# Ecological Risk Assessment of Thiosalts

By

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## Abstract

Thiosalts are sulphur compounds generated in the processing of sulphide ores, which concentrate in the mining wastewater. The most common thiosalt species are thiosulphate, trithionate, and tetrathionate. While thiosalts are not typically toxic, thiosalts can decompose resulting in pH depression.

Current industry practice of periodic checking of the water quality downstream, to assess aquatic risk clearly points to the lack of a comprehensive risk based approach in managing thiosalts. Assessing the aquatic risk to organisms requires predicting thiosalt natural degradation in pond/stream conditions and toxicity data of thiosalt species.

Due to the complex reaction pathways and pH dependence of the various thiosalt degradation reactions, assessing the risk to the environment is challenging. A novel methodology is developed for an aquatic community 'No Observed Effect Concentration' (NOEC) based on the limited toxicity data that is available for thiosalts. To analyze the indirect effect of thiosalts on pH, a new exposure model is developed to estimate the residual concentration of thiosalts and pH in the water body. 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. The results from this model are incorporated into the thiosalts risk assessment and a case study is used to illustrate the model. In this study, the exposure model predicts that trithionate and tetrathionate will degrade to sulphate ions, hydrogen sulphite ions, sulphite ions and elemental sulfur. The concentration of thiosulfate,

trithionate and tetrathionate, initially at 25 mg/L, 40 mg/L and 6 mg/L respectively, decreased over the course of the study. Over the duration of 77 hours, thiosulfate degraded completely, while the estimated residual trithionate and tetrathionate concentrations were 13 mg/L and 5.77 mg/L, respectively. The pH of the undiluted effluent was estimated to decrease from pH 9.2 to pH 5.6 within an hour of the effluent discharge and decreased further to pH 4 over a period of the next 3 days. A framework and methodology developed in this thesis can be utilized to estimate the potential direct and indirect risks of thiosalts exposure to ecological entities.

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Any work of mine is incomplete without the mention of the contribution of my wife, daughter and friends. I thank them all for the love and affection shown to me.

I dedicate this thesis to my daughter Maryam.

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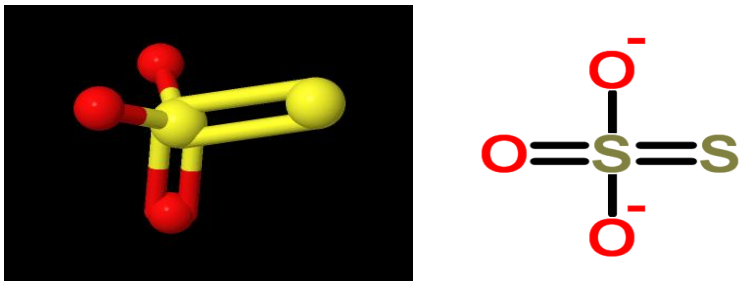
# Chapter 1: Introduction

## 1.1 Introduction to thiosalts

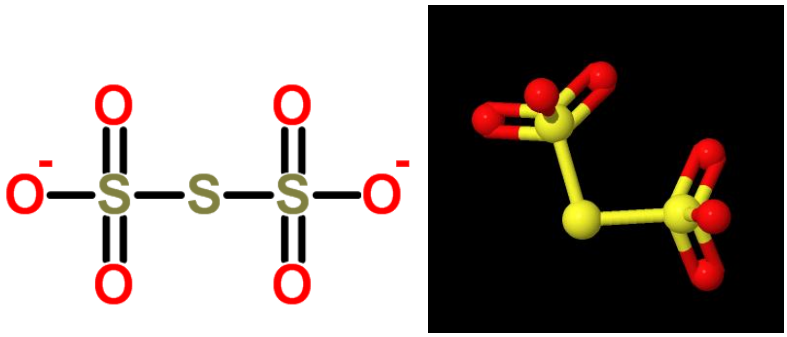
Thiosalts are partially oxidized sulfur oxyanions such as $S_2O_3^{2-}$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$ ions. These compounds, generated in the processing of sulfide ores, concentrate in mining wastewater. Figure 1 shows the general structure of thiosulfate, trithionate and tetrathionate ions. The most common sulfide ores found are pyrite ($FeS_2$) and pyrrhotite (FeS) (Bernier and Warren, 2007). Thiosalts are formed when sulfur rich ores are oxidized in mining processes such as grinding, aeration and flotation units (Kuyucak et al., 2001). Thiosalts also exist naturally in volcanic eruptions and in runoff from open pit mines containing sulfur and sulfur decomposing bacteria (Takano, 1994). Figure 2 shows the schematic of various processes involved in a mining concentrator. The schematic (Fig. 2) is shown of a concentrator at Xstrata Kidd Metallurgical site in Timmins, ON. Thiosalts present in mining effluents are collected in tailing ponds for treatment (Figure 2). They are not completely reduced in many tailing ponds by conventional treatment procedures that precede their discharge (Rolia, 1983). The key factors in the generation of thiosalts in the mining process are sulfur content in the ore, grinding and floatation pH, residence time of the effluent, temperature, dissolved oxygen in the grinding solution and air flow in floatation units (Wasserlauf and Dutrizac, 1982; Rolia, 1985; Kuyucak, 2001).

The thermodynamics of the sulfide oxidation process suggest sulfate as the result of its oxidation, but kinetic limitation results in the formation of thiosalts. Oxidation of thiosalts continues until all of the thiosalts degrade and the end product of sulfate is reached (Kuyucak and Yaschyshyn, 2007). Thiosalt oxidation reactions produce protons ($H^+$) that contribute to acidity in the effluents while in the treatment system or downstream from receiving waters (Kuyucak and Yaschyshyn, 2007). The General characteristics of acidic mine effluent are low pH, high sulfate content and high metal loading. Decomposition of thiosalts depends greatly on the oxidizing agents and the metal content in the effluents. However, the present research focuses thiosalt decomposition in the absence of metal loadings.

While thiosalts are not typically toxic, the oxidation to sulphate results in pH depression in water bodies (Rolia, 1983). The resulting sulfuric acid in the water body deteriorates the water quality and could endanger the aquatic organisms (Forsberg 2011). The relationship between thiosalt reduction and pH depression is well established by studies such as Belanger (2008) and Rolia et al. (1983). Rolia et al., (1982), observed a lowered pH of about pH 3-4 in the receiving lakes and rivers of thiosalt effluents. Apart from the ability to contribute to aquatic risk, thiosalts are also known to reduce the overall effectiveness and output in the floatation unit in a process plant (Ramachandra, 2006). Also, acidification of water bodies, apart from rendering them toxic may also result in the release of some toxic metal compounds in sediments that could further affect the aquatic assemblage (Forsberg, 2011).



(A)



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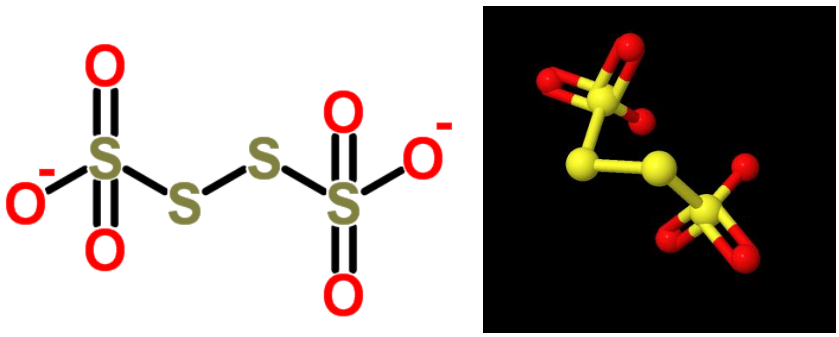


(C)

**Figure 1: 2D and 3D structures of (A) thiosulfate (B) trithionate (C) tetrathionate**

(Source: www.chemspider.com)

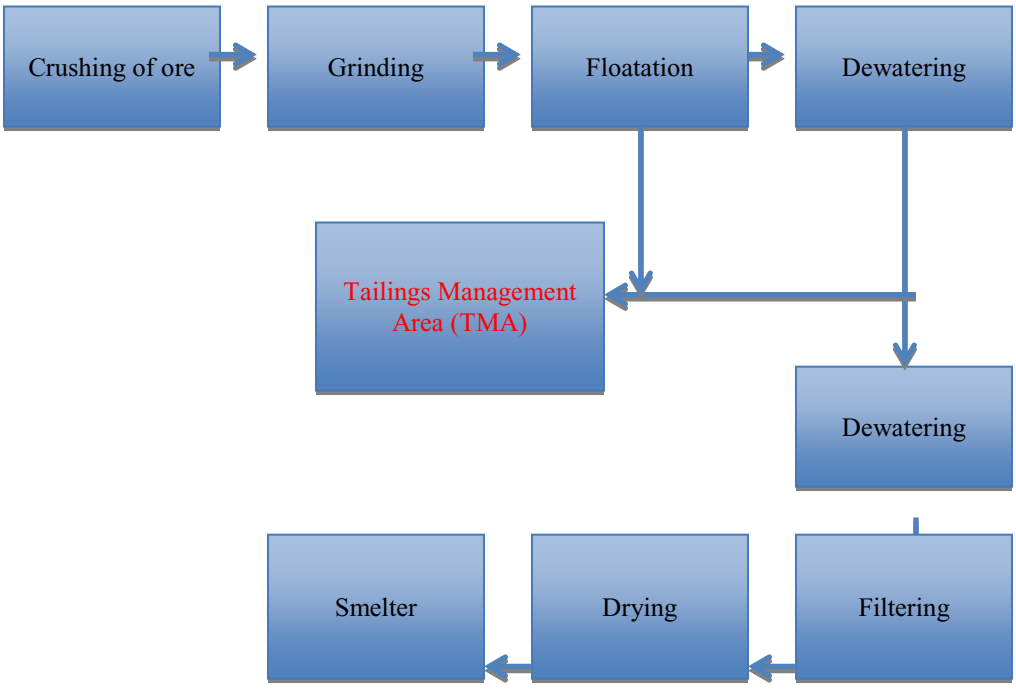



**Figure 2: Various units in pre processing facility in Kidd metallurgical site**

**Adopted from Kidd metallurgical site, Timmins, ON**

Water quality impact from sulfuric acid generation by thiosalt oxidation is particularly problematic as the oxidation of thiosalts in tailing/retention ponds is slow and their decomposition may not be complete during the pond residence time. However, thiosalts oxidation occurs at a faster pace in the receiving water body due to the action of the thiobacilli species of bacteria. The degradation of thiosalts is considered as the primary source of acidification in mining effluents; nevertheless, knowledge regarding their individual impacts is limited (Forsberg, 2011).

