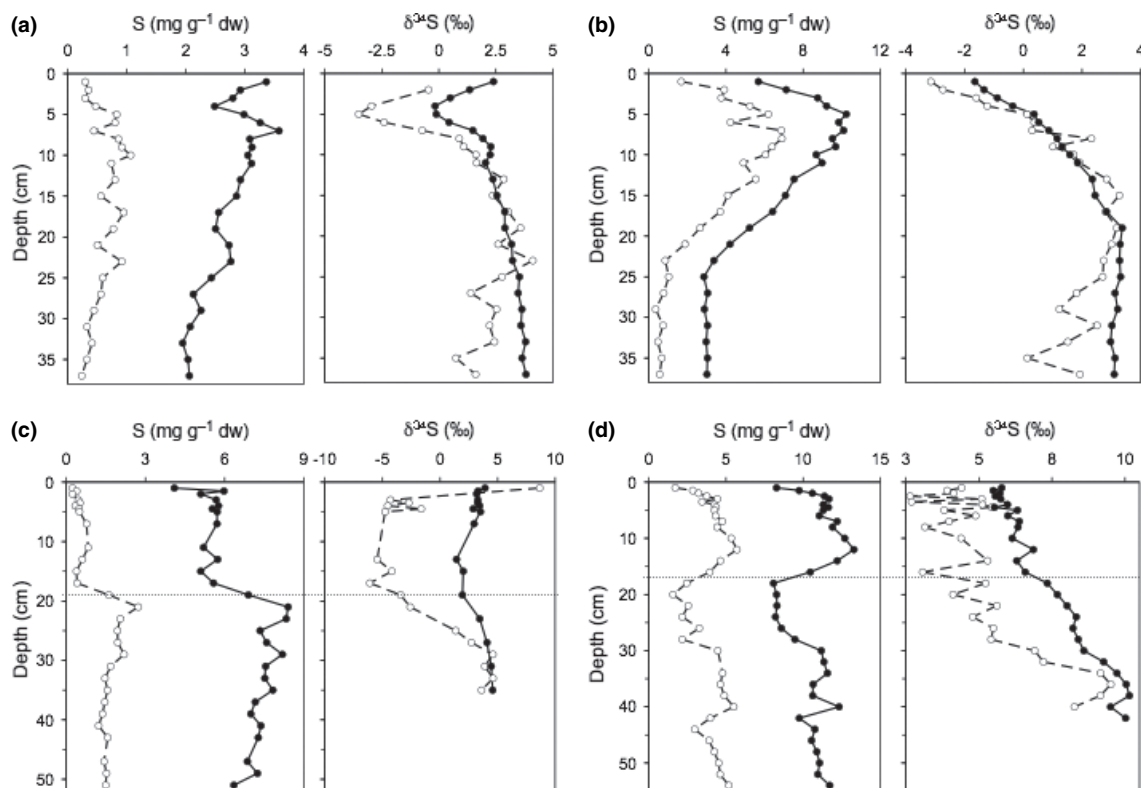


Fig. 2. Concentrations and stable sulphur isotopic compositions ($\delta^{34}\text{S}$) for total sulphur (closed circles, solid lines) and chromium-reducible sulphur (open circles, dashed line) in (a) Lake Richie, (b) Sargent Lake, (c) Lake Cadillac and (d) Houghton Lake [dotted, horizontal lines in (c) and (d) represent beginning of copper sulphate additions to Lake Cadillac and Houghton Lake, respectively, in 1940].

treatment lake (Houghton). Before industrialization (i.e. pre-1890), low rates of atmospheric sulphate deposition (Aherne *et al.* 2004) limited dissimilatory sulphate reduction in all the lakes, as evidenced by relatively constant and low concentrations of CRS deep in the sediment cores. With industrialization (post-1890), coal combustion and metal smelting ultimately increased the rates of atmospheric deposition of sulphate, to a maximum level

in 1976 (Aherne *et al.* 2004). These rates have since declined (Aherne *et al.* 2004) in response to implementation of the U.S. Clean Air Act of 1970 (Stoddard *et al.* 1999). Of the 4 study lakes, this depositional history is only recorded in the sediments of Sargent Lake (see further description in Drevnick *et al.* 2007). For the treatment lakes, the sulphate supply has been further augmented by CuSO_4 additions. It is reiterated that,

although CuSO₄ has been purposefully added to the lakes since 1940, this legacy is not seen in the sedimentary sulphur profile from Lake Cadillac. For Houghton Lake, however, it does appear the sulphate from CuSO₄ additions is being reduced to sulphide, and being transformed to CRS, with increased concentrations in the upper 20 cm of the sediment. A relevant question, therefore, is why the sedimentary sulphur profile of Houghton Lake also does not exhibit a response to industrialization, as noted in Sargent Lake? This lack of response is possibly due to significant changes in the sedimentation rate associated with logging and/or farming in the Houghton Lake watershed (Yohn *et al.* 2004).

