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Developing a novel methodology for ecological risk assessment of thiosalts

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Abstract A new methodology is developed to estimate an aquatic community toxicity threshold concentration based on the limited toxicity data that are available for thiosalts. To analyze the indirect effect of thiosalts on decreasing pH, an exposure model is developed that estimates the residual concentration of thiosalts and pH in the water body. The results from this model are incorporated in thiosalts risk assessment and a case study is used to illustrate the applicability of the proposed model. In this study, the exposure model predicts that, trithionate and tetrathionate degraded to SO_4^{2-} ions, HSO_3^- ions, SO_3^{2-} ions and elemental sulfur. The concentration of thiosulfate, trithionate and tetrathionate, initially at 25, 40 and 6 mg/L, respectively are expected to decrease. Over the duration of 77 h, thiosulfate degrades completely, while the estimated residual trithionate and tetrathionate concentrations are 13 and 5.77 mg/L, respectively. pH of the undiluted effluent is estimated to decrease from 9.2 to 5.6 within an hour of the effluent discharge and decreases further to 4 over a period of next 3 days. A framework and methodology developed in this paper can be utilized to estimate the potential direct and indirect risk of thiosalts exposure to ecological entities.

Keywords Ecological · Risk assessment · Natural degradation model · Thiosalts · Bootstrap · Aquatic quality criteria

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1 Introduction

Thiosalts are sulfur oxyanions present in the mine effluent resulting from the processing of sulfide ores. Thiosalts are produced when sulfide mineral is oxidized to sulfate under high pH in floatation unit. The thiosalts generated from the process are deposited in the tailings pond. Thiosalts being metastable compounds, their oxidation to sulfate in the tailings pond is a slow process depending on various factors such as presence of sulfur degrading bacteria, temperature and pH. The most important species amongst the thiosalts in regards to toxicity are thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_4^{2-}$) (Schwartz et al. 2006). The environmental impacts of thiosulfate, trithionate and tetrathionate (hereby referred as thiosalts) to aquatic species are a major concern to mining industries (Johnson and Hallberg 2005). Detailed information on thiosalts formation, toxicity and treatment systems used for removal of thiosalts from mine effluent is presented in Kuyucak and Yaschyshyn (2007), Dinardo and Sally (1998) and Söderlund (2008). Thiosalts are not completely oxidized nor completely removed in the tailings retention area by most effluent treatment methods (Dinardo and Sally 1998). The treated final effluent is discharged into the receiving waters such as lakes, streams and rivers. In the presence of catalysts such as copper(II) and iron(III) and *Thiobacillus* bacteria, biological and chemical processes further oxidize thiosalts downstream (Dinardo and Sally 1998; Schwartz et al. 2006; Sääf et al. 2009; Zhang and Jeffrey 2010). The presence of high concentrations of thiosalts in effluent receiving waters may result in toxicity to aquatic species due to their direct ingestion. Also, oxidation of thiosalts species results in pH depression of the water body resulting in potential aquatic risk (Schwartz et al. 2006; Dinardo and

Sally [1998]). Rolia and Chakrabarthi ([1982]) has documented acidity, as low as between pH 3 and 4, in receiving waters as far as 20 km from effluent discharge point due to oxidation of thiosalts released from few mine sites in Canada. However, recent studies such as Kuyucak and Yaschyshyn ([2007]), Falconbridge ([2006]) and Blue Note Mining ([2008]), have reported pH of around 6 in the receiving waters owing to enhanced remediation of thiosalts from effluent waters. Studies such as Corazza et al. ([2012]) and Carrasco and Chang ([2005]) have estimated the variability of contaminant concentrations in rivers using Monte Carlo simulations and compared with the contaminant criteria in aquatic media. Limited data of thiosalt toxicity to aquatic species is an abetting factor in developing criteria for thiosalt effluent discharge.