There is no specified standard for maximum thiosalt concentration for safe discharge of thiosalt effluents in the water body, although acceptable pH ranges are provided and acute toxicity studies were conducted for two aquatic species (Rolia, 1983; MMER, 2012; Schwartz et al., 2006). Since the direct ingestion of thiosalts poses no toxicity for the concentrations usually present in the effluents, the environmental standards for thiosalt are to be based on the pH depression due to oxidation (Rolia, 1983; Kuyucak and Yashchyshyn, 2007).

This research proposes a methodology to set an environmental standard for thiosalt effluents and also focuses on conducting an environmental risk assessment of the water body receiving the final thiosalt effluent. A thiosalt natural degradation model is proposed in this research that focuses on the relationship between thiosalt concentration, physical conditions of the effluent and resulting pH depression.

## 1.2 Impacts of thiosalts on rivers and streams

After their treatment from the tailings management area (Figure 2) thiosalts from the mining effluent are released into the rivers or streams. Thiosalts concentrations in the final mining effluent are typically in the range of less than 30 to 1000 ppm (Wasserlauf and Dutrizac, 1982). As mentioned earlier, usually thiosalts are not completely oxidized to form sulfate ion by treatment techniques in the tailing management area (Dinardo and Salley, 1998). High concentrations of thiosalt in tailings coupled with insufficient retention times lead to environmental problems when effluent from such tailings are discharged into water bodies (Silver and Dinardo, 1981).

Thiobacillus bacteria oxidize the thiosalts that enter the receiving water body, thus lowering the pH of the water body. Various types of Thiobacillus include thiobacillus thioparus, thiobacillus neapolitanus, thiobacillus novellus and thiobacillus denitrificans (Dinardo and Salley, 1998). Rolia et al (1982) reported pH of receiving water bodies decreasing from about pH 3 to pH 4.

## 1.3 Thiosalt effluent treatment methods

Thiosalts present in mining effluents are treated using various methods such as microbial –enhanced degradation and chemical oxidation. The treated effluent is released to the receiving water body. Prior to release in the water body, the buffering capacity of the treated effluent is increased so as to facilitate further lowering of pH in the receiving waters. Reduction of thiosalts in receiving waters is caused by various species of Thiobacillus bacteria. However, the bacteria efficiency is not stable throughout the year

in northern climates; it depends on various factors not limited to the oxygen availability, ambient temperature and availability of oxidizing agents. Various methods of thiosalt effluent treatment used by industry or that have been evaluated in a laboratory are discussed below.

1. Natural oxidation in tailings management area
2. Chemical oxidation by hydrogen peroxide
3. Increasing buffer capacity by adding carbonate or bi-carbonate
4. Biological oxidation

**Natural oxidation in tailings**

It was observed in the tailings management program of Brunswick mines that the thiosalt degradation rate followed a first order rate (Kuyucak and Yaschyshyn, 2007). The rate equation for a first order degradation is given as follows:

$C_{(t)} = C_0\, e^{-(Kt)}$

where,

$C_{(t)}$ is the residual thiosalt concentration (mg/L) in effluent after duration "t"

$C_0$ is the initial thiosalt concentration (mg/L) in the effluent

K is the degradation rate constant ($Hours^{-1}$)

t is time in hours

It was observed in the Brunswick mines tailings management that the degradation rate of thiosalts varied seasonally (Kuyucak and Yaschyshyn, 2007). As expected, the fastest rate of degradation was observed in summers and the slowest rate in winters. It is to be noted that all the thiosalts species are clubbed together and expressed in thiosulfate equivalent.

**Chemical oxidation using hydrogen peroxide**

Investigation of thiosalt oxidation using hydrogen peroxide was conducted at Kidd Metallurgical site, Timmins. Each mole of thiosalt as a thiosulfate equivalent could consume about 3.5 moles of $H_2O_2$ (Kuyucak and Yaschyshyn, 2007). The Brunswick mine investigation revealed that 0.0028 ml of $H_2O_2$ could destroy 1 mg of thiosalt from effluent waters containing 850 mg/L.

**Carbonate and bi-carbonate buffering**

The concept used in carbonate and bi-carbonate buffering is increasing the effluent pH (making highly alkaline) to minimize pH depression due to oxidation of thiosalts. Both carbonate and bi-carbonate could be used to increase the alkalinity. The buffering process is in accordance with the following equations:

$NaHCO_3 \rightarrow Na^+ + HCO^-_3$

$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$

$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$

**Biological oxidation of thiosalts**

Various bacteria are capable of oxidizing thiosulfate and polythionates to produce sulfuric acid. Presence of these bacteria in the water bodies containing thiosalts could lead to acidification of the water body. Different species of Thiobacillus bacteria become active in different pH and temperature conditions (Wasserlauf and Dutrizac, 1982). Regardless of the Thiobacillus species of bacteria, the degradation of thiosalts results in the generation of sulfate and pH depression (Dinardo and Salley, 1998):

Biological reactors are used in the removal of thiosalts from mine effluents. The most common types of bioreactors are (Dinardo and Salley, 1998)

1. Rotating Biological Contactor (RBC): The RBC reactor is a rotating shaft mounted with disks partially immersed in the effluent. Layers of microbes growing on the disks degrade the thiosalts present in the effluent.
2. Aerated packed column and tank reactors: Packed column and tank reactors consist of a large tank or tube filled with material to which microbes adhere. The effluent and air are passed through the tank or tube.
3. Packed Bed Reactor: Packed bed reactors consist of an aerated packed bed using a high surface area material. This material is used as a carrier for microbes. The remediation system consists of several compartments in series. Different thiobacteria are placed in each of the compartments to take advantage of the natural ability of different species to thrive under different conditions.

There is a need for modeling the ecological risk assessment of thiosalts to the aquatic species; especially considering the fact that the receiving water quality is checked downstream on a periodic basis, and upon identification of a concern, measures are taken to prevent deterioration.

## 1.4 Research Objective

The present work considers the following three main objectives.

1. To develop a method so that the pH of the water body is linked to the risk to aquatic species;

2. To establish an environmental standard for thiosalt effluents in the receiving waters; and
3. To model ecological risk assessment of aquatic species.

## 1.5 Organization of thesis

Chapter 1 introduces thiosalts, wherein the natural occurrence of thiosalts and generation of thiosalts from mining industries is discussed. This chapter also discusses various processes in a mine concentrator that contribute to thiosalt generation. Impacts of thiosalts on the receiving water body are also introduced. Both direct impact and indirect impacts of thiosalts are discussed. The most common thiosalt treatment techniques used in industry are briefly introduced. This chapter throws light on the purpose of this research and its novelty in environmental risk assessment.

Chapter 2 deals with the literature review of thiosalts and their behaviour in various conditions such as change in pH, temperature and the presence of oxidants. Interaction of all thiosalt species with one another and in the presence of oxidizing agents and their disproportionation reaction are investigated. Thiosalt degradation and disproportionation pathways are very complex. Sometimes a particular pathway of reduction for a thiosalt could not be pinpointed. This chapter describes the various pathways of thiosalt reduction and highlights the reactions selected and used in the present research to develop a natural degradation model. The ultimate goal of this research is to conduct an environmental risk

assessment to aquatic assemblage due to the presence of thiosalts in water bodies. The framework for risk assessment as prescribed by the US EPA is also detailed in this chapter.

Chapter 3 discusses the framework of environmental risk assessment pertinent to the present scenario of thiosalts. Each section in the framework of the environmental section is discussed in accordance with the problem of study.

Limited toxicity data of thiosalts for aquatic assemblage is one of the major challenges faced in this research. Bootstrapping methodology is used in this research to estimate the missing toxicity data on the basis of available data. Chapter 3 also details the work accomplished in this research to develop a dose response model for the aquatic assemblage based on the limited available toxicity data. Modeling of the thiosalt natural degradation in the pond and stream environment and quantifying the exposure to the aquatic organisms are also documented in this chapter.

The developed risk assessment methodology is applied to data from an actual mine site. The site selected is Kidd Metallurgical site located in Timmins, ON. Chapter 4 describes the site and the operations at the site related to the generation of thiosalts.

Chapter 5 details the results from the risk assessment case study of Kidd Metallurgical Site. The end results focus on the resultant thiosalt concentration in the water body and

the decrease in pH the thiosalt oxidation caused in the water body. Emphasis is also put on the duration required by the thiosalts to decrease the pH of the receiving water body.

# Chapter 2: Literature review

## 2.1 Introduction

The thermodynamics of the sulfide oxidation process suggest sulfate as the result of its oxidation, but kinetic limitation results in the formation of thiosalts (Silver and Dinardo, 1981). As mentioned earlier, thiosalt oxidation is very slow in tailing ponds and biological ponds and their decomposition cannot be complete during the residence time. Direct and indirect toxicity of thiosalts to aquatic species has been studied by many previous researchers (Schwartz et al., 2006; Noval and Holtze, 2009; McGeer et al., 2000) and is discussed in section 2.2. However, predicting the behaviour of thiosalts in aqueous solution is very complex as the aqueous solutions of polythionates form a complex equilibrium system. A part of the difficulty also arises due to conflicting pathways of thiosalt decomposition that may occur simultaneously. Thiosalt generation and reactivity depends on various factors such as pH, sulfide content of ores, residence time, temperature and catalysts such as microbes and metals (Wasserlauf and Dutrizac, 1982). Thiosalt natural degradation reaction pathways applicable to this research are discussed in section 2.3.

