



# A Mass-Balance Tool for Monitoring Potential Dissolved Sulfur Oxidation Risks in Mining Impacted Waters

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## Abstract

Sulfur oxidation intermediate compounds (SOIs) in mine tailings reservoir water are linked to adverse environmental impacts, such as acidity, toxicity, and oxygen consumption, and can lead to regulatory non-compliance. Their prediction and management has largely focused on a subset of SOI compounds referred to as thiosalts ( $S_nO_x^{2-}$ ), with thiosulfate ( $S_2O_3^{2-}$ ) presumed to be the dominant thiosalt species, yet no published study to date has determined if  $S_nO_x^{2-}$  and, specifically  $S_2O_3^{2-}$ , dominate SOIs in these waters. The objectives of this study were to: (1) determine sulfur mass balance across a range of mining impacted waters; (2) evaluate whether  $S_nO_x^{2-}$  compounds dominate the SOI pool for these waters; and (3) compare current industry analytical methods for thiosalts determination with a new approach proposed here. From 2014 to 2018, 52 water samples were collected from four Canadian base metal mine water management systems in Ontario, Manitoba, and Newfoundland. These samples were characterized for total sulfur (TotS) as well as individual sulfur species ( $\Sigma H_2S$ ,  $S^0$ ,  $SO_3^{2-}$ ,  $S_2O_3^{2-}$ ,  $S_3O_6^{2-}$ ,  $S_4O_6^{2-}$ , and  $SO_4^{2-}$ ). Thiosulfate was consistently found to represent only a minor component of TotS, with an average relative percentage of  $\approx 4\%$  across all samples. The reactive sulfur pool, ( $S_{react}$ ), defined here as all sulfur compounds capable of oxidation, was significant and variable, averaging  $30 \pm 25\%$  of the S budget. A direct comparison of  $S_{react}$  concentrations to thiosalts concentrations determined by either of the two currently available analytical methods (indirect acid titration method or direct  $S_2O_3^{2-}$  method by ion chromatography) indicated that  $S_{react}$  was significantly higher ( $p < 0.05$ ) for a selected suite of samples ( $n = 6$ ) collected in 2018. These results indicate that currently available methods may underreport the concentrations of oxidizable sulfur compounds in tailings reservoir water caps and receiving environmental waters.  $S_{react}$  provides a conservative, economically viable and directly comparable measurement to monitor potential dissolved sulfur oxidation risks in water discharged to receiving environments.

**Keywords** Mining water · Mass-balance · Thiosalts · Reactive sulfur · Sulfur oxidation intermediates · Monitoring tool

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## Introduction

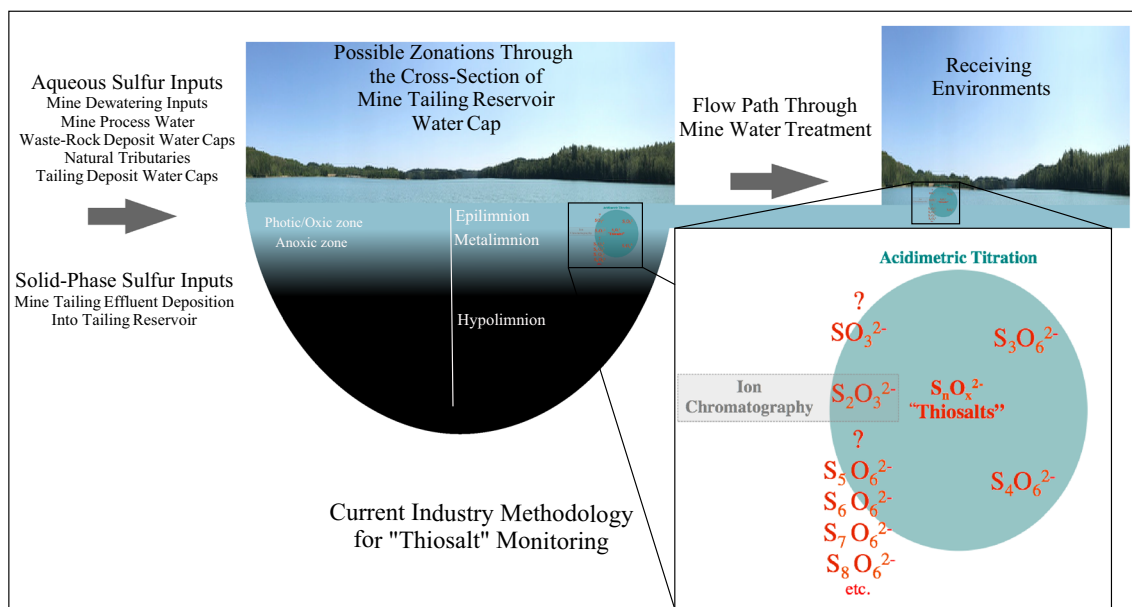
Sulfur plays a central role in many potential environmental risks associated with mining. Sulfide minerals are the predominant hosts for economically viable metals (Johnson and Hallberg 2003), resulting in abundant sulfur compounds in tailings reservoirs and other mining impacted waters (MIWs). The occurrence of sulfur oxidation intermediates (SOIs) in the dissolved phase of MIWs is a significant industry-wide concern due to their potential to generate acidity, depress oxygen, and create toxic effects in receiving environments as they oxidize. Any sulfur compound with an oxidation state less than the +6 observed in sulfate, ( $SO_4^{2-}$ ) can be oxidized and/or disproportionated through abiotic and microbially-mediated sulfur cycling

reactions (Whaley-Martin et al. 2019). Currently, mines are not required by regulators to monitor dissolved SOIs in tailings reservoirs or receiving waters, but those that do monitor a subset referred to as thiosalts. These sulfur compounds (of the general form  $S_nO_x^{2-}$ ) are commonly but not solely produced during extraction/processing of sulfide-rich ores and have been implicated in toxicity test failures (Miranda-Trevino et al. 2013). In particular, thiosulfate,  $S_2O_3^{2-}$  is a widespread, abundant thiosalt observed in mill effluents associated with sulfide ore extraction (Miranda-Trevino et al. 2013). Since these process waters are regularly discharged into tailing reservoirs, thiosalts are commonly assumed to be the dominant SOI in these waters, despite no study to date directly determining the validity of this assumption.

A lack of standardization within the industry with respect to the definition of thiosalts has resulted in different analytical methods being used. One strategy solely measures thiosulfate concentrations ( $S_2O_3^{2-}$ ) by ion chromatography (IC) and reports this as thiosalts. The other commonly used analysis employs an acidimetric titration (AT) proxy method thought to provide an indirect, but more robust measure of thiosalts species based on the assumption that  $S_2O_3^{2-}$ ,  $S_3O_6^{2-}$ , and  $S_4O_6^{2-}$  compounds are dominant (Makhija and Hitchen 1979) (See Fig. 1). Neither of these methods capture colloidal/particulate sized elemental sulfur ( $S^0$ ) or organo-sulfur compounds, which have been identified as reactive and important sulfur species that can be generated, transformed, and/or consumed through microbial sulfur cycling in aquatic environments (Gourdon and Funtowicz 1998;

Lin et al. 2013; Pokorna et al. 2007). The two currently available monitoring approaches are inconsistent in terms of how thiosalts are operationally and analytically defined. Perhaps more important, all present definitions of thiosalts potentially encompass only a subset of the SOIs that may occur in MIWs. To the best of our knowledge, there are no published sulfur mass-balance (measuring total aqueous sulfur and complementary sulfur speciation) determinations of mining waters (i.e. tailing reservoir water caps and discharge waters) to date. Thus, no direct assessment exists that has evaluated whether current thiosalts measurements capture all, or even most, of the sulfur pool that could cause downstream impacts in receiving environments through subsequent oxidation and/or disproportionation.

Similar to the variations observed in current industrial monitoring of sulfur compounds, SOI distributions reported for natural systems within the scientific literature also differ in the analytical methods as well as the specific sulfur species characterized (Boulegue 1977; Ferrer et al. 2011; Findlay 2016; Fuseler and Cypionka 1995; Kamysny et al. 2008; La et al. 1982; Lichtschlag et al. 2013; Luther et al. 1991, 2001; Warren et al. 2016). This is compounded by the analytical challenges of identifying the presence of specific SOI species as many occur at low abundance and in semi-stable states (Kamysny et al. 2008, 2009; Rozan et al. 2000). Thus, knowledge gaps across industrial and fundamental research investigations exist in the proportions and compositions of the SOI compounds in environmental waters.



**Fig. 1** Schematic diagram depicting the types of mining impacted waters this study focused on, the possible SOI species that can occur as thiosalts ( $S_nO_x^{2-}$ ) and the specific SOI species quantified by the two currently available analytical thiosalts monitoring approaches

(ion chromatography ( $S_2O_3^{2-}$ ) and acidimetric titration ( $S_2O_3^{2-}$ ,  $S_3O_6^{2-}$  and  $S_4O_6^{2-}$ ). Uncertainty remains on whether higher order polythionate species and  $SO_3^{2-}$  are being routinely captured with acidimetric titration and thus are denoted with a “?”