The current industry procedure of managing thiosalt impact is in situ measurement of thiosalt concentrations and pH in the downstream environment. There could be a time lag between preventive measures adopted in the downstream environment and the initiation of thiosalt impact, clearly pointing to the lack of comprehensive risk-based predictive approach in managing thiosalts. The challenges encountered in performing ecological risk assessment of thiosalts to aquatic assemblage are:

- Predicting natural degradation of thiosalt effluent in receiving water and quantifying the acidity in water resulting from thiosalt degradation;
- Establishing a toxicity threshold concentration (TTC) based on the limited toxicity data for freshwater species.

To overcome the above-mentioned problems, a novel exposure assessment model is developed based on thiosalt natural degradation kinetics. The developed preemptive exposure model facilitates treatment options and leads to lower risk to aquatic species. The non-parametric bootstrap technique, which is adopted in this research, estimates the missing toxicity data on the basis of a limited observed data set available from different researches (Frey and Rhodes [1999]; Jagoe and Newman [1996]).

1.1 Toxicity of thiosalts

The toxicity of thiosalts to aquatic species has been characterized under laboratory conditions and is reported in Table 1; however, the toxicity data available in the literature is very limited (Schwartz et al. [2006]; Taylor et al. [2010]). Lowest acute toxicity is reported for *Daphnia magna* (McGeer et al. [2000]; Schwartz et al. [2006]); the thiosalt concentrations in the final effluent prior to discharge are found to be less than 300 mg/L in the mine sites surveyed in Canada (Gould et al. [2004]; Kuyucak and Yaschyshyn [2007]). Aquatic toxicity is caused mainly as a result of thiosalt oxidation in downstream environment

Table 1 Toxicity of thiosalts, LC_{50} and IC_{25} values (Schwartz et al. [2006])

	Thiosulfate (ppm)	Tetrathionate (ppm)
Acute toxicity		
Oncorhynchus mykiss	>819	>742
Daphnia magna	300	750
Sublethal toxicity		
Ceriodaphnia dubia	59	562
Pimephales promelas	664.6	>891
Lemna minor	497.9	>901

(Forsberg [2011]; Schwartz et al. [2006]; McGeer et al. [2000]). Toxicity tests due to lowering of pH in the water sample were conducted for the freshwater aquatic species mentioned above. At pH below 5 in the test sample, significant mortality was observed in all of the aquatic species except *Lemna minor* (Schwartz et al. [2006]).

To accurately assess risk to aquatic community, thiosalt toxicity data from a limited number of individual species must yield a valid prediction of the effect on an entire community. The two common methods of calculating target species community TTC values are, conventional and species sensitivity distribution (SSD) approaches. The assessment factor (AF) method derives TTC criteria by multiplying an uncertainty factor to most sensitive species from the data set (Environment Canada [2007]; CCME [2007]), thus leading to a over-protective criteria and conservative risk estimates (Xing et al. [2013]). Toxicity characteristics such as LC_{50} or EC_{50} for multiple species is fit to a distribution; such a distribution is termed as SSD. For risk assessment purposes a low centile of the SSD is selected as a level to protect, or below which, the impact may be acceptable (Hanson and Solomon [2003]; Posthuma et al. [2002]). SSD approach is more reasonable than AF method and has become preferable method to derive water quality in countries such as Canada (Xing et al. [2013]). Adopting SSD approach with extremely sparse data could lead to biased/skewed risk assessment results (Posthuma et al. [2002]).

Bootstrap technique addresses the issue of quantifying the sample error that is introduced by estimating toxicity values from limited numbers of toxicity data points (Xing et al. [2013]; Shao [2000]; Frey and Rhodes [1999]). By adopting the bootstrapping technique, a specific distribution to the toxicity data need not be assigned, thereby, decreasing the uncertainty in the assessment (Jagoe and Newman [1996]; Frey and Rhodes [1999]; Xing et al. [2013]).