One of the intermediary aims of the research is to understand the degradation pathways of thiosulfate and polythionates and to develop a natural degradation model. The natural degradation model is based on thiosalt degradation kinetics that can estimate the resultant concentration of thiosalts and pH of the receiving water body. This natural degradation

model is then used in conducting the exposure assessment stage of the thiosalt risk assessment.

## 2.2 Toxicity of thiosalts

Toxicity can be classified into three categories, namely, direct toxicity, indirect toxicity and secondary effects. Direct toxicity stems from the ingestion of contaminants by aquatic species present in the water body. Indirect toxicity is caused by the lowering of the pH of the water body owing to thiosalt oxidation and secondary effects are the outcome of the changed conditions in the water body resulting from direct and indirect toxicity (Novak and Holtze, 2009). For example, thiosalts lowering of pH can cause some of the non-toxic substances to become toxic. Such an effect is termed a secondary effect. Detection of secondary toxicity effects is very complicated (Novak and Holtze, 2009). Contribution of secondary effects of thiosalts towards the aquatic environmental risk is out of the scope of this research.

Amongst the three major thiosalt species, thiosulfate is most toxic according to the limited data available (Schwartz et al., 2006; Novak and Holtze, 2009; McGeer et al., 2000). Novak and Holtze (2009) also reported that the direct toxicity of thiosalt species mixture posed less toxicity than individual species, i.e, the thiosalt mixture showed antagonistic effects behaviour. The acute toxicity of the aquatic species is summarized in terms of their Lethal Concentration (LC) 50 values and Inhibition Concentration (IC) 50 values. The Canadian Centre for Occupational Health and Safety (CCOHS) defines LC50 as the minimum concentration that if administered all at once causes death of 50% of a group of test animals. It is a measure of the acute toxicity of a material. IC 50 or half

maximal inhibition concentration is a measure of effectiveness of a Chemical of Concern (COC) in inhibiting biological or biochemical function of a target species. IC 50 refers to the concentration of thiosalts causing 50% growth inhibition in fresh water aquatic species. Toxicity data of thiosalts is limited and the available data is present for fresh water fish only (McGeer et al., 2000). The Literature throws light on acute toxicity for only two species, namely, Rainbow trout and Daphnia magna (Schwartz et al 2006). Daphnia magna is sensitive to thiosulfate while rainbow trout is more sensitive to tetrathionate.

Previous toxicity studies investigated $Na_2S_2O_3$ (or thiosulphate) solution toxicity to brook trout and smallmouth bass over a period of 24 hours. In the study, 10,000 mg/L had no effect on the considered fish species; however, 50,000 mg/L proved to be acutely toxic (McGeer et al., 2000). There was no toxicity of $Na_2S_2O_3$ observed over 7 days for rainbow trout for concentrations of up to 9200 mg/L (McGeer et al., 2000). Novak and Holtze (2009) and Schwartz et al. (2006) conducted acute toxicity studies for rainbow Trout and daphnia magna with respect to thiosulfate, trithionate and tetrathionate. Novak and Holtze (2009) calculated the LC50 value of thiosulfate to rainbow trout to be 7378 mg/L, when the fish is exposed for a period of 96 hours. The LC50 value of thiosulfate for Daphnia magna was calculated to be 1012 mg/L when exposed for duration of 48 hours (Novak and Holtze, 2009). However, Schwartz et al. (2006) reported far smaller LC50 values of thiosulfate for rainbow Trout and Daphnia magna than the values reported in Novak and Holtze (2009). The LC50 value of thiosulfate for rainbow trout was reported to be 819 mg/L for the exposure duration of 96 hours and the LC50 value of

Daphnia magna was about 300 mg/L. The LC50 values of tetrathionate for rainbow trout were established at >800 mg/L and for Daphnia magna at 750 mg/L (Novak and Holtze, 2009, Schwartz et al., 2006, Kuyucak and Yashchyshyn, 2007). McGeer et al. (2000) conducted an acute toxicity test for daphnia magna and Selesnastrum capricornutum. Selenastrum is a fresh water alga and daphnia magna is a common water flea. The reason for conducting an acute toxicity test on the species was based on the fact that the species represented different trophic levels within the aquatic ecosystem. These species are commonly used and widely accepted as the test species to assess potential toxins in the system (McGeer et al., 2000). The toxicity tests were conducted to monitor the effects in the target species from no effect to full effect. The full effect in the target species is understood as mortality for Daphnia magna or growth inhibition for Selenastrum (McGeer at el 2000). Each of the species is exposed to solutions of thiosulfate, trithionate and tetrathionate. The solutions are monitored for their pH as well because of the possibility of thiosalt oxidation during the tests. Thiosulfate and tetrathionate did not alter the pH of the solution, and very little reduction (about 5%) in their concentration in solution was observed. However, trithionate concentration showed significant reduction, i.e., it underwent oxidation resulting in a decrease in pH of the solution. It became difficult to assess the toxicity caused by trithionate as the contribution of decreased pH to growth inhibition and mortality could not be assessed separately. Acute toxicity (IC 50) of thiosulfate, trithionate and tetrathionate for Selenastrum were calculated to be 2220 mg/L, 330 mg/L and 2110 mg/L respectively. Thiosulfate proved to be most toxic to Daphnia magna followed by tetrathionate and trithionate. McGeer et al. (2000) reported

48 hour EC 50 values of thiosulfate, trithionate and tetrathionate for Daphnia magna to be 300 mg/L, 1350 mg/L and 750 mg/L respectively.

Ample measures were taken by McGeer et al. (2000) to minimize uncertainty in the EC50 value of thiosalts. The sodium salt was used to generate thiosulfate solution while potassium salt was used for trithionate solution. Toxicity of $Na^+$ and $K^+$ ions to the considered species was unlikely as their IC 50 values were 1430 mg/L and 2780 mg/L respectively, whereas the concentration of both $Na^+$ and $K^+$ ions present in the solution at the IC 50 values of thiosalts for considered species were far less than 1430 mg/L. Acute toxicity and sub lethal toxicity of various fresh water species are shown in Table 1.

**Table 1: Acute toxicity data for fresh water species**

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

As mentioned before, indirect toxicity of thiosalts is due to its oxidation resulting in generation of acid in the water body (Novak and Holtze, 2009; Schwartz et al., 2006; Frosberg, 2011). Schwartz et al. (2006) investigated the acute toxicity due to decreasing

pH of the solution with respect to various fresh water species. The fresh water species considered in the acute toxicity test conducted by Schwartz et al. (2006) were Ceriodaphnia dubia, Fathead minnow, Selenastrum capricornutum and Lemna minor. It was observed that the lower pH limit (causing no more than 50% effect) was observed to be pH 5.5. According to Metal Mining Effluent Regulations (MMER), any incident of pH decreasing below 6 is to be reported (MMER, 2012). Although studies (Schwartz et al., 2006; Novak and Holtze 2009) have reported IC 50 values for pH of a little less than 6, MMER (2012) states that a pH of 6 should be treated as a recommended best practice in industry for an effluent receiving water body.

## 2.3 Thiosalt reaction kinetics

Various researches nvestigated thiosalt reduction in alkaline, acidic and neutral mediums at varying temperatures; yet, most of the thiosalt reduction data at mesophilic temperatures is unavailable. Mizoguchi et al. (1976), Rolia et al. (1982), Meyer and Ospina (1982) and others reported thiosalt reduction reactions at temperatures above 70 $^{o}$C, 90 $^{o}$C, 110 $^{o}$C and 130 $^{o}$C. However recent studies such as Zhang and Dreisigner (2002), Zhang and Jeffrey (2010) and Miranda-Trevino et al. (2009) have focused more on thiosalt reduction reactions at naturally occurring temperatures. Other researchers such as Meyer and Ospina (1982) studied the oxidation of thiosulfate and tetrathionate in acidic conditions (pH= 3.5-4.0) while Rolia (1982) studied thiosulfate, trithionate and tetrathionate reaction kinetics in highly alkaline solutions.

The relative rates of decomposition of polythionates ($S_xO_6^{2-}$) at a given pH were given by X = 6 > 5 > 4 > 3 (Wasserlauf and Dutrizac, 1982). The general rule in thiosalt decomposition is that acid is utilized in decomposition reactions that produce elemental

sulfur; acid is formed in thiosalt decomposition reactions that produce polythionates and sulfates (Vongporm, 2008). Pathways of degradation are shown for each thiosalt in the following sections.

## Stability of thiosalts

Different species of thiosalts are stable under different conditions of pH and temperature. In this study, sensitivity of the thiosalt reactions to change in pH is considered as the primary factor. Polythionates are observed to be thermodynamically unstable in an alkaline medium (pH above 9) (Wasserlauf and Dutrizac, 1982). On the contrary, thiosulphate is observed to be generally reactive in very acidic conditions and stable under alkaline conditions. However, even in alkaline conditions as temperature is increased, thiosalts are observed to show signs of degradation. Thiosulfate reactions at elevated temperatures (for example, above $40^0$C) are not of interest in this research. In an acidic environment, thiosulfate decomposes to yield sulfur, sulfate, trithionate and tetrathionate, and also may produce or consume acid ($H^+$ ions) (Wasserlauf et al 1982, Jorgensen 1990, Rolia et al 1982). In near neutral and mild acidic conditions polythionates are found to be stable, although their stability decreases with an increase in temperature and markedly so for trithionate (Wasserlauf and Dutrizac, 1982). Table 2 shows the reactivity of thiosalts in various pH ranges (Miranda-Trevino, 2009).