The sediment samples from the other reference (Richie) and treatment (Cadillac) lakes do not reflect changes in the sulphate supply, likely because of sulphide oxidation. Although sulphide oxidation is a poorly understood process, it is known to be caused by, for example, sediment mixing and phototrophic sulphur bacteria (Holmer & Storkholm 2001), and to result in increased $\delta^{34}\text{S}$ values in the top few cm of sediment (Fry *et al.* 1995). Approximately the top 12 cm of sediments of both Lake Richie and Lake Cadillac are well-mixed (Yohn *et al.* 2003; Drevnick 2007), and Lake Richie has an abundant population of phototrophic sulphur bacteria (Gorski *et al.* 2003). Furthermore, the surface sediments from both Lake Richie and Lake Cadillac show increased $\delta^{34}\text{S}$ values (Fig. 2). Thus, it is likely that much of the sulphate that is reduced to sulphide in these two lakes is reoxidized, and subsequently lost to the overlying water column, instead of being transformed to CRS and stored in sediment. In contrast, there is no isotopic evidence of sulphide oxidation in the sediment cores from Sargent Lake and Houghton Lake and, as previously stated, these lakes tend to store their sulphur as CRS in sediment. There is, however, a caveat to the $\delta^{34}\text{S}$ data. The $\delta^{34}\text{S}$ values of the CuSO₄ added to Lake Cadillac and Houghton Lake are not known, and it is being assumed that it had little effect on the sediment $\delta^{34}\text{S}$ values. This assumption could be justified, considering the sulphate added from CuSO₄ additions is a rather small contribution to the total sulphate load to these two lakes (see below).

The TX fluxes in the sediment (Fig. 3) tell a story similar to the concentration profiles; some lakes (Sargent and Houghton) respond to increased sulphate supply, while others (Richie and Cadillac) do not. This phenomenon has been reported repeatedly (e.g. Mitchell *et al.* 1988; Giblin *et al.* 1990) for regions affected by acid deposition. Only recently has a study been conducted at a sufficiently large spatial scale (all of Sweden) to make some general inferences about sulphur pollution and sediment

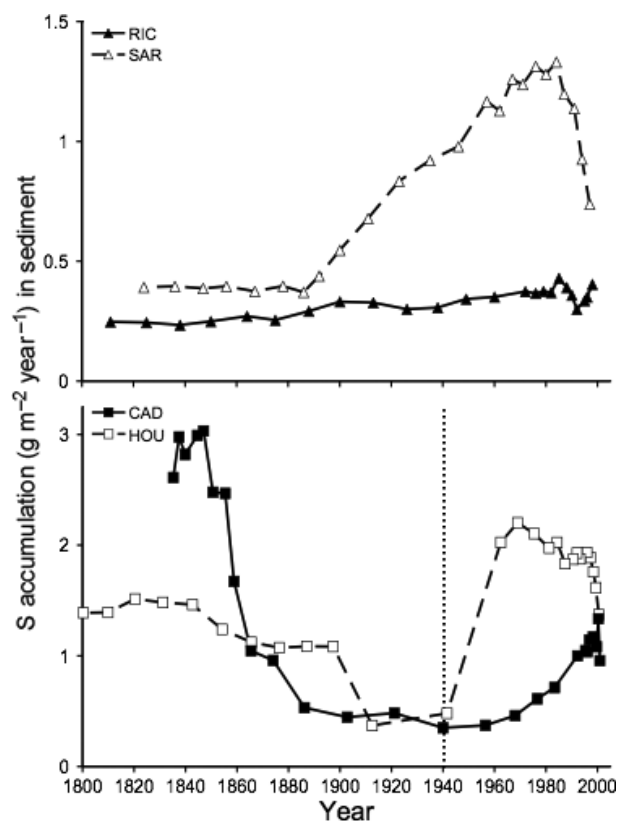


Fig. 3. Top panel: Accumulation (or flux) of total sulphur in sediment cores from Lake Richie (RIC; closed triangles, solid line) and Sargent Lake (SAR; open triangles, dashed line); Bottom panel: Lake Cadillac (CAD; closed squares, solid line) and Houghton Lake (HOU; open squares, dashed line) (dotted, vertical line in bottom panel represents beginning of copper sulphate additions to Lake Cadillac and Houghton Lake in 1940).