1.2 Thiosalt reactivity in receiving waters

Thiosalt reactivity is very complex and is dependent on physical and chemical conditions such as temperature, pH, presence of metals, and microbes. Not all of the thiosalt

species are active in similar temperature and pH ranges. Table 2 depicts pH ranges in which various thiosalts are reactive. Tetrathionate is reactive in alkaline media, trithionate is reactive in near neutral conditions and thiosulfate is reactive in acidic environment (Miranda-Trevino et al. 2009). This study focuses on thiosalts decomposition reactions at temperatures typically occurring in Northern Canada climatic regions. Studies such as Zhang and Dreisinger (2002), Zhang and Jeffrey (2010) and Miranda-Trevino et al. (2009) although limited in number have focused more on thiosalt reduction reactions at such temperatures. Xu and Schoonen (1995) studied thiosulfate decomposition in highly acidic medium (2.9 <pH> 5.2) at 20 °C. They illustrated that thiosalt disproportionation rate is far greater than other pathways of degradation. According to Xu and Schoonen (1995), thiosalt disproportionation results in elemental sulfur and sulfite as major products. At near neutral conditions, the dominant trithionate reaction is its hydrolysis to thiosulfate and sulfate (Zhang and Jeffrey 2010). The trithionate hydrolysis reaction is observed within the pH range of 5.5–10.5 as a pseudo-first-order reaction with a constant reaction $(6.2 \pm 0.2) \times 10^{-7}$ s^{-1}; the reaction rate constant is independent of the solution pH (Zhang and Jeffrey 2010). However, there is no consensus in the literature regarding the trithionate hydrolysis reaction rate. Rolia and Chakrabarthi (1982) observed the trithionate hydrolysis in the pH range of 5.5–12 with a higher reaction rate. They also observed the dependence of reaction rate on the concentration of thiosulfate. The trithionate kinetics reported by Zhang and Jeffrey (2010) was adopted in this exposure model as their reaction temperature is more consistent with

the Northern Canadian climate temperatures. Tetrathionate is highly stable in acidic conditions (Miranda-Trevino et al. 2009). At near neutral conditions and in weakly alkaline conditions, tetrathionate decomposes to trithionate and thiosulfate (Rolia 1983; Varga and Horvath 2007; Zhang and Jeffrey 2010). Tetrathionate reaction in neutral and alkaline conditions occurs via thiosulfate catalyzed rearrangement reaction (Zhang and Jeffrey 2010). Thiosalt reactions used to predict thiosalt natural degradation are reported in Table 3.

2 Materials and methods

2.1 Risk assessment

The framework of the risk assessment of thiosalts developed in this paper is demonstrated in Fig. 1. It is based on principles of ecological risk assessment developed by U.S. Environmental Protection Agency (EPA) (1992, 1998). Environmental risk assessment contains four different steps of hazard identification, exposure assessment, dose–response, and risk characterization. This study primarily focuses on the scientific gaps in exposure assessment modeling and characterization of dose–response threshold in thiosalt risk assessment.

2.1.1 Hazard identification

The hazards associated with thiosalts to aquatic organisms could be summarized as:

Table 2 Investigation of the thiosalt reactivity based on pH and temperature

	pH 2	pH 4	pH 7	pH 9
4 °C	Thiosulfate	No reaction	No reaction	Tetrathionate
15 °C	Thiosulfate	Trithionate	Trithionate	Tetrathionate
30 °C	Thiosulfate and trithionate	Trithionate	Trithionate	Thiosulfate, trithionate and tetrathionate

Table 3 Reactions used in exposure model

Equation numbers	Reaction rates	pH and temperature range	Reactions	References
1	1.38×10^3 L/mol/h	9.2–11; Not given	$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$	Zhang and Dreisinger (2002)
2	1.9×10^{-3} h^{-1}	7.1–9.2; Room temperature	$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	Miranda-Trevino et al. (2009)
3	Not given	7.1–9.2; Not given	$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-}$	Varga and Horvath (2007)
4	14.6×10^{-3} h^{-1}	4–7.1; Room temperature	$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	Mizoguchi et al. (1976), Zhang and Jeffrey (2010)
5	0.66 L/mol/s	2.9–5.6; Room temperature	$2S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + SO_3^{2-} + 2S^0$	Xu and Schoonen (1995)