**Table 2: Reactivity of thiosalts in various pH ranges**

| | pH = 2 | pH = 4 | pH = 7 | pH = 9 |
|---|---|---|---|---|
| 4 $^o$C | Thiosulfate | No reaction | No reaction | Tetrathionate |
| 15 $^o$C | Thiosulfate | Trithionate | Trithionate | Tetrathionate |
| 30 $^o$C | Thiosulfate and trithionate | Trithionate | Trithionate | Thiosulfate, trithionate and tetrathionate |

**Thiosulfate reaction**

Three pathways of thiosulfate decomposition are oxidation, reduction and disproportionation reaction pathways. Jorgensen (1990) studied thiosulfate decomposition pathways in anoxic sediments in river and lake samples in Denmark. Jorgensen (1990) observed that of the sediments from the lake and river samples, 6% of their $S_2O_3^{2-}$ had undergone oxidation, with a 50% reduction and a 44% disproportionation reaction.

Reduction of thiosulfate to $H_2S$ by $SO_4^{2-}$ reducing bacteria is given by the following reaction (Jorgensen, 1990):

$S_2O_3^{2-} + 8FeOOH + 14H^+ \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 11H_2O$ --(1)

Thiobacilli bacteria oxidize the thiosulfate by the following reaction (Jorgensen, 1990):

$S_2O_3^{2-} + CH_3COO^- + H^+ \rightarrow 2HS^- + 2CO_2 + H_2O$ --(2)

Thiosulfate disproportionation follows the following reaction (Jorgensen, 1990):

$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + HS^- + H^+$ --(3)

Mizoguchi et al. (1976) studied the disproportionation of thiosulfate under highly acidic conditions and temperatures ranging from $70^0$C-$150^0$C. Mizoguchi et al. (1976) proposed the following reaction for thiosulfate decomposition:

$5S_2O_3^{2-} + 6H^+ \rightarrow 2S + 2S_4O_6^{2-} + 3H_2O$ -- (4)

$S_2O_3^{2-} + H^+ \rightarrow S + HSO^-_3$ --(5)

$3S_2O_3^{2-} + 2H^+ \rightarrow 4S + 2SO_4^{2-} + H_2O$ --(6)

However, the thiosulfate decomposition reaction proposed by Mizoguchi et al. (1976) are not relevant since this study focuses on the thiosulfate decomposition reaction at temperatures typical of pond conditions.

Xu and Schoonen (1995), however, contradicted the findings of Mizoguchi et al. (1976) regarding the dominant pathway of thiosulfate decomposition. Xu and Schoonen (1995) studied thiosulfate decomposition in a highly acidic medium (2.9 <pH>5.2) at $20^0$C. They illustrated that the thiosalt disproportionation rate is far greater than other pathways of degradation. According to Xu and Schoonen (1995) thiosalt disproportionation results as elemental sulfur and sulfite as major products. The reaction is shown below:

$2S_2O_3^{2-} + H^+ \rightarrow HSO^-_3 + SO_3^{2-} + 2S$ --(7)

Though thiosulfate is stable in alakaline conditions, Rolia and Chakrabarti (1982) investigated the decomposition of thiosulfate in alkaline conditions at 75-85 $^0$C. The thiosulfate oxidation reaction by Rolia and Chakrabarti (1982) is as follows

$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$ --(8)

Thiosulfate degradation was also investigated in the presence of catalysts such as pyrite and hematite to produce tetrathionate (Xu and Schoonen 1995). Pyrite oxidation of thiosulfate is according to the following reaction:

$FeS_2 + 6Fe(H_2O)_6^{3+} + 3H_2O \rightarrow Fe^{2+} + S_2O_3^{2-} + 6Fe(H_2O)_6^{2+} + 6H^+$ --(9)

**Trithionate reactions**

Zhang and Jeffrey (2009) investigated the kinetics of trithionate reactions at near neutral conditions. At near neutral conditions the dominant trithionate reaction is its hydrolysis to thiosulfate and sulfate (Reaction 10). Zhang and Jeffrey (2009) observed that the hydrolysis reaction is observed within the pH range of 5.5 to 10.5. The trithionate hydrolysis reaction is a pseudo first order reaction with a reaction rate constant of (6.2±

0.2) * $10^{-7}$ $s^{-1}$. Even though the reaction is active in a range of pH the reaction rate constant is independent of the pH (Zhang and Jeffrey 2009).

$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$ --(10)

In strongly alkaline solutions, trithionate degrades to thiosulfate and sulfite according to Reaction (11) (Zhang and Jeffrey 2009).

$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$ --11)

In alkaline conditions, Rolia et al. (1982) and Wasserlauf and Dutrizac (1982) reported that the rate of trithionate decomposition was greatly increased by an increase in temperature. An experiment was conducted at pH 10 and a temperature of $80^0$C to observe trithionate reaction. The results from the test closely agree with the stoichiometry of the hydrolysis reaction (10).

Rolia et al. (1982), reported that reaction (10) is active in a pH range of 5.5 to 12, although the temperatures at which the reaction (10) is active are from 70 – $85^0$C. The effect of initial thiosulfate concentration on the trithionate decomposition rate was also reported by Rolia et al. (1982). At pH 5.5 – 8 and at temperatures between 85 -$100^0$C, the presence of thiosulfate concentration accelerated trithionate decomposition.

**Tetrathionate reactions**

Tetrathionate is highly stable in acidic conditions (Miranda-Trevino 2010). At near neutral conditions and in weakly alkaline conditions it decomposes to trithionate and thiosulfate (Rolia 1982; Varga and Horvarth 2007; Zhang and Jeffrey 2009). A tetrathionate reaction in neutral and alkaline conditions occurs via the thiosulfate catalysed rearrangement reaction (Zhang and Jeffrey 2009). The rearrangement of polythionates is according to the following equation:

$2S_xO_6^{2-} \rightarrow S_{x-1}O_6^{2-} + S_{x+1}O_6^{2-}$ (X>3) –(12)

Trithionate cannot rearrange according to the equation (12), as thiosulfate cannot be formed from the interactions of polythionates (Zhang and Jeffrey 2009). The reaction (12) is strongly catalysed by the presence of thiosulfate. Thus tetrathionate in near neutral conditions rearranges to trithionate and pentathionate. In the same near neutral pH conditions, Varga and Horvath (2007) proposed that decomposition of tetrathionate in the presence of thiosulfate took place with the following reactions:

$S_4O_6^{2-} + S_2O_3^{2-} \rightleftarrows S_5O_6^{2-} + SO_3^{2-}$ --(13)

$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-}$ --(14)

As mentioned before, trithionate hydrolysis is a dominant reaction in near neutral conditions. Thus the trithionate formed from the rearrangement of tetrathionate is further degraded to thiosulfate, sulphate ions and $H^+$ ions. The tetrathionate hydrolysis pathway in strongly alkaline conditions is not well defined. Even though tetrathionate hydrolysis may follow the trithionate hydrolysis pathway (Reaction 10), the polythionates generated by such a reaction would be highly unstable in an aqueous solution. Tetrathionate is one of the principal products in thiosulfate degradation in the gold leaching process. This degradation often occurs in the presence of ammonia, copper and oxygen. As an alternative for such a process Zhang and Dreisinger (2002) studied the decomposition of polythionates in alkaline solutions in the absence of oxygen, ammonia and copper. The experiments were conducted in the temperature ranges of 22 – 40 $^oC$. The tetrathionate degradation in alkaline medium may be represented by the following equations (Zhang and Dreisinger 2002):

$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$ --(15 a)

$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O$ --(15 b)

First tetrathionate is degraded to thiosulfate and trithionate. The trithionate generated is further degraded into thiosulfate and sulphite. The overall tetrathionate degradation reaction is given by Zhang and Dreisinger (2002) as:

$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$ --(16)

Rolia and Chakrabarti (1982) investigated the kinetics of decomposition of trithionate and tetrathionate in alkaline solutions. It was observed that in highly alkaline solutions tetrathionate degraded to thiosulfate and trithionate (Rolia and Chakrabarti 1982; Varga and Horvath 2007). However the reaction (15 b) proposed by Zhang and Dreisinger (2002) was found to be non-dominant by Rolia and Chakrabarti (1982). The trithionate decomposition reaction was observed to be much slower than the tetrathionate degradation reaction. The experiments conducted by Rolia and Chakrabarti (1982) were carried out in the presence of an oxidant such as dissolved oxygen. An intermediate step in the process of risk assessment is developing a natural degradation model for thiosalts. It is assumed that dissolved oxygen is the only oxidant available in the water body. Therefore, the reactions proposed by Rolia and Chakrabarti (1982) were selected and used in the natural degradation model. Zhang and Dreiseinger (2002) reported the tetrathionate degradation reaction (Reaction 16) at the pH range of 10 and higher. Rolia and Chakrabarti (1982) observed the same reaction from pH 9.2 upwards. Tetrathionate degradation in a highly alkaline solution is a first order reaction with respect to both tetrathionate and hydroxyl ions ($OH^-$). The reaction rate constant also differed between the researchers by an order of magnitude. Rolia and Chakrabarti (1982) reported a

reaction rate of 0.17 $Lmol^{-1}S^{-1}$ while Zhang and Dreisinger (2002) reported a rate of 1.71 $Lmol^{-1}S^{-1}$.