A sulfur mass-balance approach can determine whether currently employed thiosalts methods are sufficiently conservative for monitoring potential SOI related risks. The authors of this study could only identify one research article from the academic literature (Edwards et al. 1992) that provided both total sulfur and sulfate concentrations for natural water samples. Notably, mass-balance determinations are standard practice in studies examining other elements in aquatic systems where multiple possible oxidation states under environmental settings result in complex chemical speciation—i.e. arsenic (Komorowicz and Bara 2016; Whaley-Martin et al. 2012) and selenium (Robberecht and Van Grieken 1982). Thus, it appears that this fundamental approach is being underutilized in the field of aquatic sulfur biogeochemistry. The underlying hypothesis of this study was that current thiosalts monitoring efforts, regardless of which available analytical method used, may underestimate the concentration of SOIs that occur in MIWs. Thus, the first objective of this research was to apply a sulfur mass-balance approach combining measurement of total sulfur concentrations (TotS) with sulfur speciation to assess the relative proportions of thiosalts compounds in MIWs including tailings reservoirs and receiving environments (post-treatment) from a range of mines. The second objective was to compare current thiosalts monitoring methods with a new procedure for determining reactive sulfur, proposed here, as a more conservative sulfur-monitoring tool.

## Materials and Methods

### Sample Collection

In 2014 and 2015, 27 water samples were collected from seven sites within the water treatment system of a Ni/Cu mine located about 30 km northwest of Sudbury, Ontario. The sites consisted of the water cap of a “tailings reservoir” (38 m depth) and six water inputs (WasteRock<sub>1</sub>, WasteRock<sub>2</sub> (constant water bodies overlying wasterock piles)), a mine dewatering stream, and pipes (DP<sub>1</sub>, DP<sub>2</sub>, and DP<sub>3</sub>) that discharge water into the tailings reservoir. In 2018, additional tailings reservoir and receiving environment water samples were collected from May to August from the Sudbury, Ontario mine water system (processed on-site) and three additional mine sites in Flin Flon, Manitoba, Snow Lake, Manitoba, and BaieVerte, Newfoundland. The Sudbury samples were processed on site whereas the samples for mines 2–4 were shipped to the University of Toronto and processed on arrival there (supplemental Table S-1). The sampling methods have been described previously in detail (Whaley-Martin et al. 2019). Briefly, water samples from an approximate depth of 0.5 m were collected using telescopic pole water samplers with a  $\approx$  500 mL polyethylene or a

glass bottle that had been rinsed with site water three times immediately prior to use. Water samples from depths in the tailing reservoirs were collected with Van Dorn samplers from the Sudbury, Ontario Mine from a floating platform accessible by boat and directly from a boat at the Flin Flon, Manitoba secondary tailing reservoir. In total, across years, seasons, mines, sites, and different water depths within these systems, 52 water samples were targeted for TotS and SOI speciation analyses. Water cap physico-chemical parameters [temperature, pH, dissolved oxygen (%) and conductivity] were determined onsite using a YSI 600 XLM (Sudbury, Ontario), a ProDSS water quality meter (Flin Flon and Snow Lake, Manitoba) and a Thermo Scientific Orion A329 portable multiparameter meter (BaieVerte, Newfoundland). ORP measurements were converted to Eh by adding the half cell potential of the reference electrode and are shown in the supplemental information section.

### Total Aqueous Sulfur Analysis

MIW samples for total dissolved sulfur (TotS<sub>aq</sub>) analyses were filtered on site (0.45  $\mu$ m and 0.2  $\mu$ m membrane filters, Pall Acrodisc<sup>®</sup> 25 mm Supor<sup>®</sup> membrane) after transfer with 60 mL syringes (pre-rinsed with site water) into 50 mL polypropylene centrifuge tubes. The centrifuge tubes were pre-acid spiked for preservation to achieve a final concentration of 0.2% HNO<sub>3</sub> (Optima grade, Fisher Chemical). Samples were stored at 4 °C until shipment to the Commonwealth Scientific and Industrial Research Organization (CSIRO), Lucas Heights Laboratories, Australia for TotS analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian730 ES (Mulgrave, Australia) (supplemental Table S-2). Sulfur calibration standards were prepared from certified reference stock solutions (AccuStandard New Haven, CT, USA) in 2% v/v HNO<sub>3</sub>. The S concentration was determined by measuring signal intensity at the 181.972 nm sulfur emission line. The Varian fast automated curve-fitting technique (FACT) was used to correct for any background or inter-element interferences. In the development of this method, spectral interferences from calcium and manganese using the operating conditions specified in Table S-2 were found to be negligible. The use of ICP-AES for measuring sulfur in environmental samples has been confirmed in previous studies (Prietz et al. 1996; Reisman et al. 2007; Wu et al. 2009). The limit of detection (LOD) for sulfur was 1 mg/L (calculated as three times the standard deviation of the mean blank). A paired two-sample t-test revealed no statistically significant difference ( $p=0.4$ ) between TotS<sub>aq</sub> concentrations in the 0.2 and 0.45  $\mu$ m filtered water samples. Thus, mass-balance calculations were carried out with the dissolved S defined as the the <0.45  $\mu$ m filtered fraction, except for two samples where only the <0.2  $\mu$ m fraction was available for analyses.

## Derivatization of Thiosulfate and Sulfite for HPLC–UV/VIS

Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) and sulfite ( $\text{SO}_3^{2-}$ ) analyses were determined by HPLC–UV/VIS using a method adapted from Rethmeier et al. (1997), which involves derivatization of thiosulfate and sulfite with monobromobimane to create fluorescent products detectable following chromatographic separation (Table 1). Immediately after sampling, 50  $\mu\text{L}$  of water samples were derivatized by adding 50  $\mu\text{L}$  of acetonitrile, 50  $\mu\text{L}$  of 50 mmol/L HEPES (4-(2-hydroxyethyl) piperazine-1-ethanesulfonic acid,  $\geq 99.5\%$ , Sigma)/5 mmol/L of EDTA (ethylenediaminetetraacetic acid, 99.4–100.6%, Sigma Aldrich) ( $\text{pH}=8.0$ , adjusted with NaOH) buffer, and 10  $\mu\text{L}$  of 48 mmol/L monobromobimane ( $> 97\%$ , Sigma Aldrich) in acetonitrile in 2 mL glass amber vials. The derivatization reaction was carried out in the dark for 30 min, after which 100  $\mu\text{L}$  of methanesulfonic acid ( $\approx 100$  mmol) ( $\geq 99.5\%$ , Sigma Aldrich) was added to stop the reaction. These derivatized samples were stored in the dark at 4  $^\circ\text{C}$  during transport and kept frozen before LC-fluorescence detection.

The monobromobimane derivatized waters were analyzed on a Shimadzu LC-20AD prominence liquid chromatograph (LC) coupled to a fluorescence/UV/VIS detector. LC separations of  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$  derivatives were achieved using an Alltima™ HP C<sub>18</sub> reversed phase column (150 mm  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ , Grace™) held at 35  $^\circ\text{C}$  using an isocratic mobile phase of 70% of 0.25% acetic acid v/v ( $\text{pH}$  3.5 adjusted with 1 N NaOH) and 30% methanol at 1.5 mL/min for 6 min, when it was lowered to 0.85 mL/min for 9 min. The excitation wavelength was set to 380 nm and the emission wavelength 478 nm. The sulfite peak eluted at  $\approx 2.3$  min and thiosulfate eluted at  $\approx 3.5$  min. Calibration curves were prepared using commercially available standards of sodium thiosulfate (Sigma Aldrich, 99% purity) and sodium sulfite (Sigma Aldrich,  $\geq 98\%$  purity). Detection limits were 0.05 mmol/L for thiosulfate and 0.01 mmol/L for sulfite, the lowest standards run where linearity was maintained.

## Elemental Sulfur Analysis by HPLC–UV/VIS

Water samples for elemental sulfur analysis were also collected across all years. A subset of the filtered MIWs collected in 2014/15 ( $n=12$ ) were sub-sampled by pipetting 200  $\mu\text{L}$  directly into amber 2 mL glass vials and immediately frozen for later analysis. After thawing to room temperature, chloroform was added and the sample vials were shaken for  $\approx 10$  s, and phases were allowed to separate to achieve a 1:1 solvent to water ratio. The chloroform layer was then removed with a chloroform pre-rinsed glass syringe and placed into a 4 mL glass vial and the aqueous phase was

rinsed 2–3 more times with chloroform (each time allowing a phase separation). The chloroform extracts collected for each sample were combined. Samples were gently blown down under pure  $\text{N}_2$  gas to a 100  $\mu\text{L}$  final volume and run through HPLC–UV/VIS on an Alltima™ HP C<sub>18</sub> reversed phase column with a 1 mL/min flow rate through a room temperature column and an isocratic mobile phase of 95% methanol and 5% water (held for 10 min). The absorbance wavelength for  $\text{S}^0$  was 263 nm and the elemental sulfur peak eluted at  $\approx 8$  min. Calibration standards were constructed through serial dilution of commercially available elemental sulfur (32.065 g/mol ( $\approx 99\%$ , Fisher Scientific) with chloroform. Detection limits for elemental sulfur were 0.075 mmol/L, the lowest standard run where linearity was maintained.