sulphur accumulation (Bindler *et al.* 2008). First, lakes near industrial centres generally have more sulphur in their newer, top sediments than in their older, bottom sediments. Second, lakes located distant from industrial centres have sediments exhibiting a variety of sulphur profiles, but most frequently exhibit no difference from the top of the sediment to the bottom, or else actually have less sulphur in their top sediments than their bottom sediments. Bindler *et al.* (2008) suggested this latter condition was the 'pre-pollution norm' for lakes, and that it can be maintained, even in the face of pollution (e.g. Cadillac), with sufficient sulphide oxidation (Dornblaser *et al.* 1994; Eimers *et al.* 2006). It is interesting to note that the only known other lake studied for the effects of CuSO₄ additions on sedimentary sulphur had a TS profile characteristic of this pre-pollution norm, being strikingly. It is interesting to note that the only known other lake (Figure Eight Lake; Manning *et al.* 1988) studied for the effects of CuSO₄ additions on sedimentary sulphur had a

TS profile characteristic of this pre-pollution norm, being strikingly. It is interesting to note that the only known other lake (Figure Eight Lake; Manning *et al.* 1988) studied for the effects of CuSO₄ additions on sedimentary sulphur had a TS profile characteristic of this pre-pollution norm, being strikingly similar to that seen for Lake Cadillac. Those researchers reported that the low TS concentrations near the sediment surface were due to inhibition of pyrite formation. We agree with this explanation and hypothesize that the inhibition was due to sulphide oxidation. Sulphur isotopes, however, were not measured in that study.

Although there is good agreement between the timing and quantities of CuSO₄ additions with sulphur accumulation in the sediment of Houghton Lake (i.e. linear regression with log-transformed data, $n = 12$, $r^2 = 0.852$, $P < 0.001$), it is difficult to unequivocally relate the two observations because CuSO₄ additions contribute only a minor portion of sulphate to the total sulphate load for this large lake in any given year. At the peak of the CuSO₄ programme for Houghton Lake, 18 736 kg of sulphate (plus 12 394 kg of copper) were added to the lake in 1977. Although not a trivial quantity of sulphate, when spread out over the entire area of the lake, it amounts to ≈ 2.3 kg sulphate ha⁻¹, a rather small quantity, compared to the annual wet deposition of sulphate. The nearest National Atmospheric Deposition Program station (MI53; 100 km west of Houghton Lake), for example, measured 23.3 kg sulphate ha⁻¹ in 1979, the first year of the station operation (National Atmospheric Deposition Program 2008). The annual rates of wet deposition of sulphate at the station have declined since 1979, but have always remained at a sufficiently high level that the sulphate added from CuSO₄ additions amounted to no more than 10% of the sulphate added from wet deposition (Appendix I). Purposeful additions of sulphate to lakes (e.g. for acidification experiments) have added sulphate at rates at least 2.5 times greater than wet deposition, in order to elicit effects on sedimentary sulphur (Kelly *et al.* 1995; Urban *et al.* 2001). Furthermore, atmospheric deposition is only one of two major natural sulphate sources to Houghton Lake, with watershed inputs also likely being important (Driscoll *et al.* 2001). It seems unlikely, therefore, that the comparatively small quantity of sulphate added from CuSO₄ additions is important in the lake's overall sulphur budget. Indeed, the TS flux in sediment for 1942 was 0.5 g m⁻² year⁻¹ (5 kg ha⁻¹ year⁻¹), increasing to 2 g m⁻² year⁻¹ (20 kg ha⁻¹ year⁻¹) by 1962. Additions of CuSO₄ cannot quantitatively explain this increase, unless there was some unknown mechanism focusing sulphate/sulphide to the deepest portion of the lake. A possi-

bility is that a spike in sulphate concentrations, in combination with a pulse of organic matter (e.g. dead algae deposited after CuSO₄ dosing), could lead to high instantaneous sulphate reduction rates that result in an intense accumulation of sulphur over a short time interval.

Overall, this study could not unequivocally link CuSO₄ additions to any changes in sedimentary sulphur in Lake Cadillac and Houghton Lake. There are at least three reasons this link cannot be established. First, the quantity of sulphate added from CuSO₄ additions is a rather insignificant quantity, compared to other sulphate inputs. The typical annual addition of 1–3 kg ha⁻¹ of sulphate is perhaps not sufficient to alter the biogeochemical cycling of sulphur or, consequently, other ecosystem processes dependent upon sulphur cycling (e.g. mercury methylation and phosphorus immobilization). Second, sulphate from CuSO₄ additions is reduced to sulphide in lakes with well-mixed sediments, but is subsequently re-oxidized to sulphate and lost to the overlying water column, instead of being transformed to CRS and stored in the sediment. Third, it might be more pertinent to study contemporary processes than simply sediment archives (e.g. dissimilatory sulphate reduction, sulphide oxidation). Sediment archives are very useful for studying historical deposition of conservative substances, but less useful for substances that might change and/or diffuse out of sediment during the post-deposition period. If more work is to be done to investigate the effects of CuSO₄ additions on sulphur cycling, it is suggested such efforts focus on understanding the effects on dissimilatory sulphate reduction and sulphide oxidation during, and after, the narrow window in the spring and summer when CuSO₄ is applied, and also studying a larger number of lakes to account for the variability associated with individual lake sediment responses to CuSO₄ additions.