Varga and Horvarth (2007) also proposed tetrathionate degradation in a highly alkaline medium. Tetrathionate, if left for a long time in a highly alkaline medium, decomposes to thiosulfate and sulphite through the following reaction (Varga and Horvarth 2007):

$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$ --(17)

Other researchers have shown that the decomposition of tetrathionate is highly dependent on the alkalinity of its solution. In weakly alkaline solutions (pH <9) tetrathionate rearranges to trithionate and pentathionate as previously mentioned and shown in Reaction (12) (Varga and Horvarth 2007; Zhang and Jeffrey 2009). In weakly alkaline solutions both trithionate and pentathionate were found to be stable. As the alkalinity of the solution rises slightly, pentathionate decomposes to thiosulfate according to the following reaction:

$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O$ --(18)

Thus, tetrathionate decomposition in slightly alkaline solutions is given by the overall process shown in Reaction (19) (Varga and Horvarth 2007):

$4S_4O_6^{2-} + 6OH^- \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O$ --(19)

Reaction (19) shown above is applicable for pH <12. For pH > 12, disproportioning of trithionate starts to show according to the Reaction (20) shown below:

$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O$ --(20)

Another disproportionation of trithionate observed at pH =13 is as follows (Varga and Horvarth 2007)

$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + H_2O$ --(21)

The overall degradation of tetrathionate according to Varga and Horvarth (2007) is given by the following processes:

$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$ --(22)

$4S_4O_6^{2-} + 10OH^- \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 5H_2O$ --(23)

Even though tetrathionate is observed to be very stable in highly acidic conditions, Drushcel et al. (2003) observed that in the presence of $O_2$ and $Fe^{3+}$ tetrathionate oxidizes to sulphate at $25^0$C. The degradation rate of the reaction is pseudo-first order with a reaction rate of $10^{-11}$ $S^{-1}$. Tetrathionate oxidation reaction in the presence of excess Fe and $O_2$ is given by the following reaction (Drushcel et al., 2003):

$S_4O_6^{2-} + 3Fe^{3+} + 2.75\ O_2 + 4.5\ H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+$ --(24)

The kinetics of tetrathionate oxidation was found to be several orders of magnitude slower than the formation of polythionates from thiosulfate in acidic, $Fe^{3+}$ solutions.

**Biological oxidation of thiosalts**

As mentioned earlier, various bacteria are capable of oxidizing thiosulfate and polythionates to produce sulfuric acid. Table 3 shows various bacteria that can decompose thiosalts and the pH ranges in which they are active.

**Table 3: Thiosalt decomposing bacteria and their pH ranges**

| Name | pH charateristics | Reference |
|---|---|---|
| Thiobacillus thiooxidans | Range 1.0 to 6.0<br>Optimum 2.0 to 3.0 | Dinardo and Salley (1998) |
| Thiobacillus thioparus | Optimum near neutral | Dinardo and Salley (1998) |
| Thiobacillus neapolitanus | Range 4.5 to 7.8<br>Optimum 7.0 | Dinardo and Salley (1998); Wasserlauf and Dutrizac (1982) |
| Thiobacillus novellus | Range 5 to 9<br>Optimum at 7.0 | Dinardo and Sally (1998) |
| Thiobacillus denitrificans | Range 6 to 8 | Dinardo and Sally (1998) |
| Thiobacillus ferrooxidans | Optimum 1 to 4 | Wasserlauf and Dutrizac (1982) |
| Thiobacillus A2 | Range 7.0 to 9.0 | Wasserlauf and Dutrizac (1982) |

Trithionate is highly inert to degradation by normal chemical reagents in near neutral pH conditions (Wasserlauf and Dutrizac, 1982). However degradation of trithionate by T. neapolitanus under aerobic and anaerobic conditions proceeds rapidly in contrast to its degradation behaviour in chemical reagents. The reaction pathways of thiosalts bio-oxidation are complex; researchers have identified many pathways for thiosalt degradation based on the bacterial species and effluent conditions (Dinardo and Sally, 1998). The general tendency in bio-oxidation of thiosalts is decreased pH. Different bacteria in the thiobacilli species differ with respect to their optimum degradation conditions. Thiobacillus ferroxidans operate in the pH range of 1 to 4; Thiobacillus neapolitanus functions best at near neutral condtions and Thiobacillus A2 functions under slightly alkaline conditions. The degradation of thiosalts by thiobacteria was drastically inhibited at a pH higher than 9, suggesting that degradation process in highly alkaline conditions is followed by chemical oxidation (Dinardo and Sally, 1998). Thiobacillus A2 rapidly oxidizes thiosulfate but does not oxidize or produce polythionates. However, Thiobacillus neapolitanus oxidises both polythionates and thiosulfate; thiosulfate is oxidized at a faster rate than polythionates. Thiobacillus ferrooxidans oxidizes polythionates at a faster rate than thiosulfate. Table 3 shows various thiobacteria and the optimum conditions for their action. Overall aerobic oxidation of thiosalts by thiobacilli bacteria is given by the following equations:

$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$ --(25)

$S_3O_6^{2-} + 2O_2 + 2H_20 \rightarrow 2S0_4^{2-} + 4H^+$ --(26)

$S_4O_6^{2-} + 7/2\ O_2 + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+$ --(27)

$2S^0 + 3O_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+$ --(28)

## 2.4 Frame work of Risk Assessment

Risk assessment is defined as the process of assessing magnitudes and probabilities of the adverse effects of anthropogenic/natural activities. The goal of risk-based environmental regulation is to balance the degree of risk to be permitted against the cost of risk reduction and against competing risks (Suter et al., 1993). The framework of the risk assessment of a contaminant in general is demonstrated in Figure 3, which is based on the principles of ecological risk assessment (US EPA, 1977).

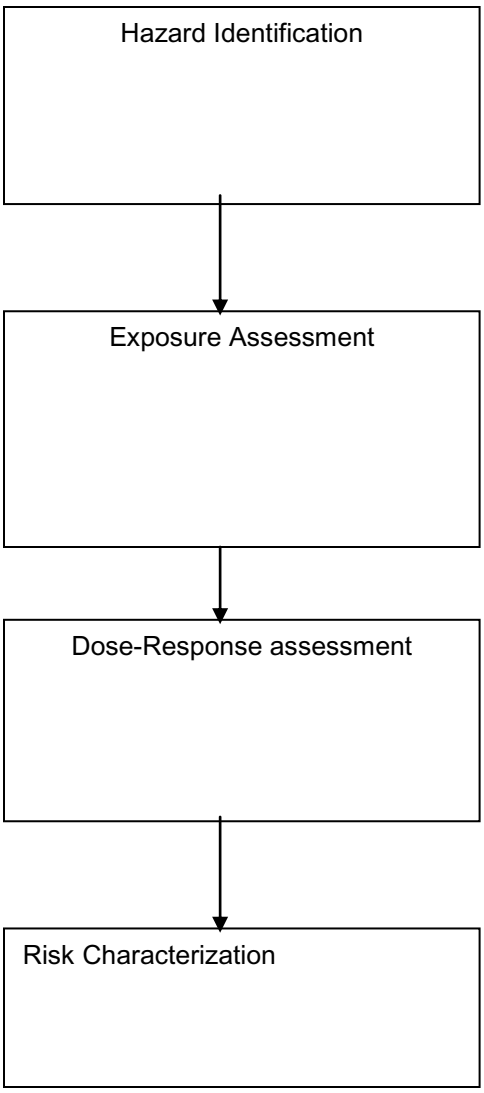



**Figure 3: Framework of risk assessment of thiosalts**

**Hazard Identification**

This is defined as the process of determining whether human or animal exposure to a chemical of concern (COC) could cause an increase in the incidence of a health concern or whether exposure to a non-human receptor, like fish, birds or other wildlife, might

affect them adversely (Paustenbach, 2002). The chemicals of concern in this research are thiosalts. The aquatic effects of a thiosalt may be of such minor significance that the aquatic organism is able to carry on its functioning in a normal manner and that only under conditions of additional stress (e.g., changes in pH) can a chemically induced effect be detected. On other hand, at sufficiently high concentrations, thiosalts may have the capacity to cause illness or death to some aquatic life.

**Exposure Assessment**

This is the process of measuring or estimating the intensity, frequency, and duration of human or animal exposure to an agent currently present in the environment. The exposure to the target species can be modeled/simulated or could be obtained from field data.

**Dose response relation**

This is the process of characterizing the relation between the dose of an agent administered or received and the incidence of an adverse health effect in the exposed population, and of estimating the incidence of the effect as a function of exposure to the agent (Suter et al., 1993).

Human data on exposure to the agent of interest are often not available and regulation is based on experimental studies involving species that are administered in doses far higher than those of regulatory interest. The toxicity data obtained from the test species (usually rodents) are then extrapolated or interpolated to human toxicity values. Uncertainty factors ($10^{-x}$), where x could be 10, 100 or 1000, account for the discrepancy in toxicity values.

**Risk Characterization**

This is the process of estimating the incidence of a health effect under the various conditions of human or animal exposure described in the exposure assessment. Risk characterization is performed by combining the results from both exposure and dose response assessments. Risk is quantified by calculating the ratio termed Hazard Index (HI).

$$\text{Hazard Index} = \frac{\text{Exposed Concentration}}{\text{Threshold contaminant concentration}}$$

If the HI of the contaminant is above 1, then there is a possibility of risk caused to the considered species or environment. However, a probabilistic approach is warranted when the chance of exceedance of the exposure over the threshold value can be quantified. When there are multiple contaminants in the environment, then the sum of HI of all contaminants together should be less than 1. However, the impact of individual contaminants does not always add to the impact on the group constituting those individual components. Sometimes the risk associated with the group can be higher (Synergistic effect) or lower (antagonistic effect) than the sum of the risks from its constituent contaminants. Consideration of these effects further helps to quantify risk from the contaminants to a species or an environment.

# Chapter 3: Risk Assessment of thiosalts: methodology

## 3.1 Overview of methodology

The framework of risk assessment established by USEPA was outlined in Chapter 2. This chapter focuses on the application of the risk assessment framework to thiosalts. The chapter outlines the scientific gaps in exposure assessment modeling and the characterization of a dose-response threshold in thiosalt risk assessment. The methodology of the present study is discussed below and is presented in Figure 4.