Fig. 1 A developed methodology for risk assessment of thiosalts
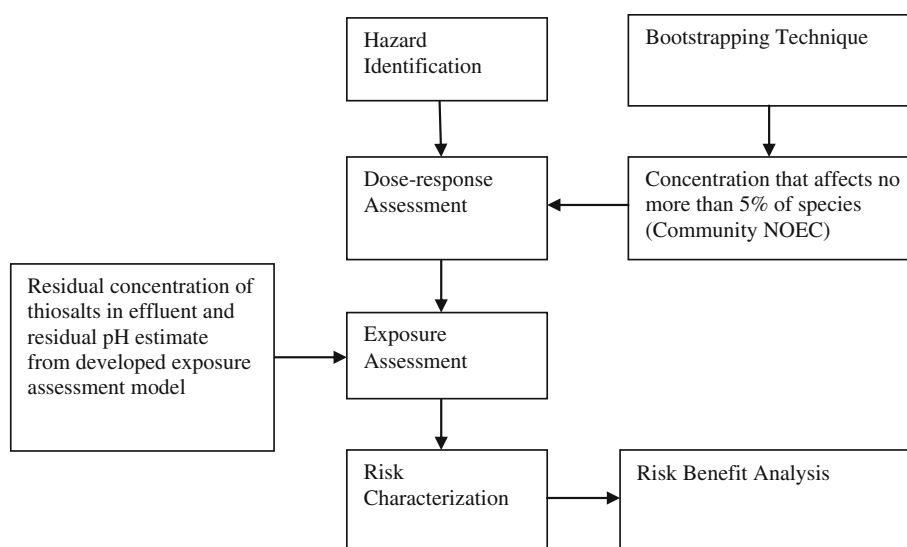
- Direct toxicity due to ingestion of thiosalts;
- Indirect toxicity due to pH depression.

The scope of this research is limited to the ecological impacts of chemical oxidation of thiosalts in the presence of dissolved oxygen only. Oxidation of thiosalts in the presence of *Thiobacillus* bacteria or other catalysts such as Cu^{2+} and Fe^{3+} is out of the scope of this research. However, the present methodology could be extended to simulate thiosalt behavior and subsequent risk from thiosalts in the presence of such catalysts as well.

2.1.2 Exposure assessment

Exposure of aquatic species to thiosalts contaminants is estimated using an exposure assessment model developed as part of this research. The developed exposure assessment model is based on the understanding of the relationship between acid producing (oxidation) and acid consuming (disproportionation) pathways of thiosalts and their reaction kinetics.

Reactions of various species of thiosalts over a range of temperatures and pH are taken from the literature (Table 3). It should be noted that most of these expressions are derived from single species experiments, and therefore may not represent the kinetics of mixed solutions. It is also assumed that no heavy metal or other catalyst is present and abiotic conditions prevail in the water body. Some researchers have given varied reaction rates of the same reaction, and the rates differ by order of magnitude. However, the purpose here is to demonstrate the method. More complex reaction rates, once determined, can be added. It is also assumed that the mining effluent is undiluted in the receiving water body thus simulating a worst-case scenario.

The input parameters in the model are initial pH of the effluent, and concentrations of thiosulfate, trithionate and tetrathionate as three major thiosalt contaminants. The methodology for the exposure assessment model developed as a part of this study is illustrated in Fig. 2. Initial pH of the water body is measured and subsequent active thiosalt reactions are identified. Thiosalt reaction would continue to progress until thiosalt is completely degraded or the pH of the solution changes to the point that the reaction is no longer active. Based on this concept and the reaction rates, change in $[H^+]$ concentration or change in thiosalt species concentrations are calculated.

2.1.3 Dose–response assessment

The target species for risk assessment are aquatic organisms on which toxicity tests were conducted; hence, there is no requirement for uncertainty factor in determining TTC. The minimum allowable pH leading to 50 % mortality in the mining effluent for all the species mentioned in Table 1 except *L. minor* is 5.5 (Schwartz et al. 2006; Rolia 1983).