## Analysis of Dissolved $\Sigma\text{H}_2\text{S}_{\text{aq}}$

Total dissolved aqueous  $\Sigma\text{H}_2\text{S}_{\text{aq}}$  was determined on 27 samples at the Sudbury, Ontario mine immediately after collection to limit sulfide loss through rapid abiotic oxidation. The methylene blue spectrometric method (HACH Company, Loveland, CO, USA) was used as a rapid *in situ* technique for sulfide quantification (Reese et al. 2011; Azizi et al. 2015; Risacher et al. 2018). For waters collected at depth in the Sudbury tailings reservoir with a VanDorn water sampler, all sample ports were kept closed while water was extracted through a small port within one minute of bringing the sampler up to the boat in an attempt to limit aeration of the water samples prior to analysis. A 10 mL water sample taken with a sterile 10 mL pipette was eluted within 30 s of collection into a pre-charged 15 mL Falcon tube containing 0.5 mL of “Reagent 1” to which 0.5 mL “Reagent 2” was then immediately added, according to USEPA Method 8131 as adapted wastewater analysis. Details of this methodology are described at [https://www.nemi.gov/methods/metho\\_d\\_summary/7418/](https://www.nemi.gov/methods/metho_d_summary/7418/). After 5 min of reacting, samples were analyzed on site to obtain dissolved  $\Sigma\text{H}_2\text{S}_{\text{aq}}$  concentrations using spectrometric analysis with a HACH DR2800 (HACH Co., Loveland, CO, USA) together with internal calibration curves derived by the manufacturer. Sulfide concentrations were not included in the mass-balance concentrations as the methodology could not rule out some potential loss during the VanDorn sampling of anoxic samples despite rapid collection and analyses within 1 min of bringing the bottle to the surface of the reservoir.

## Analysis of Dissolved $\text{SO}_4^{2-}$ Through Spectrometric and Ion Chromatographic Methods

Water samples for dissolved  $\text{SO}_4^{2-}$  analyses were analyzed on site (Ontario mine) or were analyzed on arrival at the University of Toronto Laboratory (other three mine

**Table 1** Physico-chemical parameters and sulfur speciation for mining impacted water bodies ( $n = 27$ ) at the Sudbury, Ontario mine (2014–2015)

	Mining impacted water (MIW)	pH	°C	Specific conductance ( $\mu\text{S}/\text{cm}^2$ )	$\text{O}_2$ (%)	Total S ( $<0.45 \mu\text{m}$ ) (mmol/L)	Total S ( $<0.2 \mu\text{m}$ ) (mmol/L)	$\text{S}-\text{SO}_4^{2-}$ (mmol/L) <sup>a</sup>	$\text{S}-\text{S}_2\text{O}_3^{2-}$ (mmol/L)	$\text{S}-\text{SO}_3^-$ (mmol/L)	$\text{S}-\text{S}^0$ (mmol/L) <sup>a</sup>	$\text{H}_2\text{S}$ ( $\mu\text{mol/L}$ )	Unresolved aqueous SOI pool (mmol/L)	$\text{S}_{\text{react}}$ (mmol/L)	$\text{S}_{\text{react}}$ proportion of total S Pool (%)
Sep-14	Waste rock <sub>1</sub>	3.64	15.4	2572	100	$9.7 \pm 0.03$	N/A	$4.0 \pm 0.5$	$1.4 \pm 0.3$	$< 0.01$	$< 0.02$	$< \text{LOD}$	4.3	5.7	59
	Waste rock <sub>2</sub>	3.47	15.3	N/A	61	$10.9 \pm 0.12$	N/A	$3.8 \pm 0.5$	$1.6 \pm 0.02$	$< 0.01$	N/A	$< \text{LOD}$	5.5	7.1	65
	Mine dewatering	7.01	13.2	2673	98	$7.9 \pm 0.05$	N/A	$4.1 \pm 0.5$	$0.95 \pm 0.3$	$< 0.01$	N/A	$0.87 \pm 0.01$	2.85	3.8	48
	Tailings reservoir 2 m	6.92	16.4	2244	28	$10.3 \pm 0.02$	N/A	$5.7 \pm 0.5$	$1.1 \pm 0.3$	$< 0.01$	$< 0.02$	0.12	3.5	4.6	45
Nov-14	Tailings reservoir 21 m	7.66	15.9	2262	5	$9.4 \pm 0.64$	N/A	$6.04 \pm 0.5$	$1.6 \pm 0.07$	$< 0.01$	$< 0.02$	$< \text{LOD}$	1.76	3.4	36
	Waste rock <sub>2</sub>	4.05	4.2	2303	83	$8.1 \pm 0.75$	$9.4 \pm 0.07$	$6.8 \pm 0.5$	$0.67 \pm 0.2$	$0.04 \pm 0.05$	$< 0.02$	$0.17 \pm 0.01$	0.63	1.3	16
	Mine dewatering	6.66	7.3	N/A	100	$7.4 \pm 0.01$	$7.4 \pm 0.07$	$6.5 \pm 0.5$	$0.68 \pm 0.01$	$0.02 \pm 0.01$	$< 0.02$	$0.35 \pm 0.01$	0.22	0.9	12
	Discharge pipe (DP <sub>1</sub> )	3.56	6.3	1824	N/A	$5.3 \pm 0.43$	$4.4 \pm 0.64$	$4.3 \pm 0.5$	$0.61 \pm 0.05$	$< 0.01$	$< 0.02$	$2.6 \pm 0.01$	0.39	1	19
	Tailings reservoir 2m	6.63	8.2	2232	N/A	N/A	$9.6 \pm 0.10$	$6.8 \pm 0.5$	$0.14 \pm 0.01$	$< 0.01$	$< 0.02$	$< \text{LOD}$	2.66	2.8	29
	Tailings reservoir 21m	7.23	8.1	2231	N/A	N/A	$9.8 \pm 0.04$	$7.2 \pm 0.5$	$0.14 \pm 0.00$	$< 0.01$	$< 0.02$	$< \text{LOD}$	2.46	2.6	27

Table 1 (continued)

Mining impacted water (MIW)	pH	°C	Specific conductance ( $\mu\text{S}/\text{cm}^2$ )	$\text{O}_2$ (%)	Total S ( $<0.45 \mu\text{m}$ ) (mmol/L)	Total S ( $<0.2 \mu\text{m}$ ) (mmol/L)	$\text{S}-\text{SO}_4^{2-}$ (mmol/L) <sup>a</sup>	$\text{S}-\text{S}_2\text{O}_3^{2-}$ (mmol/L)	$\text{S}-\text{SO}_3^-$ (mmol/L)	$\text{S}-\text{S}^0$ (mmol/L) <sup>a</sup>	$\text{H}_2\text{S}$ ( $\mu\text{mol/L}$ )	Unresolved aqueous SOI pool (mmol/L)	$\text{S}_{\text{react}}$ (mmol/L)	Proportion of total S Pool (%)
May-15														
Mine dewatering	5.16	15.8	1447	98	$6.3 \pm 0.03$	$6.3 \pm 0.01$	$6.21 \pm 0.5$	$0.2 \pm 0.01$	$0.041 \pm 0.01$	N/A	$0.23 \pm 0.01$	< LOD	0.09	1
Discharge pipe 1 (DP <sub>1</sub> )	2.75	15.4	1875	94	$5.8 \pm 0.25$	$5.5 \pm 0.20$	$6.6 \pm 0.5$	$0.21 \pm 0.01$	$0.08 \pm 0.02$	N/A	$0.07 \pm 0.01$	< LOD	< LOD	< LOD
Discharge pipe 2 (DP <sub>2</sub> )	3.91	15.6	3699	100	$13 \pm 0.11$	$11.8 \pm 0.01$	$9.0 \pm 0.5$	$0.19 \pm 0.03$	< 0.01	N/A	$1.7 \pm 0.01$	3.81	4	31
Discharge pipe 3 (DP <sub>3</sub> )	6.23	13.7	N/A	95	N/A	N/A	$0.8 \pm 0.1$	$0.14 \pm 0.02$	< 0.01	N/A	$0.01 \pm 0.01$	N/A	N/A	N/A
Tailings reservoir 2.5 m	7.05	8.9	2130	21	$8.3 \pm 0.02$	$8.3 \pm 0.035$	$8.5 \pm 0.5$	$0.26 \pm 0.05$	< 0.01	N/A	$0.14 \pm 0.01$	< LOD	< LOD	< LOD
Tailings reservoir 3.5 m	7.01	8.5	2135	10	$8.3 \pm 0.03$	$8.4 \pm 0.015$	$8.5 \pm 0.5$	$0.18 \pm 0.04$	< 0.01	N/A	$0.29 \pm 0.02$	< LOD	< LOD	< LOD
Tailings reservoir 15 m	7.21	7.3	2147	2.5	$8.4 \pm 0.03$	$8.4 \pm 0.03$	$8.6 \pm 0.5$	$0.16 \pm 0.02$	< 0.01	N/A	$0.44 \pm 0.02$	< LOD	< LOD	< LOD
Tailings reservoir 2 m	7.28	15.4	1803	13	$8.3 \pm 0.02$	$8.2 \pm 0.01$	$2.6 \pm 0.5$	$0.20 \pm 0.04$	< 0.01	N/A	$0.24 \pm 0.01$	5.5	5.7	69
Tailings reservoir 4 m	8.25	14.5	1757	3.9	$8.4 \pm 0.01$	$8.4 \pm 0.04$	$1.6 \pm 0.5$	$0.23 \pm 0.04$	< 0.01	N/A	$0.65 \pm 0.06$	6.57	6.8	81
Tailings reservoir 30 m	8.45	10.5	1581	0.4	$8.3 \pm 0.01$	$8.3 \pm 0.03$	$2.0 \pm 0.5$	$0.14 \pm 0.00$	< 0.01	N/A	$0.75 \pm 0.04$	6.16	6.3	76