The possibility of hazard from thiosalts to aquatic organisms could consist of either of the following two ways:

1. Direct toxicity due to ingestion of thiosalts; and
2. Indirect toxicity resulting from pH depression.

Exposure of the target species to thiosalts can be obtained from field data targeting mining effluents. It can also be estimated using an exposure model developed as part of this research. The developed exposure model estimates the concentration of thiosalts (thiosulfate, trithionate and tetrathionate) remaining in the effluent and the time required to reach the concentration and pH under given conditions of temperature and catalyst. The methodology employed to develop the exposure model is discussed in section 3.3 of this chapter. In this research, the target species for risk assessment are aquatic organisms on which toxicity tests were conducted; hence, there is no requirement for extrapolation of data. The toxicity data available for thiosalts is shown in Table 1 of Chapter 2. One of

the challenges in this study was the limited toxicity data available to establish thiosalt direct toxicity (Schwartz et al. 2006; Taylor et al. 2010); characterizing risk using a limited data set could lead to a very conservative risk assessment. To accurately assess risk to the aquatic community, a method that will yield a valid prediction of the effect on an entire community from a limited number of individual species, is required. The bootstrapping technique was used to predict the missing toxicity data, based on available data. Using the randomly generated toxicity data, aquatic risk threshold concentrations were established. The bootstrapping technique is discussed in detail in the sections to follow.

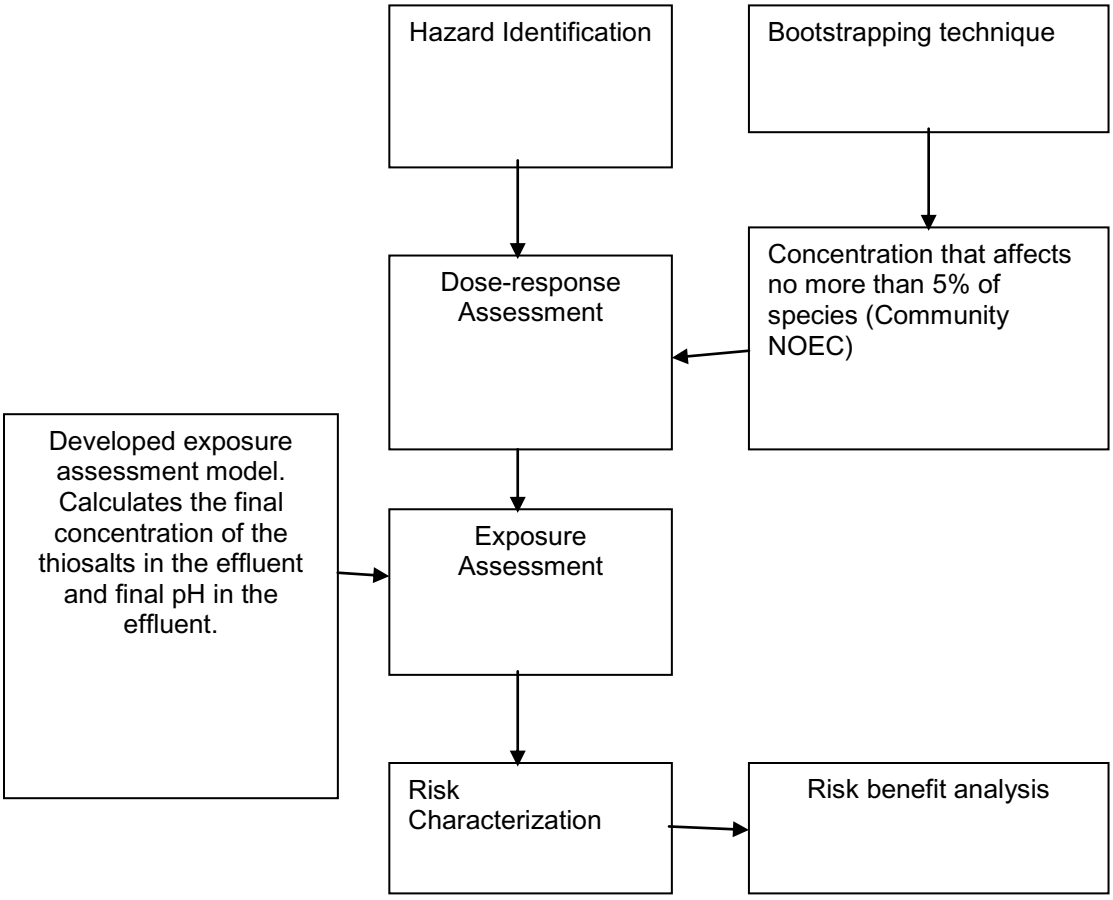



**Figure 4: Risk assessment of thiosalts-methodology**

## 3.2 Dose response assessment

### 3.2.1 Dose assessment end points

Exposure response modeling is the evaluation of the health effects on a species due to exposure/ingestion of a particular quantity of the contaminant (www.epa.gov/risk/index.htm). Selecting assessment endpoints is an important part of ecological risk assessment. Assessment endpoints are the expressions of the actual environmental value to be protected (Paustenbach, 2002) and they also define the target of the assessment that is to be achieved. According to Paustenbach (2002), two elements are needed to define assessment end points. First is the specific valued entity. This entity could be a species, a functional group or a community. In the present research, the entity is the fresh water aquatic community. The second element needed to determine the assessment end point is the attribute or characteristic of the entity that is to be protected. In the present study it is mortality of the aquatic species. The goal of the present research is to establish the No Observed Effect concentration (NOEC) of the thiosalts in an aquatic environment. The NOEC is defined as the highest concentration in a toxicity test that has no statistically significant adverse effect or acceptable effects on the exposed population of test organisms as compared with the controls (Jagoe et al, 1996). It is an important tool in ecological risk assessment as it is used to characterize risk by its comparison with the exposed concentration of the contaminant (Xing et al., 2013).

### 3.2.2 Determining NOEC value

To assess risk to a community, effects data for a limited number of individual species must yield a valid prediction of the effect on an entire community.

The two common methods of calculating community NOEC are:

1. The Assessment Factor (AF) method that determines NOEC by taking the smallest known critical toxicity value of a species in a community and dividing this value by an arbitrary assessment factor, for example 10. This factor is used to counter the variabilities present in the species sample (Environment Canada, 2007; Xing et al., 2013).
2. Assuming that the critical values or the LC50 values of species follow a specified distribution, and selecting a low percentile of the toxicity distribution as a level below which the impact may be termed acceptable (Hanson and Solomon, 2003; Posthuma et al., 2002).

**AF approach**

According to Environment Canada (2007), a predicted no effect concentration is derived from the minimum critical toxicity value and represents the concentration of a substance in the environment that is not expected to induce any adverse effects in a population. Predicted no effect concentrations are calculated by dividing the minimum critical toxicity value (LC50 in this research) by an appropriate assessment factor.

The assessment factors may vary in magnitude and are used to account for, but not limited to:

1. Extrapolation from single species laboratory test to ecosystem impacts

2. Quality and quantity of data available
3. Variations in sensitivity between species or between individuals within a species.

The AF approach is used by many regulatory agencies for deriving threshold effect concentrations. However, it is considered as a Tier 1 approach for calculating threshold concentration for a contaminant, and as such gives a very conservative contaminant threshold concentration (Wijngaarden et al. 2010). If only a single toxicity value is available, there is an uncertainty about the relevance of this value to other organisms and hence a large assessment factor (e.g., 1000) is used (Environment Canada, 2007; Xing et al., 2013).

**Species Sensitivity Distribution approach**

Living organisms constitute a vast diversity of physiology, behaviour and other characteristics. Thus different species respond differently to a compound at a given concentration, which is otherwise termed as sensitivity. The statistical distribution function of the variations and sensitivity of various species to a particular physiological or biological factor yields Species Sensitivity Distributions (SSD). SSD is estimated from a sample of toxicity data and is a cumulative distribution function of the data. SSDs are increasingly used in ecological risk assessment procedures to establish water quality criteria or NOEC (Xing et al., 2013). An example of an SSD is shown in Figure 5.

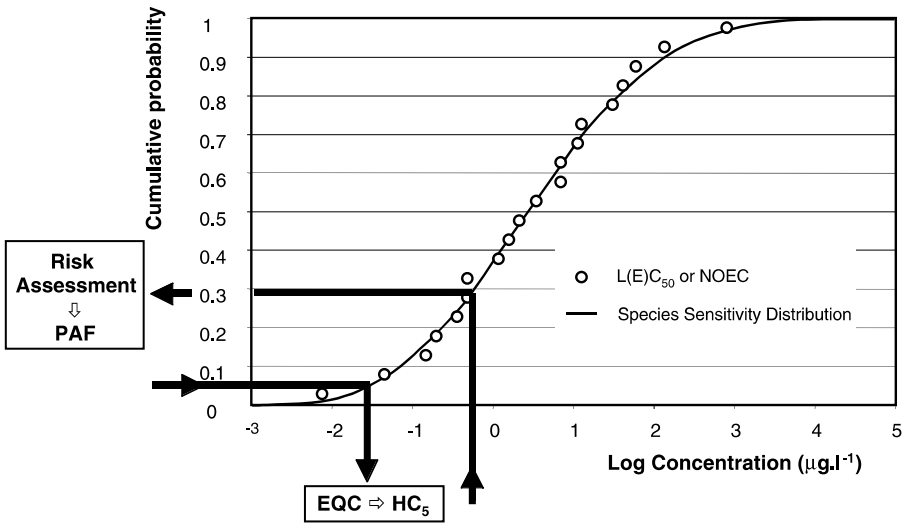



**Figure 5: SSD expressed as a cumulative distribution function**

Source: Posthuma et al. (2002).

The dots in Figure 5 are the measured toxicity data points. The curve is fitted species sensitivity distribution. The X-axis in Figure 5 represents the exposed contaminant concentration of the organisms and the Y-axis represents the percentage of species affected due to the corresponding concentration. The arrows in Figure 5 indicate that an SSD can be used in a 'forward' as well as 'inverse' way.