A methodology using bootstrapping technique is proposed to estimate TTC that can be used in ecological risk assessment of thiosalts. This concentration should affect no more than 5-percentile of the aquatic species. Since acute toxicity data of thiosalts is available for only two (*D. magna* and *Oncorhynchus mykiss*) aquatic species, it was assumed that the available data represents the extreme toxicity data points for the aquatic species for which ecological risk assessment is to be performed. Random data points are generated between the LC50 values for Rainbow trout and *D. magna* for both thiosulfate and tetrathionate. It was assumed that the probability distribution of the randomly generated data between the toxicity points of 300
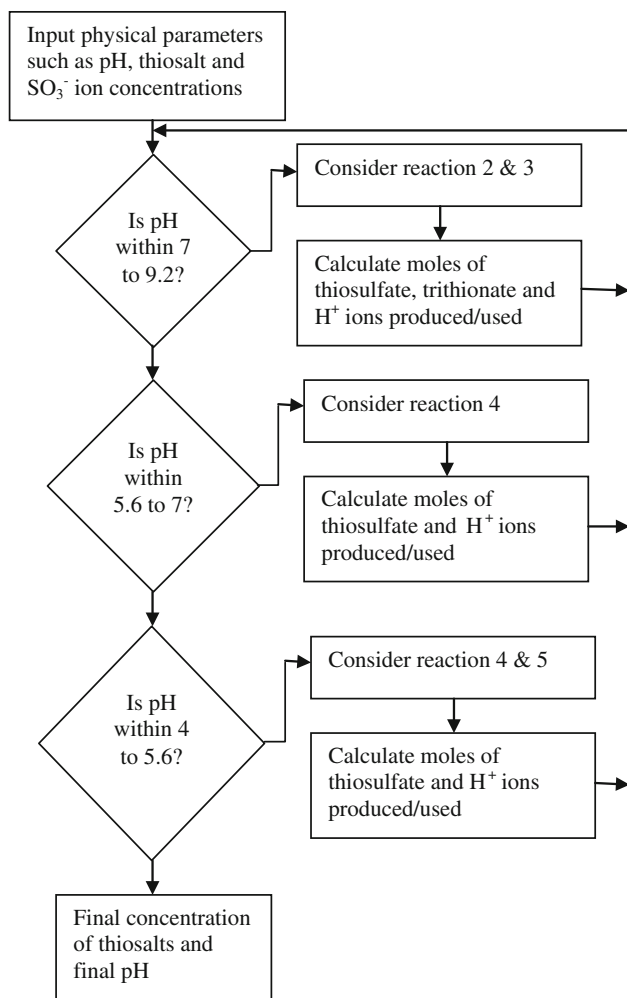
Fig. 2 Methodology for the developed exposure assessment model

Fig. 3 Framework for the developed bootstrapping methodology for NOEC

Table 4 Check for convergence of thiosulfate data

Distributions	Simulation 1 (parameters)	Simulation 2 (parameters)
Weibull	4.05 (β), 16.70 (θ)	3.98 (β), 15.97 (θ)
Normal	559.37 (μ), 4.20 (s)	559.60 (μ), 4.04 (s)
Logistic	559.43 (μ), 2.37 (s)	559.60 (μ), 2.33 (s)

and 819 ppm for thiosulfates follows a uniform distribution. Similarly, randomly generated data for tetrathionate also follows a uniform distribution with its extreme points being 742 and 750 ppm. The framework of the developed methodology is demonstrated in Fig. 3. The assumptions in the model are taken to simplify the complexity in determining no observed effect concentration (NOEC) of thiosalts. *D. magna* and Rainbow trout are considered as the most sensitive species to direct thiosalt toxicity. Since the LC_{50} values is available for these two aquatic species only, assuming that all the LC_{50} values lie within this range leads to a safe protection criteria.