**Table 1** (continued)

	Mining impacted water (MIW)	pH	°C	Specific conductance (μS/cm <sup>2</sup> )	O <sub>2</sub> (%)	Total S (<0.45 μm) (mmol/L)	Total S (<0.2 μm) (mmol/L)	S-SO <sub>4</sub> <sup>2-</sup> (mmol/L) <sup>a</sup>	S-S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mmol/L)	S-SO <sub>3</sub> <sup>-</sup> (mmol/L)	S-S <sup>o</sup> (mmol/L) <sup>a</sup>	H <sub>2</sub> S (μmol/L)	Unresolved aqueous SOI pool (mmol/L)	S <sub>react</sub> (mmol/L)	S <sub>react</sub> proportion of total S Pool (%)
July 22 2015	Tailings reservoir 1 m	6.97	19.4	2246	63	8.4 ± 0.02	8.3 ± 0.01	1.4 ± 0.5	0.10 ± 0.35	< 0.01	N/A	0.19 ± 0.01	6.9	7	83
	Tailings reservoir 3.5 m	7.28	17.5	2235	11	8.4 ± 0.02	8.4 ± 0.01	2.2 ± 0.5	0.10 ± 0.02	< 0.01	N/A	0.18 ± 0.01	6.1	6.2	74
	Tailings reservoir 10 m	8.34	14.3	2223	2.5	8.4 ± 0.05	8.5 ± 0.01	1.7 ± 0.5	0.10 ± 0.04	< 0.01	N/A	0.37 ± 0.03	6.6	6.7	80
Nov-15	Waste rock <sub>1</sub>	3.7	9.9	2415	99	8.9 ± 0.14	8.4 ± 0.03	5.4 ± 0.5	0.15 ± 0.02	< 0.01	< 0.02	0.16 ± 0.02	3.35	3.5	39
	Waste rock <sub>2</sub>	N/A	N/A	N/A	N/A	10 ± 0.52	11.2 ± 0.1	5.8 ± 0.5	0.16 ± 0.02	< 0.01	< 0.02	0.18 ± 0.01	4.04	4.2	42
	Discharge pipe 3 (DP <sub>3</sub> )	6.57	9.3	1819	97	1.2 ± 0.02	1.2 ± 0.01	0.7 ± 0.1	0.12 ± 0.01	< 0.01	< 0.02	0.23 ± 0.02	0.38	0.5	42
	Tailings reservoir 1.3 m	6.35	11.0	2220	39	8.8 ± 0.07	8.7 ± 0.02	6.8 ± 0.5	0.26 ± 0.02	< 0.01	< 0.02	1.3 ± 0.02	1.74	2	23

N/A not analyzed

<sup>a</sup>Sulfate determinations determined through spectroscopy were assumed to have an error of 0.5 mmol/L, which was larger than the triplicate error in all cases but consistent with methodology limitations that were determined for samples run in parallel through ion chromatography



sites). Samples were collected in clean 250 mL or 1 L Nalgene sample bottles that had been rinsed with the sample three times, then filled to leave no headspace, and refrigerated at 4 °C until analysis (24–48 h). Concentrations of dissolved  $\text{SO}_4^{2-}$  were determined using spectrometric analysis (*USEPA SulfaVer 4 Method 8051*) with a HACH DR2800 (HACH Co., Loveland, CO, USA). To attain concentrations within the range of the spectrometric calibration curves, all mine waters were diluted by a factor of 20 (500  $\mu\text{L}/10\text{ mL}$ ). Previous research (Reisman et al. 2007) has shown that dilution factors greater than 40 can have a significant effect on sulfate recovery in similar types of mining waters using the *SulfaVer 4 Method 8051*. Thus, while not relevant for the waters under investigation here, the authors of this study recommend instead using ion chromatography to determine sulfate concentrations in any mine waters that require significant dilution for analysis. External standard curves and QA/QC check standards were analyzed with known dissolved  $\text{SO}_4^{2-}$  concentrations (prepared from a certified stock of 100 mg/L, Lab-Chem (> 99%) with an instrumental error of  $\pm 0.5\text{ mmol/L S-SO}_4^{2-}$ ).

To determine if any interferences caused by mining water matrices were significantly affecting dissolved  $\text{SO}_4^{2-}$  concentrations determined by spectrometric analysis, two additional quality assurance/quality control measures were taken. Parallel analysis of mine water matrices through internal ion chromatography and spectrometry was carried out on 15 mine water samples (supplemental Table S-3) selected from a frozen archive of water samples. Samples were thawed and run for dissolved  $\text{SO}_4^{2-}$  concentrations using laboratory-based ion chromatography at the CSIRO Land and Water Laboratory, Lucas Heights, NSW, Australia and the field-relevant spectrometric methods utilized above. The chromatographic separation of dissolved  $\text{SO}_4^{2-}$  was achieved with an anion column (Shodex IC SI-904E) using a Shimadzu LC-20 coupled to a Shimadzu CDD-10AVP detector with a Dionex ACCRS 500 anion suppressor. Detailed ion chromatographic parameters are summarized in Table S-2. The mobile phase consisted of an acetonitrile–water (5:95 v/v) solution containing 3.2 mmol/L of  $\text{NaHCO}_3$  and 3.2 mmol/L of  $\text{Na}_2\text{CO}_3$  at 1 mL/min. Dissolved  $\text{SO}_4^{2-}$  concentrations for the ion chromatography method were determined by preparing a calibration curve using a 1000  $\mu\text{g/mL SO}_4^{2-}$  standard (AccuStandard®); detection limits for  $\text{SO}_4^{2-}$  were found to be 0.3 mg/L. For a third quality control check, the spectrometrically determined dissolved  $\text{SO}_4^{2-}$  concentrations of the Sudbury receiving environment waters were compared to concentrations determined by an external commercial laboratory as part of the mine’s federally regulated monitoring program.

## Sulfur Mass Balance Determination

Quantification of the “reactive sulfur pool” ( $S_{\text{react}}$ ) adopted in this study was based on the approach described by Edwards et al. (1992). The difference between the 0.45  $\mu\text{m}$  filtered  $\text{TotS}_{\text{aq}}$  and  $\text{S-SO}_4^{2-}$  concentration was assigned as the “reactive sulfur pool” ( $S_{\text{react}}$ ). This pool includes all specific aqueous SOI species that were directly measured (e.g.  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ) and any other SOI compounds of oxidation state  $< +6$  that were indirectly captured in the  $\text{TotS}_{\text{aq}}$  measurement (excluding dissolved  $\Sigma\text{H}_2\text{S}$ ).

## Industry Thiosalts Methods: Ion Chromatography and Acidimetric Titration

From May to August 2018, 25 water samples from tailing reservoirs and their respective receiving environments from the four mines were collected in 125 mL high-density polyethylene (HDPE) bottles, frozen, and shipped to an external commercial laboratory that carries out thiosalts analysis by IC. External laboratory analysis of thiosulfate, trithionate, and tetrathionate was completed by ion chromatography using a Dionex ion chromatograph with OmniPac PAX-100 analytical guard columns and a variable wavelength detector. The commercial laboratory was reporting concentrations of thiosulfate as thiosalts and provided concentrations of trithionate and tetrathionate on request. Six parallel samples from two of the four mining treatment systems were also analyzed for thiosalts through acidimetric titration by an in-house mine laboratory following a method adapted specifically for mining effluents (Makhija and Hitchen 1979). Both the IC methods and acidimetric titration methods included quality assurance/quality control (QAQC) samples consisting of method blanks and standards of known sodium thiosulfate ( $\text{NaS}_2\text{O}_3^{2-}$ ) concentration, with recoveries well within the acceptable recovery limits of 95% to 105%.

## Statistical Analysis

All data organization, calculations, and statistical tests (two-sample T-tests, Pearson R correlation coefficient) were carried out with Microsoft® Excel® Version 14.7.7.