**'Forward' approach**

In the 'forward' approach the risk associated with the exposed contaminant concentration is determined. In Figure 5, the arrow from the log concentration axis, i.e., X-axis to Y-axis represents the forward approach. In this approach, if one knows the concentration in the target species then one can calculate the probability of Potentially Affected Fraction (PAF). PAF is defined as the percentage of the organisms that can be potentially affected due to their exposure to the corresponding concentration.

**'Inverse' approach**

The 'inverse' approach is used when we know the environmental protection criteria or standard and intend to back calculate the corresponding maximum allowable exposed concentration in the organism. Thus the risk is considered as given and corresponding concentration, which causes that risk, is to be determined. For example, for a desired ecological risk criterion of no more than 5% of the aquatic organisms being affected, the corresponding value on the X-axis from the fitted curve is to be determined. This concentration is the maximum allowable concentration of the contaminant that the organism could be exposed to (Postuma et al 2002).

As mentioned above, in order to perform risk assessment, determining or setting the ecological risk criteria is of utmost importance. In this research, concentration of the thiosalts affecting no more than 5 percent ($HC_5$) of the aquatic community is selected as the ecological risk criterion. Therefore the concentration of thiosalts corresponding to the $HC_5$ is termed as a NOEC. The percentage of the species affected is termed as the Fraction Affected (FA). Since the present research is about derivation of environmental quality criteria, the inverse approach is adopted to predict the concentration that protects 95 percent of the species.

**SSD Construction**

Constructing an SSD requires three steps.

1. Toxicity data is collected for the organisms. The data set should be statistically and ecologically representative of the community or set of species of interest. In general, chronic toxicity data is preferred when deriving environmental quality

criteria, but for ecological risk assessment, acute toxicity data are often used owing to greater availability of data and ease of interpretation.

2. Once the data set is obtained, it is described by a specified distribution like normal, lognormal or log logistic. The selection of distribution comes from known data.
3. The output of SSD can be interpreted using a 'forward' or an 'inverse' approach as mentioned in a prior section.

**Advantages and difficulties in SSD approach**

Different protective levels in the environment can be derived using the SSD approach thereby avoiding unnecessary or unwarranted remediation. The SSD approach is more robust and has fewer uncertainties when compared to the AF approach (Xing et al. 2013). Acute toxicity data of thiosalts for aquatic organisms are very sparse; precise data is present for two aquatic species only; Rainbow trout and Daphnia magna. With such a small toxicity data set, assigning a distribution might lead to skewed results. Also, it is not statistically viable to describe a data set of two data points with a distribution. Studies (Xing et al. 2013; Verdonck et al. 2001; Wijngaarden et al. 2010) have suggested that a minimum data set of 10 toxicity points are required to develop an SSD.

### 3.2.4 Bootstrap technique

The bootstrap technique adopted in this research addresses the issues of the AF approach mentioned above, and also the inherent problems of generating SSD using sparse toxicity data (i.e. fewer than 10). 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 et al. 1996).

Since toxicity data of thiosalts is available for only two aquatic species, we assume 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 of rainbow trout and Daphnia magna for both thiosulfate and tetrathionate. There are no toxicity data available in literature for trithionate; hence this chemical is not considered for the present risk assessment. The methodology of NOEC determination is shown in Figure 6 and is further explained in detail below.

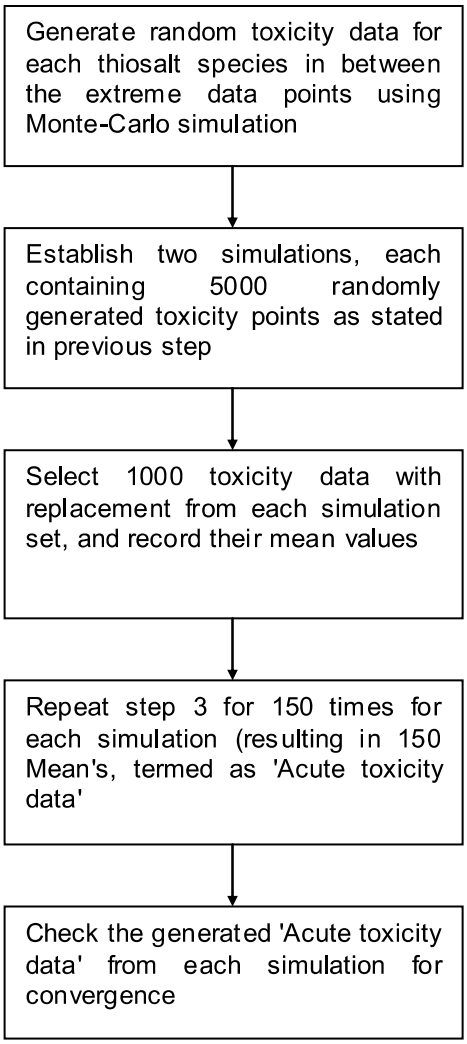



**Figure 6: Determining NOEC using bootstrap technique**

Various steps involved in the random data generation and NOEC determination are explained in detail below.

**Simulation algorithm**:

1. Random toxicity data are generated for each of the thiosalt species, namely thiosulfate and tetrathionate using @RISK. It is assumed that the randomly generated data between the toxicity points of 300 ppm and 819 ppm for thiosulfates followed a uniform distribution. Similarly, randomly generated data for tetrathionate also follows a uniform distribution with its extreme toxicity points being 742 ppm and 750 ppm.
2. Two data sets, referred to as simulation 1 and simulation 2, are generated with each of the data set containing 5000 randomly generated toxicity data points.
3. Randomly select 1000 data points with replacement from each simulation set, and record their mean.
4. Step 3 is repeated 150 times for each simulation, thus resulting in 150 means.
5. These 150 mean points are hereby called 'Acute toxicity data generated' using the bootstrapping technique.
6. 'Acute toxicity data generated' from each simulation are checked for convergence.

**Check for convergence**:

1. Using @RISK software, the simulations data are fitted with distribution. Refer to Appendix Figures A.1 – A.6 for information about the distributions and their parameters.
2. Weibull, Normal and Logistic distributions are fitted to the data.
3. Two simulations are said to be converged if the fitted distribution parameters of each simulation match the other simulation or are in close proximity. Results for the confirmation of convergence are presented in the Appendix

**Determination of 5-percentile concentration**:

1. 150 acute toxicity data generated from each of the two simulations are joined as an acute toxicity data set for thiosulfate and tetrathionate, thus resulting in 300 data points for thiosulfate and another 300 data points for tetrathionate.
2. These data points for each of the thiosalt species are sorted in ascending order.
3. The $15^{th}$ data point for each of the thiosalt species represents the 5-percentile concentration. Table 11 in section 5.1 presents the 5-percentile concentration for thiosulfate and tetrathionate.

**Selecting best fitting distribution for the toxicity data**

1. Three goodness of fit tests, namely, the Chi-Square test, Anderson-Darling test, and Kolmogorov-Smirnov test were considered for the study.
2. First, using the Chi-square test, the distributions that fit to the toxicity data are ranked.

3. Second, using the Anderson-Darling test, the ranks of thiosulfate toxicity data are as follows.
4. Additionally, the Kolmogorov-Smirnov test is used to rank the toxicity data distribution.
5. Now adding the ranks of each distribution from all goodness of fit tests gives a number for each of the distributions. The distribution with the least number is termed the best distribution. For example, normal distribution is ranked 3 according to the chi square test, and ranked 2 and 3 according to the A-D test and K-S test respectively. Summing up all the ranks, i.e., 3+2+3 = 8.

## 3.3 Exposure Assessment Model

To perform the thiosalt risk assessment, the exposed concentration of the target species (aquatic organisms) to the contaminant is to be determined. This could be obtained from in-situ field observation or by estimating using an exposure assessment model. The exposure model developed should establish the relationship between exposure time and residual concentration and also determine the variations of pH with respect to exposure time. The residual concentration and the pH of the water body are compared with their corresponding allowable or acceptable limits to determine risk. To determine the concentration and pH of the water body, understanding the thiosalt degradation pathways is essential. Degradation pathways of thiosulfate, trithionate and tetrathionate were discussed in detail in Chapter 2. From the available literature, reactions of thiosalts in the temperature range of 20 $^{0}$C-40 $^{0}$C were selected and grouped as shown in Table 4. 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.

**Table 4: Thiosalts degradation reactions used in the exposure model**

| Reaction rates | Equation numbers | pH and temperature range | Reaction | Reference |
|---|---|---|---|---|
| $1.38*10^{3}$ $LMol^{-1}h^{-1}$ | 1A | 9.2 to 11; Not given | $4S_4O_6^{2-} + 6\ OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$ | Zhang and Dreisigner (2002) |
| 0.66 $LMol^{-1}S^{-1}$ | 5A | 2.9 to 5.6; Room temperature | $2S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + SO_3^{2-} + 2S^0$ | Xu and Schoonen (1995) |
| $14.6*10^{-3}$ $h^{-1}$ | 4A | 4 to 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) |
| $1.9*10^{-3}$ $h^{-1}$ | 2A | 7.1 to 9.2; Room temperature | $S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$ | Miranda-Trevino et al. (2009) |
| Not given | 3A | 7.1 to 9.2; Not given | $S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-}$ | Varga and Horvarth (2007) |

**Assumptions in the model**

1. The pH of the effluent receiving water body is slightly basic.
2. It is assumed that no heavy metal or other catalyst is present and abiotic conditions prevail in the water body.
3. It is also assumed that the mining effluent is undiluted in the receiving water body, thus simulating a worst-case scenario.

The parameters that are to be input in the model are the 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 part of this study is illustrated in Fig 2. Initial pH of the water body is measured and subsequently 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, the change in $[H^+]$ concentration or change in thiosalt species concentrations are calculated.