Logistic, Normal and Weibull distributions are fitted to the data from each simulation. The toxicity data generated is checked for convergence by comparing the distribution characteristics from each simulation as explained in Table 4. Once the convergence of data from both simulations is confirmed, the 5-percentile concentration value is calculated from the 300 toxicity data points (150 from each
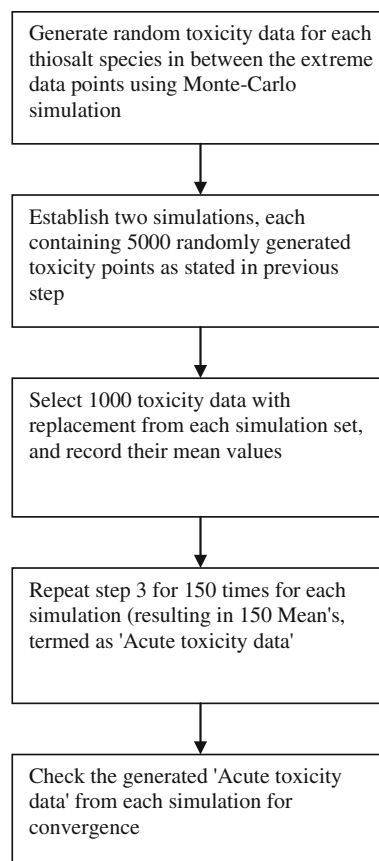
simulation). The toxicity data generated from the bootstrap technique is fit to a distribution amongst Logistic, Normal, and Weibull distributions. After fitting a particular distribution, the distributions are ranked according to goodness-of-fit tests. The final rank is obtained by summing all the ranks of the goodness tests for a distribution. The distribution with least rank is determined as the best fit.

2.1.4 Risk characterization

The TTC is compared with the exposure concentration. The hazard index (HI) was calculated as:

HI = exposed concentration/TTC.

If the exposure concentration is higher than the maximum allowable concentration, i.e., HI >1, the site may pose risk to aquatic organisms and risk remediating actions are warranted. Also, the final pH of the water body was determined and compared with the maximum allowable pH to investigate the indirect toxicity of the thiosalts concentrations.

3 Results

3.1 Threshold of toxicity

Distributions are ranked in accordance to their goodness-of-fit tests as shown in Table 5. The R^2 value for Logistic, Normal and Weibull distributions are calculated and are 0.992, 0.997 and 0.953, respectively.

All the distributions have a good fit index, and the 5-percentile concentrations for all the distributions do not differ significantly. As a result, it can be safely assumed the Normal distribution is appropriate for the toxicity data generated for thiosalts. The 5-percentile concentrations of thiosulfate from each of the distributions are presented in Table 6. The 5-percentile concentrations established for thiosulfate and tetrathionate are estimated to be 552 and 745 mg/L, respectively.

3.2 Exposure to thiosalts

Mine effluent data are selected from Kidd Metallurgical Mine Site in Canada as described in Kuyucak and Yaschyshyn (2007); aquatic risk assessment is conducted to demonstrate the developed risk assessment model. Initial input parameters used in the exposure assessment model are presented in Table 7.

Table 5 Goodness-of-fit test rankings

Goodness test	Logistic	Normal	Weibull
A–D test	4	2	3
χ^2 test	4	3	2
K–S test	1	3	4
Final rank	Second	First	Second

Table 6 Distributions versus 5-percentile concentrations

Distributions	5-Percentile concentration (mg/L)
Normal	552.71
Logistic	552.60
Weibull	552.46

Table 7 Input parameters for the considered case study

Input parameters	Values
Initial pH	9.2
Thiosulfate (mg/L)	25
Trithionate (mg/L)	40
Tetrathionate (mg/L)	6

Depending upon the initial pH conditions, the reactions of thiosalts are chosen by the exposure assessment model. Since the pH of effluent in the case study is in between 7.1 and 9.2, the active reactions in this pH range are reactions (2) and (3).