## Results

### Comparison of $[\text{SO}_4^{2-}]$ Measured Using Spectrometry vs. Ion Chromatography

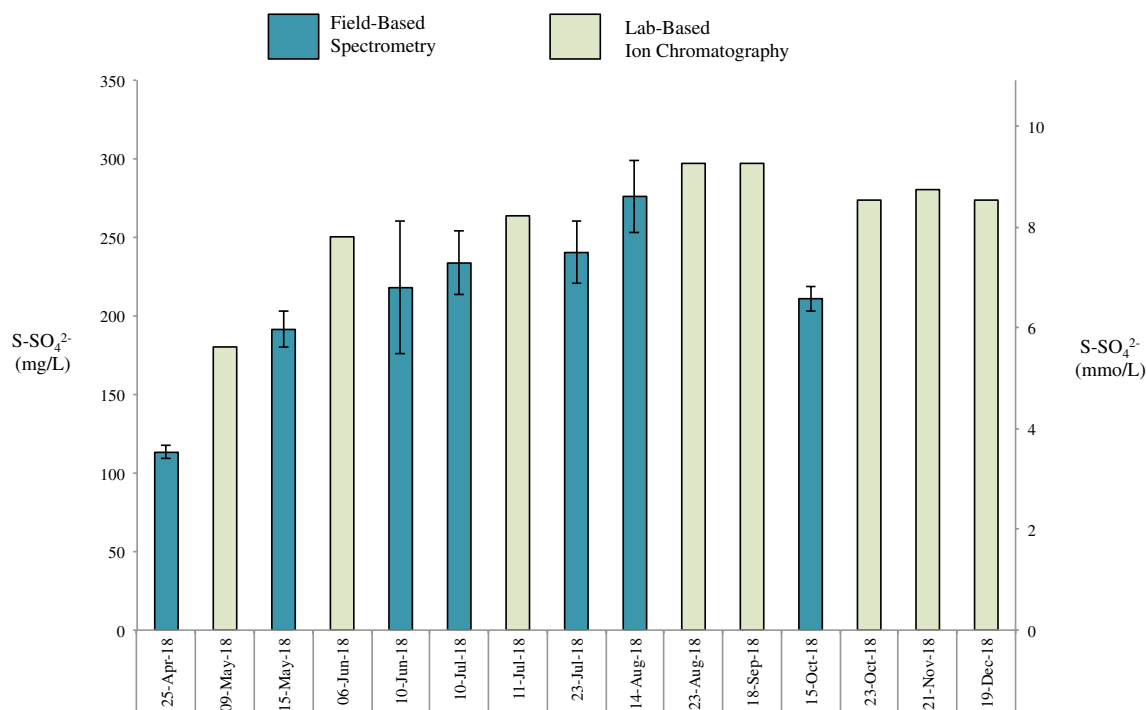
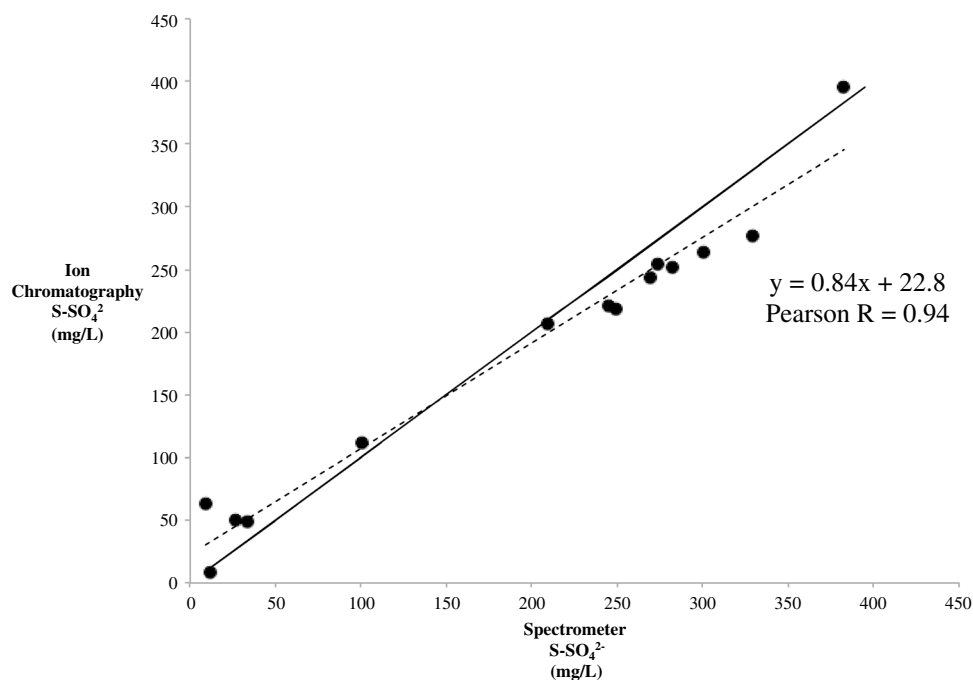
Dissolved  $\text{SO}_4^{2-}$  concentrations determined by field-relevant spectrometric methods showed excellent agreement with those determined using the lab-based IC method (Pearson R correlation coefficient = 0.94,  $p < 0.0001$ ) in the 15 archived



mine water samples that were tested (Fig. 2). A slight offset from the 1:1 line may be present at higher concentrations ( $\approx 250$  to  $350$  mg/L  $\text{S-SO}_4^{2-}$ ) with the spectrometry slightly underestimating concentrations determined by IC. This trend

was also noted in  $\text{SO}_4^{2-}$  analyses at the Sudbury receiving water's monitoring station (Fig. 3). In this instance, comparison was between the field based-methods and  $\text{SO}_4^{2-}$  concentrations determined through an external laboratory. The

**Fig. 2** Linear relationship between sulfate concentrations measured using a portable field instrument (spectrometry) and laboratory based ion chromatography (sample locations and dates are listed in the supporting information in supplemental Table S-4.)



**Fig. 3** Sulfate concentration comparison at the regulated monitoring station receiving waters (Sudbury, Ontario mine) measured using a portable field instrument (spectrometry) and ion chromatography (external commercial laboratory analyses)

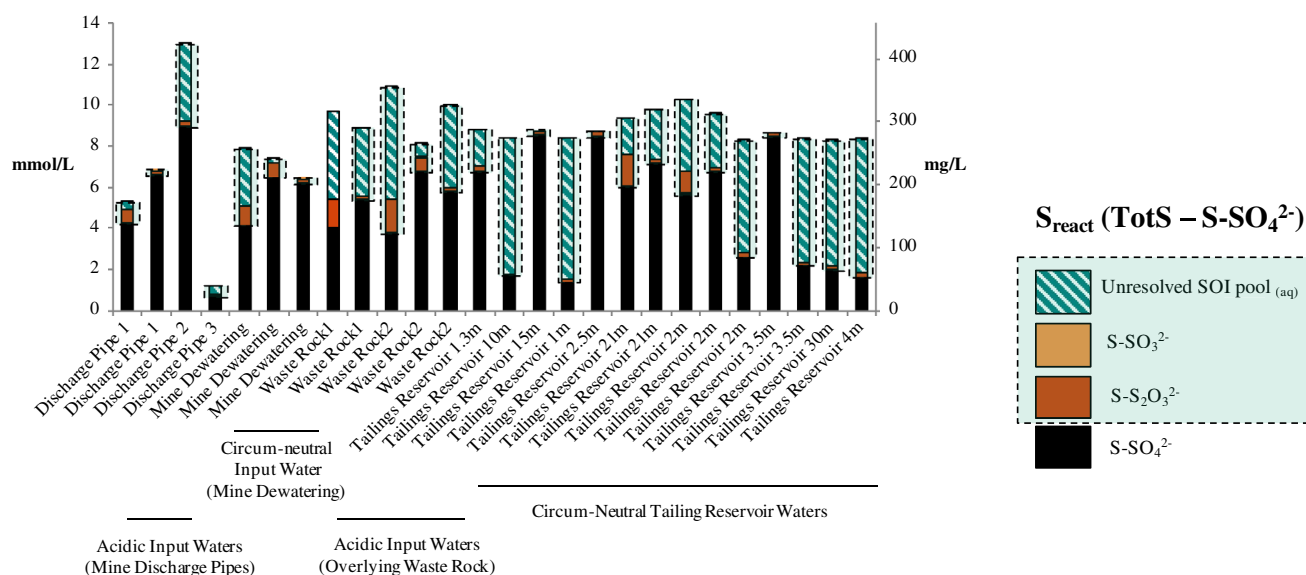
small error was considered acceptable as a slight underestimation of  $\text{SO}_4^{2-}$  concentrations results in a more conservative estimate of risk utilizing the mass-balance approach. Continuous validation of sulfate concentration measurements made by field spectrometric equipment by comparison with laboratory IC measurements using split samples is recommended QA/QC to ensure there are no analytical interferences that may result in inaccurately reported sulfate concentrations. These results validate the use of this field portable instrument to measure  $\text{SO}_4^{2-}$  concentrations in mining waters requiring a  $\leq 20$  times dilution factor for analysis.

### Sulfur Mass Balance Determinations

A wide range in pH, temperature, dissolved oxygen concentrations (Table 1), and Eh (Fig. S-2) were observed in the MIWs sampled at the Sudbury, Ontario mine site between 2014 and 2015. Comparison of the Eh–pH field data with the stability field diagram for reduced sulfur species in natural waters (Druschel et al. 2003) indicated that only one sample (July 2015, Sudbury Mine Tailings reservoir, 30 m depth) was in the range where sulfide would be expected to dominate sulfur speciation if the system was in thermodynamic equilibrium. In the remaining samples, mildly oxidizing conditions favour the stability of SOI's such as sulfite and dithionate. Some caution should be applied when applying thermodynamic predictions to mine water systems as they are subject to frequent inputs of SOIs; thus, assuming that the systems are in thermodynamic equilibrium is questionable. The relative importance of water residence times, thermodynamic vs. kinetic control of sulfur speciation in mine

wastewaters, and the role of biotic vs. abiotic processes will be the subject of forthcoming publications.