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APPENDIX

Quantities of copper sulphate (CuSO_4) and the proportion that is sulphate (SO_4) added to Lake Cadillac and Houghton Lake, Michigan, 1944–2003, and rates of SO_4 addition, and for comparison, SO_4 wet deposition measured at nearest National Atmospheric Deposition Program station (MI53; dots indicate data were not collected or available for that year)

Year	Lake Cadillac			Houghton Lake			Wet deposition. SO_4 (kg ha ⁻¹)
	CuSO_4 (kg)	SO_4 (kg)	SO_4 (kg ha ⁻¹)	CuSO_4 (kg)	SO_4 (kg)	SO_4 (kg ha ⁻¹)	
Appendix I							
1944	.	.	.	272	164	0.02	.
1945	.	.	.	0	0	0.00	.
1946	.	.	.	272	164	0.02	.
1947	.	.	.	0	0	0.00	.
1948	.	.	.	726	437	0.05	.
1949	.	.	.	7303	4395	0.54	.
1950	.	.	.	2449	1474	0.18	.
1951	.	.	.	3266	1966	0.24	.
1952	.	.	.	22 952	13 814	1.70	.
1953	.	.	.	16 556	9965	1.23	.
1954	.	.	.	16 057	9664	1.19	.
1955	.	.	.	19 731	11 876	1.46	.
1956	.	.	.	13 426	8081	1.00	.
1957	.	.	.	15 105	9091	1.12	.
1958	.	.	.	15 195	9146	1.13	.
1959	.	.	.	24 267	14 606	1.80	.
1960	.	.	.	24 585	14 797	1.82	.
1961	.	.	.	23 678	14 251	1.76	.

APPENDIX (Continued)

Year	Lake Cadillac			Houghton Lake			Wet deposition. SO ₄ (kg ha ⁻¹)
	CuSO ₄ (kg)	SO ₄ (kg)	SO ₄ (kg ha ⁻¹)	CuSO ₄ (kg)	SO ₄ (kg)	SO ₄ (kg ha ⁻¹)	
1962	.	.	.	20 865	12 558	1.55	.
1963	.	.	.	25 174	15 152	1.87	.
1964	.	.	.	27 442	16 517	2.04	.
1965	.	.	.	25 220	15 179	1.87	.
1966	.	.	.	23 360	14 060	1.73	.
1967	.	.	.	22 770	13 705	1.69	.
1968	.	.	.	24 494	14 742	1.82	.
1969	.	.	.	8618	5187	0.64	.
1970	.	.	.	11 793	7098	0.88	.
1971	.	.	.	10 546	6347	0.78	.
1972	.	.	.	11 079	6668	0.82	.
1973	5216	3140	2.08	11 294	6798	0.84	.
1974	4522	2722	1.80	10 206	6143	0.76	.
1975	4774	2873	1.90	19 278	11 603	1.43	.
1976	7348	4423	2.93	4082	2457	0.30	.
1977	5491	3305	2.19	31 130	18 736	2.31	.
1978	2858	1720	1.14	14 061	8463	1.04	.
1979	4445	2675	1.77	13 789	8299	1.02	23.34
1980	5897	3549	2.35	13 835	8327	1.03	23.24
1981	5443	3276	2.17	13 993	8422	1.04	21.05
1982	5443	3276	2.17	16 261	9787	1.21	22.45
1983	7257	4368	2.89	17 214	10 360	1.28	21.98
1984	7257	4368	2.89	17 463	10 511	1.30	28.00
1985	7257	4368	2.89	17 010	10 238	1.26	26.25
1986	7257	4368	2.89	17 026	10 247	1.26	26.75
1987	7257	4368	2.89	12 701	7644	0.94	19.25
1988	7257	4368	2.89	8845	5324	0.66	16.92
1989	5987	3604	2.39	12 927	7781	0.96	16.50
1990	22.58
1991	3175	1911	1.27	4491	2703	0.33	19.42
1992	3175	1911	1.27	6350	3822	0.47	20.38
1993	.	.	.	0	0	0.00	23.64
1994	2214	1332	0.88	0	0	0.00	17.44
1995	2223	1338	0.89	0	0	0.00	13.78
1996	2858	1720	1.14	8 981	5405	0.67	15.87
1997	2295	1381	0.92	0	0	0.00	13.35
1998	3169	1907	1.26	4940	2973	0.37	15.11
1999	3175	1911	1.27	4940	2973	0.37	13.28
2000	79	48	0.03	0	0	0.00	13.18
2001	68	41	0.03	0	0	0.00	14.88
2002	100	60	0.04	0	0	0.00	12.56
2003	0	0	0	0	0	0.00	15.99

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