Of these two reactions, reaction (2) is the one that could alter the pH of the water body as [H$^+$] ions participate in it. The other reaction is just a degradation reaction with no direct effect on pH. These two reactions will be active until the pH of the water body decreases to 7. H$^+$ ions released by lowering of pH from 9.2 to 7 were calculated based on reaction rates and stoichiometry. Figure 4 illustrates the trend in natural thiosalt degradation in receiving water body. On the basis of the reaction rate of Eq. 2, effluent pH changed from 9.2 to 7 within an hour as presented in Fig. 5. Also, the thiosalt concentrations present originally in the discharged effluent underwent no significant change within this period (Fig. 4). Trithionate hydrolysis (reaction (4)) at near neutral conditions decreased the effluent pH from 7 to 5.6 within an hour from effluent discharge. However, the loss of trithionate in that hour was very small as well (Fig. 4). The active reactions in the pH range of 5.6–4 are reactions (4) and (5); both of the reactions alter the pH of the water body. Depending upon their corresponding reaction rates, final thiosalt concentrations and pH is estimated (Table 8). The final concentration of trithionate is estimated to be 13 mg/L. Thiosulfate is completely degraded into HSO$_3^-$ and SO$_3^{2-}$ ions and elemental sulfur after 60 h from the time of discharge. The profile of the pH of the water body resulting from natural degradation of thiosalts is shown in Fig. 5. The pH of the water body rapidly decreases from its initial condition of 9.2–5.6 within first hour of effluent discharge. The final pH of the effluent was estimated to be pH 4 after 77 h from time of discharge.

3.3 HIs from thiosalts

The thiosalt concentrations present in mining effluents from the case study (Table 8) were far lesser than the maximum allowable concentrations determined by bootstrapping technique. The HIs calculated are presented in Table 9. The results discussed are for a worst-case scenario considering no dilution of the effluent in the receiving waters. However,
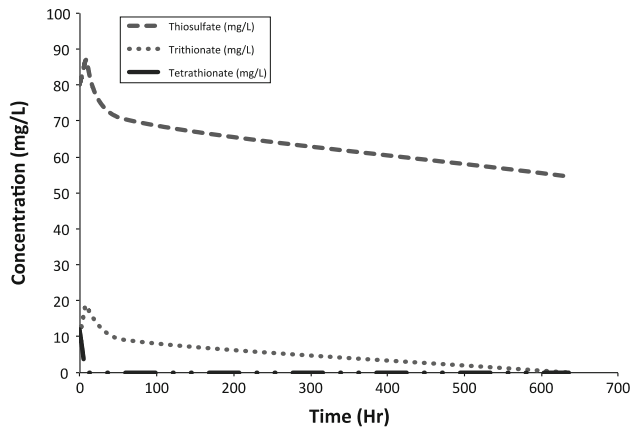
Fig. 4 Thiosalts concentration profile

Table 8 Final results from exposure assessment model

Time after effluent discharge	Effluent pH	Thiosulfate (mg/L)	Trithionate (mg/L)	Tetrathionate (mg/L)
0	9.2	25	40	6
<1	7	25	39.9	5.9
<1	5.6	25.1	39.7	5.9
60	5.6	0	18.7	5.9
77	5.6	0	13.04	5.9

Fig. 5 pH profile of the effluent

incorporating dilution factors, the results for the acidity of the receiving water is shown in Table 10.

4 Discussion

Hydrolysis of 1 mol of trithionate (reaction (4)) produces 1 mol thiosulfate and 2 mol H^+ ions while reaction (5) involving thiosulfate consumes the H^+ ions. Both of the reactions occur simultaneously. The rate of trithionate hydrolysis is far slower than thiosulfate disproportionation reaction. Thus, for the concentrations considered in the case study, pH of the effluent remains at about 5.6 until 60 h after discharge as shown in Fig. 5. Concentrations of thiosulfate and trithionate initially showed no significant change until the pH of the water reached 5.6. This is because at near neutral conditions, even a small change in $[H^+]$ could lead to drastic change in pH. Direct toxicity due to ingestion of thiosalts proved not a concern for this study. However, the rapid decline of effluent pH from 9 to 5.6 (Fig. 5) and water body's continued acidic conditions over the next 77 h can be a source of toxicity in the aquatic assemblage. Sharp drop in pH of a solution could have many implications especially towards the aquatic toxicity, as the scope for acclimation by the species to the changing conditions is limited. Although it is evident from the literature (Rolia and Chakrabarthi 1982; Forsberg 2011) that more severe acidic conditions prevailed in the freshwater ecosystems due to thiosalt oxidations as a result of mine effluents in Canada. Such acidic conditions in the water body could be the result of thiosalt oxidation in the presence of microbes, Fe^{2+} and Cu^{3+} (Jorgensen 1990; Bernier and Warren 2007). Effluent receiving water body for the Kidd Metallurgical Site is the Porcupine River; downstream of Porcupine River (near-field) was monitored for water quality. It was observed that the pH at the downstream reached a low of 6 and mostly varied between pH of 7.5 and 6.2 during the monitoring period. These observations are consistent with the results of the natural degradation model presented in Table 10 and illustrated in Fig. 6. This proposed exposure model is robust as it may include thiosalt reactions as when they are established, thus making it a viable tool for exposure assessment of thiosalts to aquatic assemblage.