Total dissolved ( $<0.45 \mu\text{m}$ ) sulfur concentrations  $[\text{TotS}]_{\text{aq}}$  in the input waters that discharge into the tailings reservoir (WasteRock<sub>1</sub>, WasteRock<sub>2</sub>, mine dewatering stream, discharge pipes (DP<sub>1</sub>, <sub>2</sub>, and <sub>3</sub>) averaged  $7.9 \pm 3 \text{ mmol/L}$  (1.2–13 mmol/L). These concentrations were not statistically different (two sample t-test,  $p=0.40$ ) from the mean  $[\text{TotS}]_{\text{aq}}$  in the tailings reservoir, which averaged  $8.6 \pm 0.6 \text{ mmol/L}$  (8.3–10.3 mmol/L). For mass-balance calculations, all sulfur species concentrations are reported as mmol of sulfur (as the atom) within the individual chemical species (e.g.  $\text{S-SO}_4^{2-}$ ) (Table 1). In 2014 and 2015,  $\text{S-SO}_4^{2-}$  concentrations for all waters at the Sudbury Mine water system ranged from 0.7 to 9 mmol/L (average  $5.0 \pm 2.6 \text{ mmol/L}$ ). Thiosulfate ( $\text{S-S}_2\text{O}_3^{2-}$ ) concentrations were an order of magnitude lower, ranging from 0.1 to 1.6 mmol/L (average  $0.4 \pm 0.5 \text{ mmol/L}$ ) and only four of the 27 sampled waters were found to have detectable  $\text{S-SO}_3^{-}$  concentrations, with a maximum of 0.08 mmol/L. Thus,  $\text{S}_2\text{O}_3^{2-}$  comprised an average of  $5 \pm 5\%$  proportion of the TotS dissolved pool in the 2014–2015 waters (Table 1). Elemental sulfur ( $\text{S-S}_0$ ) concentrations were all  $< \text{LOD}$ , and sulfide ( $\text{S-SH}_2\text{S}$ ) concentrations were consistently low, ranging from  $< \text{LOD}$  to  $2.6 \mu\text{mol/L}$ . Measurement of  $\text{S}_{\text{react}}$ , determined as the difference between  $[\text{TotS}_{\text{aq}}]$  and  $[\text{S-SO}_4^{2-}]$  revealed variable, but frequently high, proportions in the 2014/15 MIW samples, ranging from non-detect to 83% of total S (Fig. 4; Table 1). In 2014/15,  $\text{S}_{\text{react}}$  concentrations across all inputs and the TailRes ranged from non-detect to 7.1 mmol/L (average  $3.3 \pm 3 \text{ mmol/L}$ ) (Fig. 4; Table 1). For the two samples



**Fig. 4** Dissolved sulfur speciation ( $\text{S mg/L}$  and  $\text{S mmol/L}$ )  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$  and unresolved S pool of mining impacted waters from 2014–2015 for the northern Ontario Sudbury mine water system

where total dissolved sulfur ( $<0.45 \mu\text{m}$ ) fraction was unavailable, the total dissolved sulfur ( $<0.2 \mu\text{m}$ ) concentrations were used in the mass balance.

### Cross-Mine Relative Abundance of Thiosalts

A wide range in concentration was observed for  $\text{TotS}_{0.45 \mu\text{m}}$  (50–496 mg/L; 1.6–15.5 mmol/L) as well as all individually measured S species: sulfate ( $\text{S-SO}_4^{2-}$ ) (3–365 mg/L; 0.09–11.4 mmol/L), thiosulfate ( $\text{S-S}_2\text{O}_3^{2-}$ ) ( $<0.1$ –25 mg/L;  $<0.003$ –0.8 mmol/L), trithionate ( $\text{S-S}_3\text{O}_6^{2-}$ ) ( $<1$ –3.5 mg/L;  $<0.03$  to 0.1 mmol/L) and tetrathionate ( $\text{S-S}_4\text{O}_6^{2-}$ ) ( $<0.1$ –7.4 mg/L;  $<0.03$ –0.23 mmol/L) across the four mine tailings reservoirs sampled in 2018 (Table 2; Fig. 5a). Concentrations of  $\text{TotS}_{0.45 \mu\text{m}}$  in the receiving environments collected between April and August 2018 ( $n=10$ ) ranged from 12 to 294 mg/L (0.04–9.2 mmol/L) and sulfate ( $\text{S-SO}_4^{2-}$ ) concentrations ranged from 12 to 276 mg/L (0.04–8.6 mmol/L). Concentrations of SOI species in receiving environments water determined by IC ranged between  $<0.1$  to 4.5 mg/L ( $<0.003$ –0.14 mmol/L) for thiosulfate,  $<1$  mg/L ( $<0.03$  mmol/L) for trithionate, and between  $<0.1$  and 0.69 mg/L ( $<0.03$ –0.02 mmol/L) for tetrathionate (Fig. 5b; Table 3).

### Comparison of $\text{S}_{\text{react}}$ and Industry Thiosalts Methods

Six of the 2018 MIW samples from the Flin Flon and Snow Lake mines were analyzed for TotS (ICP-AES),  $\text{SO}_4^{2-}$  (spectrometry), SOI species (thiosulfate, trithionate, and tetrathionate) by IC (commercial laboratory) and in parallel for thiosalts by the acid titration method through the Flin Flon mine's internal laboratory (Tables 2, 3; Fig. 6). For each of these MIW samples, the acid titration determined bulk thiosalts concentrations were consistently, but not statistically significantly, higher ( $p=0.14$ ) than the thiosulfate concentrations determined by IC (Fig. 6; Tables 2 and 3). For a direct comparison with  $\text{S}_{\text{react}}$ , the titration-measured bulk thiosalts concentration (supplemental Tables S-5 and S-6) was assumed to comprise only  $\text{S}_2\text{O}_3^{2-}$  (representative S mass proportion); thus, the S concentration was calculated to be 55% of that value (Fig. 6). In this instance,  $\text{S}_{\text{react}}$  concentrations were found to be higher than both the titration thiosalts method ( $p<0.054$ ) and the IC thiosalts method ( $p<0.012$ ).

## Discussion

### Comparison of Thiosalts and $\text{S}_{\text{react}}$ Pools

The results of this study assessing 52 water samples collected from tailing reservoirs, input waters, and receiving environments across four mines showed that currently accepted industry thiosalts monitoring methods

underestimate the dissolved sulfur compounds available for oxidation, i.e. those that represent risk for receiving environments. The current assumption in thiosalts monitoring is that thiosulfate and/or polythionates dominate the SOI pool and thus monitoring need only concern them. Thus, there was a focus throughout this study in comparing the concentrations and relative proportions of these compounds with the more comprehensive  $\text{S}_{\text{react}}$  pool, defined as all S occurring in oxidation states less than +6 (i.e.  $\text{TotS-S-SO}_4^{2-}$ ).  $\text{S}_{\text{react}}$  was a variable and significant S pool present across all mines at  $30 \pm 25\%$  of the overall sulfur distribution (Fig. 4). The  $\text{S}_{\text{react}}$  identified by the mass-balance approach represents a large dissolved sulfur component present in MIWs that may be typically unquantified in current industrial determinations of thiosalts. Identification of the composition of this dissolved S pool is the subject of ongoing research but, based on the Eh–pH plot for the Sudbury samples, would appear to be potentially composed, at least in part, by dithionate ions. The considerable and perhaps surprising fluctuation in sulfur speciation has been noted within mine water treatment systems previously (Rivett and Oko 1971) and may be attributed to considerable seasonal fluctuations (i.e. lake turnover) and/or mining operational changes within the system. The corresponding lack of decrease in  $\text{TotS}_{\text{aq}}$  indicated that this fluctuation is not attributed to increased precipitation/dilution processes. This has relevance beyond a single site, as expanded sampling in 2018 of tailing reservoirs and receiving environments at the active mine sites in Flin Flon, Snow Lake, and Baie Verte demonstrated the consistent presence, but varying proportion of  $\text{S}_{\text{react}}$  (Figs. 6, 7) throughout spring/summer months.

In all MIWs sampled, thiosulfate was consistently found to occur in low proportions, averaging  $\approx 4\%$  of the overall sulfur pool (Figs. 3, 4, 5). Not surprisingly, since both currently used thiosalts monitoring methods assume thiosulfate dominance, both captured significantly smaller proportions of the overall S pool available for oxidation than that determined by the “analytical window” of  $\text{S}_{\text{react}}$  proposed here (Fig. 5). Further, the two analytical methods currently used to monitor thiosalts generated different values (Fig. 6), with concentrations from the AT method consistently higher than those determined through the IC method. As stated earlier, because the term thiosalts is currently an operationally defined term with no standardized definition or analytical method; caution is therefore required when comparing reported thiosalts concentrations across mines and through time.

### Sulfur Speciation in Mining Impacted Waters

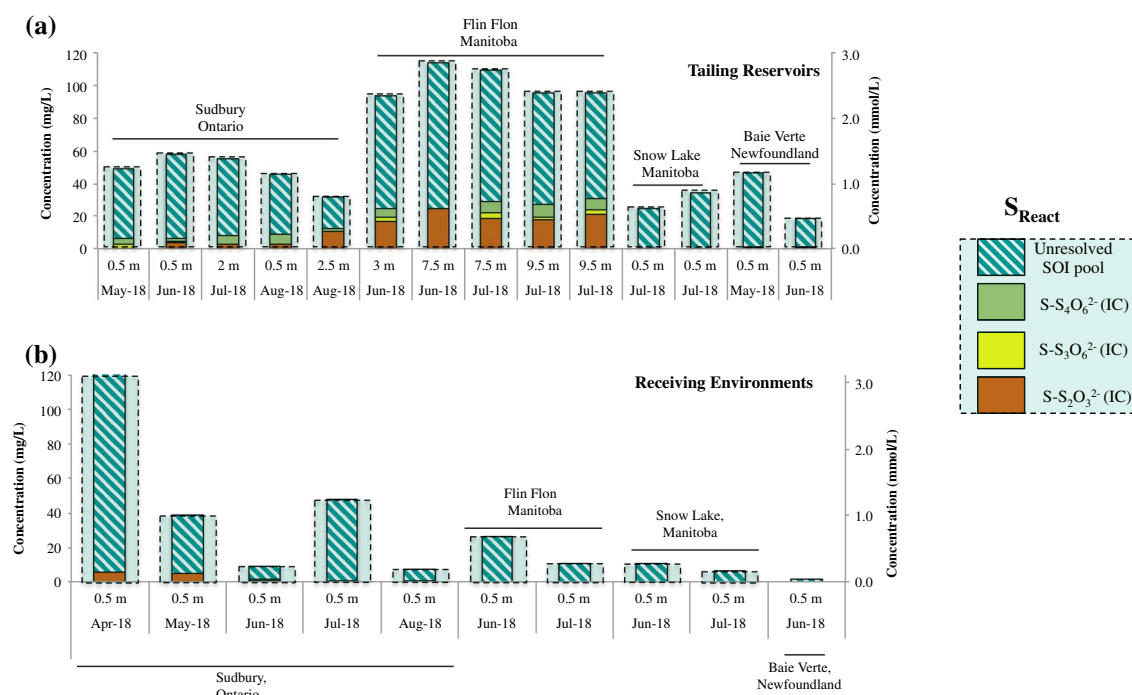
Thiosulfate is identified in the literature to play a significant role in microbial oxidative pathways (i.e. Borilova et al. 2018;

**Table 2** Tailing reservoir water sample concentrations of thiosulfate, trithionate, tetrathionate, TotS<sub>0.45 μm</sub> and S<sub>react</sub> between May and August 2018 across four mines in (1) Sudbury, Ontario (2) Flin Flon, Manitoba (3) Snow Lake, Manitoba and (4) Baie Verte Newfoundland. Shaded grey = samples analyzed for thiosalts through ion chromatography (IC) and unshaded indicates samples analyzed for thiosalts through acidimetric titration

Field Site Location	Mine water type	Field date collected	Depth	Thiosalts method	Bulk thio-salts	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mg S/L)	S <sub>3</sub> O <sub>6</sub> <sup>2-</sup> (mg S/L)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> (mg S/L)	Unresolved SOI (mg S/L)	SO <sub>4</sub> <sup>2-</sup> mg S/L	TotS <sub>0.45 μm</sub> (mg S/L)	S <sub>React</sub> (mg S/L)
Sudbury, Ontario	Tailings reservoir	May 2018	0.5 m	IC	-	0.3 (0.17)	5 (2.5)	6 (3.4)	43	586 ± 42 (196) <sup>a</sup>	245 ± 2	49
	Tailings reservoir	June 2018	0.5 m	IC	-	5.8 (3.3)	2 (1.0)	3.8 (2.2)	52	740 ± 20 (247) <sup>a</sup>	305 ± 1	58
	Tailings reservoir	July 2018	2 m	IC	-	4.5 (2.6)	< 2	10 (5.7)	48	753 ± 58 (251) <sup>a</sup>	307 ± 1	56
	Tailings reservoir	August 2018	0.5 m	IC	-	5.2 (3.0)	< 2	10 (5.7)	37	807 ± 31 (269) <sup>a</sup>	315 ± 2	64
	Tailings reservoir	August 2018	2.5 m	IC	-	19 (10.9)	< 2	2.1 (1.2)	20	840 ± 53 (280) <sup>a</sup>	312 ± 2	32
Flin Flon, Manitoba	Tailings reservoir	August 2018	10 m	IC	-	14 (8.0)	< 2	1.7 (0.97)	28	860 ± 20 (287) <sup>a</sup>	324 ± 4	37
	Tailings reservoir(primary)	June 2018	0.4 m	IC	-	27 (15.4)	< 2	< 0.2	152	986 ± 23 (329) <sup>a</sup>	496 ± 26	167
	Tailings reservoir(primary)	June 2018	0.4 m	AT	27.4	-	-	-	-	986 ± 23 (329) <sup>a</sup>	496 ± 26	167
	Tailings reservoir (secondary)	June 2018	3 m	IC	-	29 (17)	6 (3.0)	8.4 (4.8)	69	973 ± 12 (325) <sup>a</sup>	419 ± 7	94
	Tailings reservoir (secondary)	June 2018	3 m	AT	71	-	-	-	-	973 ± 12 (325) <sup>a</sup>	419 ± 7	94
	Tailings reservoir (secondary)	June 2018	7.5 m	IC	-	43 (25)	< 2	< 0.2	89	1093 ± 23 (365) <sup>a</sup>	479 ± 4	114
	Tailings reservoir (secondary)	June 2018	7.5 m	AT	102	-	-	-	-	1093 ± 23 (365) <sup>a</sup>	479 ± 4	114
	Tailings reservoir (secondary)	July 2018	7.5 m	IC	-	33 (19)	7 (3.5)	12 (6.9)	81	947 ± 128 (316) <sup>a</sup>	426 ± 4	110
	Tailings reservoir (secondary) Rep 1	July 2018	9.5 m	IC	-	31 (18)	4 (2.0)	13 (7.4)	69	1067 ± 31 (356) <sup>a</sup>	452 ± 3	96
	Tailings reservoir (secondary) Rep 2	July 2018	9.5 m	IC	-	37 (21.2)	5 (2.5)	12 (6.9)	65	1067 ± 31 (356) <sup>a</sup>	452 ± 3	96
Snow Lake, Manitoba	Tailings reservoir Rep 1	July 2018	0.5 m	IC	-	0.6 (0.3)	< 2	0.2 (0.1)	25	653 ± 23 (218) <sup>a</sup>	243 ± 1	25
	Tailings reservoir Rep 1	July 2018	0.5 m	AT	15.3	-	-	-	-	653 ± 23 (218) <sup>a</sup>	243 ± 1	25
	Tailings reservoir Rep 2	July 2018	0.5 m	IC	-	< 0.2	< 2	< 0.2	35	600 ± 5 (200) <sup>a</sup>	235 ± 3	35
BaieVerte, Newfoundland	Tailings reservoir	May 2018	0.5 m	IC	-	< 0.2	< 2	0.6	46	9.3 ± 5 (3.1) <sup>a</sup>	50 ± 0.8	47
	Tailings reservoir	June 2018	0.5 m	IC	-	< 0.2	< 2	< 0.2	17	97 ± 6 (32) <sup>a</sup>	51 ± 0.4	19

N/A not analyzed

<sup>a</sup>All sulfur species concentrations are listed as concentrations of the entire sulfur species and listed in brackets below these concentrations have been converted to the concentrations solely of S for mass balance determinations



**Fig. 5** Concentrations (mg/L and mmol/L) of the unresolved S pool, tetrathionate, trithionate and thiosulfate in 2014/2015 MIWs from a mine in **a** tailings reservoirs from May to August 2018 and **b** receiving environments from April to August 2018 (1) Sudbury, Ontario; (2) Flin Flon, Manitoba; (3) Snow Lake, Manitoba; and (4) Baie Verte, Newfoundland

Newfoundland, showing relative proportions of thiosalts species (thiosulfate, tetrathionate) to overall S concentration. The proportion of the S pool included in  $S_{\text{react}}$  ( $\text{TotS}_{\text{aq}} - \text{SO}_4^{2-}$ ) is indicated with a dashed line within the legend. Where available, replicate errors are provided in the corresponding Tables 2 and 3

Mangold et al. 2011; Mora et al. 2016; Warren et al. 2008; Whaley-Martin et al. 2019) and is ubiquitous in these MIW systems, albeit at low concentrations. At least two potential sources for thiosulfate have been identified in these systems. Tailings that are sub-aqueously deposited in the Sudbury, Ontario tailings reservoir were found to contain high concentrations of  $\text{S}_2\text{O}_3^{2-}$  (3–5 mmol/L) and thus are a likely consistent source into the reservoir water cap. However,  $\text{S}_2\text{O}_3^{2-}$  was also detected in waste rock leachate inputs (WasteRock1 and WasteRock2, Fig. 4; Table 2), indicating that in situ biological oxidation production pathways may also be involved. The presence of tetrathionate in the 2018 MIW samples was consistent with Wolkoff and Larose (1975), who detected tetrathionate in MIW using a cerium(IV)-fluorescence detection LC system. Klatt and Polerecky (2015) hypothesized that oxidation of thiosulfate and tetrathionate to sulfite and ultimately sulfate, may be a prevalent pathway that has been overlooked due to the current emphasis in the literature on traditional microbial pathways such as thiosulfate oxidation directly to sulfate. The analytically unresolved S compounds pool of  $S_{\text{react}}$  may include variable compositions and high order polythionates and/or minor amounts of organo-sulfur compounds. Polysulfides may be present in anoxic bottom waters. As water flows through tailing reservoirs and post-treatment oxygenated

receiving environments, it seems logical that progressive SOI oxidation (biological and/or abiotic) would occur.

Our results also demonstrated that a large proportion of  $S_{\text{react}}$  can occur as currently unresolved S species, even when high resolution S speciation techniques are employed (Figs. 4, 5; Tables 1, 2). These results indicate that understanding and predictions of system behavior (e.g. potential pH decreases, toxicity) would be enhanced by simultaneous measurement of individual SOIs to reveal the key compounds that occur in MIW systems (water system management components on site as well as receiving environment) and how they vary by season, treatment process, and operational schedules.