Table 9 Hazard indices

Target species	TTC of thiosulfate (mg/L)	TTC of tetrathionate (mg/L)	Exposed concentration (mg/L)	Hazard index at thiosulfate (unitless)
Oncorhynchus mykiss	552.71	745.88	54.56	0.098
Daphnia magna	552.71	745.88	54.56	0.098

Table 10 Effect of dilution factors on effluent pH

Dilution factors	Thiosulfate (mg/L)	Trithionate (mg/L)	Tetrathionate (mg/L)	Duration pH reaches 5.5 (h)	Final pH
1	0	13	5.77	60	4
10	0	0	0.59	46	4.69
20	0	0	0.29	47	4.99
500	0.1	0	0.01	N/A	5.6
1000	0.05	0	0	N/A	6.36

N/A not applicable
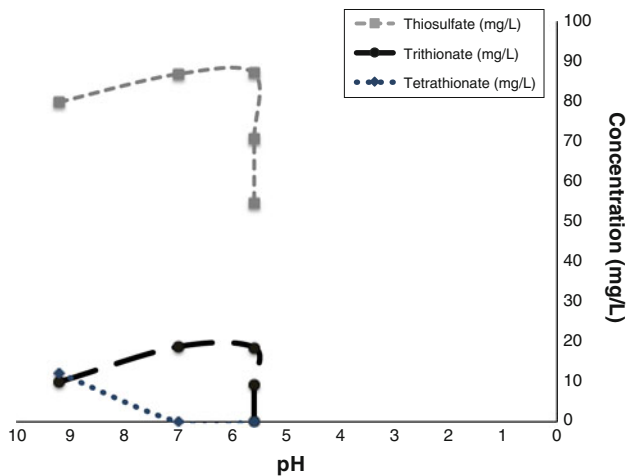
Fig. 6 Thiosalt concentration attenuation versus corresponding effluent pH

4.1 Drawbacks in the model

Predominant pathways of thiosalt species degradation are complex and not always have a clear predominant pathway under known pH ranges in real site conditions. This could be due to presence of multiple oxidizing agents like *Thiobacillus* bacteria, copper(II) and iron(III) to name few. For example, reaction of tetrathionate in alkaline conditions (pH >9.2; Table 6) could occur at near neutral conditions, albeit at a very slow pace (Zhang and Jeffrey 2010).

The model is based on limited data and assesses only abiotic conditions. Caution is urged on using above values for treatment system design. However, as more reaction data becomes available, the information can easily be integrated into the above model for better and more accurate predictions.

5 Conclusion

A novel methodology for ecological risk assessment of thiosalts is developed. The bootstrapping technique is adopted and applied to determine the TTC of thiosalts species. This technique helps to generate important missing toxicity data, thereby decreasing the uncertainty in the risk assessment methodology. A new exposure assessment methodology based on the relationship between acid producing and consuming pathways of thiosalts species is developed. The new methodology assists in estimating the final concentration of thiosalts species in the water body; which in turn predicts the resulting pH. The priority of applying this new methodology is to demonstrate the combined risk due to pH depression along with thiosalts concentration. It is observed that pH depression effect is far more severe with respect to ecological risk as compared to risk caused by thiosalts concentration. This novel methodology provides a unique mechanism of assessing risk of the substances, which primarily may not be much toxic, however, their presence develop threading environment for ecological species.

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