## Conclusions

Both of the currently available thiosalts-monitoring methods are predicated on the assumption that thiosulfate alone or thiosulfate and polythionates are the dominant SOI species in MIWs. This study showed that these methods can both underestimate the reactive sulfur concentrations, which may cause down-gradient environmental impacts due to oxidation. Within the waters sampled in this study across

**Table 3** Receiving environment water sample concentrations of thiosulfate, trithionate, tetrathionate, TotS<sub>0.45 µm</sub> and S<sub>react</sub> between May and August 2018 across four mines in (1) Sudbury, Ontario (2) Flin Flon, Manitoba (3) Snow Lake, Manitoba and (4) Baie Verte Newfoundland. Shaded grey = samples analyzed for thiosalts through ion chromatography (IC) and unshaded indicates samples analyzed for thiosalts through acidimetric titration

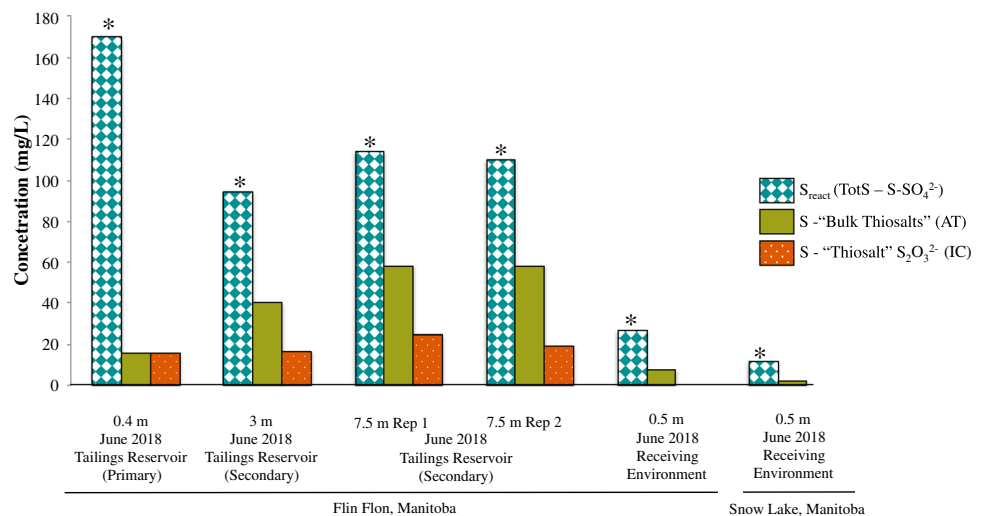
Field site location	Mine water type	Field date collected	Depth	Thio-salts method	Bulk thiosalts	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mg S/L)	S <sub>3</sub> O <sub>6</sub> <sup>2-</sup> (mg S/L)	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> (mg S/L)	Unresolved SOI (mg S/L)	SO <sub>4</sub> <sup>2-</sup> (mg S/L)	TotS <sub>0.45 µm</sub> (mg S/L)	S <sub>react</sub> (mg S/L)
Sudbury, Ontario	Receiving environment	April 2018	0.5 m	IC		10 (5.5)	N/A	N/A	128	338 ± 5 (113)	246 ± 3	133
	Receiving environment	May 2018	0.5 m	IC		7.8 (4.5)	< 2	1.2 (0.69)	28	580 ± 12 (193)	227 ± 2	34
	Receiving environment	June 2018	0.5 m	IC		1.8 (1.0)	< 2	0.3 (0.2)	6.8	653 ± 42 (218)	226 ± 3	8
	Receiving environment	July 2018	0.5 m	IC		0.6 (0.3)	< 2	0.4 (0.2)	47	740 ± 20 (247)	294 ± 1	47
	Receiving environment	August 2018	0.5 m	IC		0.5 (0.3)	< 2	< 0.2	6.7	827 ± 23 (276)	283 ± 4	7
Flin Flon, Manitoba	Receiving environment	June 2018	0.5 m	IC		< 0.2	< 2	< 0.2	27	513 ± 23 (171)	198 ± 2	27
		June 2018	0.5 m	AT	12.7	–	–	–	–	513 ± 23 (171)	198 ± 2	27
	Receiving environment	July 2018	0.5 m	IC		< 0.2	< 2	< 0.2	11	327 ± 12 (109)	120 ± 1	11
	Receiving environment	June 2018	0.5 m	IC		< 0.2	< 2	< 0.2	0.4	35 ± 1 (11.6)	12 ± 1	0.4
Baie Verte, Newfoundland	Receiving environment	June 2018	0.5 m	AT	3.5	–	–	–	–	35 ± 1 (11.6)	12 ± 1	0.4
	Receiving environment	July 2018	0.5 m	IC		< 0.2	< 2	< 0.2	6	326 ± 12 (109)	115 ± 1	6.0
	Receiving environment	June 2018	0.5 m	IC		< 0.2	< 2	< 0.2	2	58 ± 3 (19)	21 ± 1	2.0

N/A not analyzed

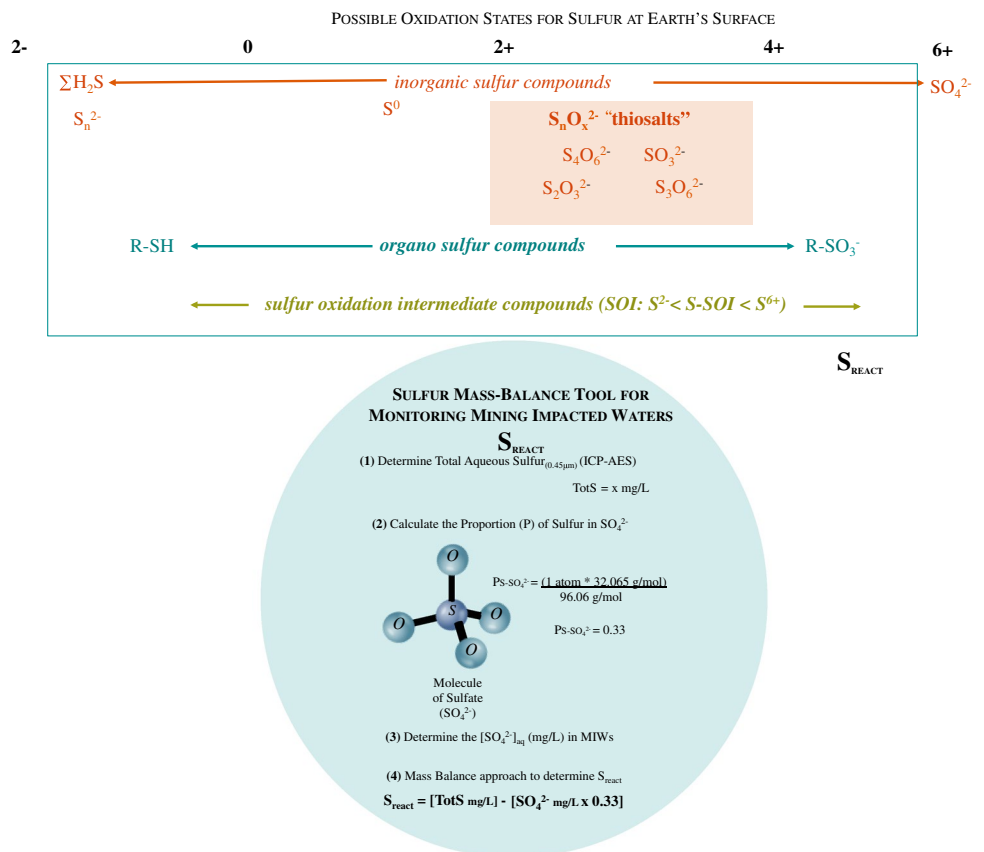
<sup>a</sup>All sulfur species concentrations are listed as concentrations of the entire sulfur species and listed in brackets below these concentrations have been converted to the concentrations solely of S for mass balance determinations



**Fig. 6** Comparison of concentrations of  $S_{\text{react}}$  (TotS– $\text{SO}_4^{2-}$ , S-bulk thiosalts (acidimetric titration (AT)) and S– $\text{S}_2\text{O}_3^{2-}$  (ion chromatography (IC) for MIW from tailings reservoirs and receiving environments in June 2018 from the active mine sites in Flin Flon and Snow Lake, Manitoba. “\*” Concentrations determined by the  $S_{\text{react}}$  method were significantly higher at a 90% confidence interval when compared to the AT method ( $p=0.054$ ) and a 95% confidence interval ( $p=0.012$ ) for the IC method



**Fig. 7** Proposed method for monitoring sulfur pools in the mining impacted waters where TotS and  $\text{SO}_4^{2-}$  allow for the determination of the  $S_{\text{react}}$  pool through simple mass-balance; and the potential array of oxidation states of sulfur and known sulfur compounds that can exist at the earth's surface. Thiosalts ( $\text{S}_n\text{O}_x^{2-}$ ) occupy a small oxidation range of the potential inorganic and organic SOI compounds ( $\text{S}^{2-} < \text{S-SOI} < \text{S}^{6+}$ ) that participate in oxidation reactions



four mine water treatment systems, including tailings reservoirs and receiving environments, thiosulfate accounted for, on average, only 4% of the overall sulfur budget, while  $S_{\text{react}}$  concentrations were commonly significantly greater. The simple mass balance approach proposed here (Fig. 7) allows a conservative quantification of the entire reactive sulfur pool ( $S_{\text{react}} = \text{TotS}_{\text{aq}} - \text{S-SO}_4^{2-}$ ). This tool provides a

comprehensive measure of dissolved S that has the potential to cause environmental impacts through oxidation. Thus, we recommend that MIW monitoring efforts, to facilitate effective prediction and mitigation of negative environmental occurrences, would benefit from routine total sulfur measurements alongside  $\text{SO}_4^{2-}$  to capture other sulfur compounds available for oxidation.

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