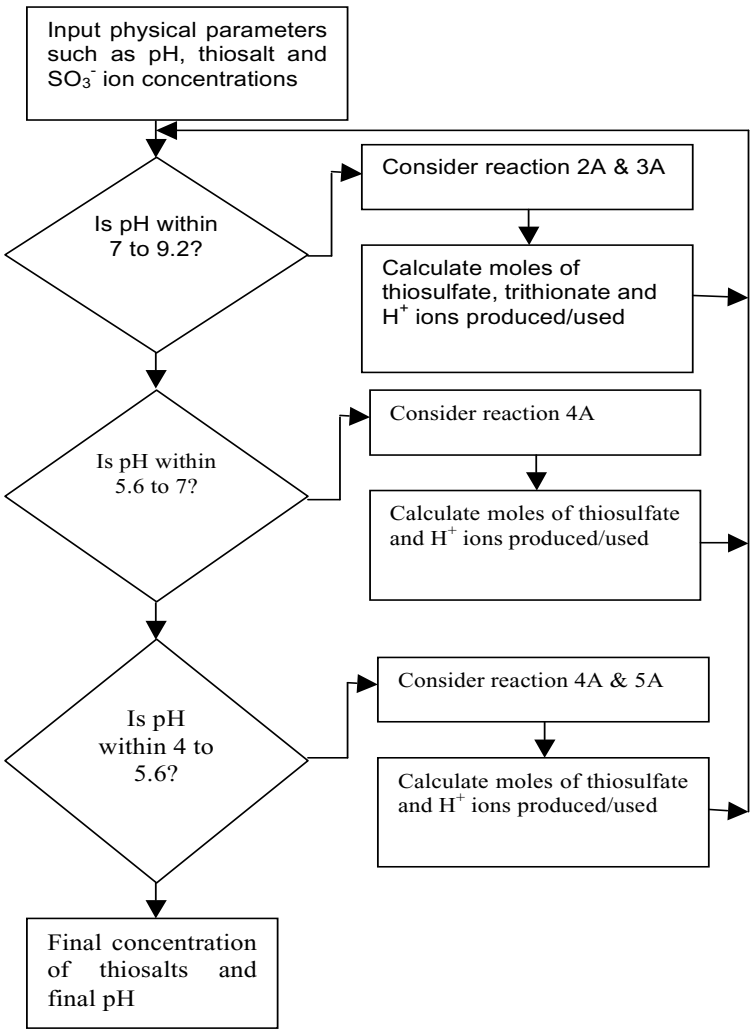



**Figure 7: Methodology of exposure model**

An example is demonstrated for the exposure model to assist explanation. Assume a scenario where the final effluent from a mining industry is released into a stream. The hypothetical initial downstream concentrations are presented in Table 5.

**Table 5: Downstream conditions of a hypothetical scenario**

| **Input Parameters** | **Value** |
|---|---|
| Initial pH | 8.5 |
| Thiosulfate | 80 mg/L |
| Trithionate | 10 mg/L |
| Tetrathionate | 12 mg/L |

Depending upon the initial pH conditions, the reactions of thiosalts are chosen by the exposure assessment model. If the pH is in between 7.1 and 9.2, the active reactions in this pH range are as shown in reactions 2A and 3A.

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \quad (2A)$$

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \quad (3A)$$

Of these two reactions, reaction 2A 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. Although 3A does generate trithionate, which is a reactant in 2A, it does not have an impact on the outcome of the reaction 2A. This is because reaction 2A is a zero order reaction i.e., the reaction rate doesn't depend on the concentration of the reactant. These two reactions will be active until the pH of the water body decreases to 7.1. For the reactions that take place, the pH of the water body should be within a range and moles/L of both trithionate and $H^+$ ions should be present. If either of the mentioned conditions

does not happen, the reaction stalls. Therefore, moles/L of trithionate and $H^+$ ions that can take part in the reaction are the minimum between these two. The total $H^+$ ions available for reaction are equal to the number of moles/L of $OH^-$ ions actually present in the solution and subtract $10^{-7}$ moles/L. Results from this segment of the exposure model are shown in Table 6. Assuming the reaction (2A), the pH change from 8.5 to 7 is instantaneous.

**Table 6: Results from first segment of the exposure assessment model**

| | |
|---|---|
| Resultant concentration of thiosulfate | 80.8 mg/L |
| Resultant concentration of trithionate | 10.8 mg/L |
| Resultant concentration of tetrathionate | 10.6 mg/L |
| Resultant pH | 7 |

Since the resultant pH (7) from this segment of exposure model falls in the pH range of 5.6 to 7, the active reactions is as follows:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \quad \textbf{(4A)}$$

Trithionate is the only species active in this pH range, and this reaction will continue until trithionate is completely used up or the resultant pH from the reaction reaches 5.6. The maximum mole/L of $H^+$ ions that can be released in this stage of model are $10^{-5.6}$ mole/L ($H^+$ molar concentration at pH 5.6). Once this molar concentration of $H^+$ ions is reached, the reaction curtails, in spite of the presence of other participants in the reaction. Molar concentration of $[H^+]$ ions released according to reaction 4A is established and consequently molar concentration of $[S_3O_6^{2-}]$ used by the reaction is back calculated. If

back calculated [$S_3O_6^{2-}$] is greater than [$S_3O_6^{2-}$] available in the solution, then using the [$S_3O_6^{2-}$] available in the solution, [$H^+$] ions released in the reaction are calculated, thus establishing the pH of the water body. The results from this segment of the model are shown in Table 7. The pH change in this stage of the exposure model is instantaneous as well.

**Table 7: Results from second segment of the exposure assessment model**

| | |
|---|---|
| Resultant concentration of thiosulfate | 87.15 mg/L |
| Resultant concentration of trithionate | 1.18 mg/L |
| Resultant concentration of tetrathionate | 10.63 mg/L |
| Resultant pH | 5.6 |

The resultant pH lies in the range of 5.6 to 4. The active reactions in this pH range are as follows:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad \textbf{(4A)}$$

$$2S_2O_3^{2-} + H^+ \rightarrow HSO_3 + SO_3^{2-} + 2S \qquad \textbf{(5A)}$$

Both the reactions in this pH range alter the pH of the water body, as is evident from reactions 4 and 5. The reaction rate of Equation (4A) is 3 magnitudes higher than the reaction of rate of Equation (5A). Hence the pH of the water body decreases to 4 instantaneously (in about 12 seconds). The time taken for pH to increase back to 5.6 is 150 hours or 6.25 days. The final result from the exposure assessment model is demonstrated in Table 8.

**Table 8: Final result from exposure assessment model**

| | |
|---|---|
| Final Concentration of thiosulfate | 62.38 mg/L |
| Final Concentration of trithionate | Completely used up, hence, 0 mg/L |
| Final Concentration of tetrathionate | 10.63 mg/L |
| Final pH of the water body | 5.6 |

**Limitations in the exposure model**

1. The exposure model is based on thiosalt degradation pathways. However, predominant pathways of thiosalt species degradation are complex and there is not always a predominant pathway(s) due to changing pH and species. This could also be due to the presence of multiple oxidizing agents such as thiobacillus bacteria, Copper (II) and Iron (III) to name a few. For example, the 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).
2. 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.
3. Some researchers have given varied reaction rates of the same reaction, and the rates differ by an order of magnitude. For example, for the same tetrathionate degradation reaction (16) in Chapter 2, proposed by both Rolia and Chakrabarti (1982) and Zhang and Dreiseinger (2002), two different reaction rates were provided. Zhang and Dreiseinger (2002) reported a rate of 1.71 $Lmol^{-1}S^{-1}$, while Rolia and Chakrabarti (1982) reported a rate of 0.17 $Lmol^{-1}S^{-1}$.

4. The model is based on limited data and assesses only abiotic conditions; however, as more reaction data becomes available, the information can easily be integrated into the above model for better and more accurate predictions.

# Chapter 4: Case study of thiosalts effluents at Kidd Metallurgical site

## 4.1 Description of the site

Kidd Metallurgical Site (Kidd Metsite) located in Timmins, Ontario and under operation by Xstrata Copper Canada is considered for the case study of ecological risk assessment of thiosalt effluents. The facility produces copper, zinc, cadmium, indium and nickel concentrate. Figure 2 presented in chapter 1 of this document showed the layout of the various units in the processing plant. The plant consists of a railroad for transporting loads in and out of the plant; an ore receiving building, one fine crushing plant, three ore grinding and floatation units, one concentrate handling unit, one thickened tailings management area, facilities for water supply, maintenance and metallurgical testing. The main source of feed for the plant is the sulfide copper-zinc ore from the mine located 30 km northeast of the site. The sulfide mineral is predominantly pyrite. Tailings and waste water from the processing facility are sent to the Tailings Management Area (TMA) for treatment and disposal. Figure 8 shows photograph of the actual mine site and Figure 9 shows the layout of the plant and its TMA.

**Figure 8: Copper-Zinc ore site that feeds Kidd Metallurgical site, Timmins, ON**

The tailings management area (TMA) is 1250 hectares located north of the plant (Figure 9). A pumping system is used to pump the tailings through two 4.5 km tailings lines to the TMA. The high-density thickened tailings are set in a conical shaped deposit with approximately 2% side slopes. Overflow water from the tailing thickener is collected in TMA in ponds A and C. Ponds A and C are used as primary settling ponds. Water from the ponds A and C is treated with lime and is flowed to pond D. Low density sludge metal precipitates are allowed to settle in pond D. Treated water from pond D is sent to the Porcupine River following final pH adjustments. The current method of thiosalts remediation used is natural degradation in the TMA in combination with added increased lime to offset pH decline in ponds A and C. Since 2009, a $H_2O_2$ thiosalt oxidation plant was commissioned at the site in addition to the previous effluent remediation techniques.

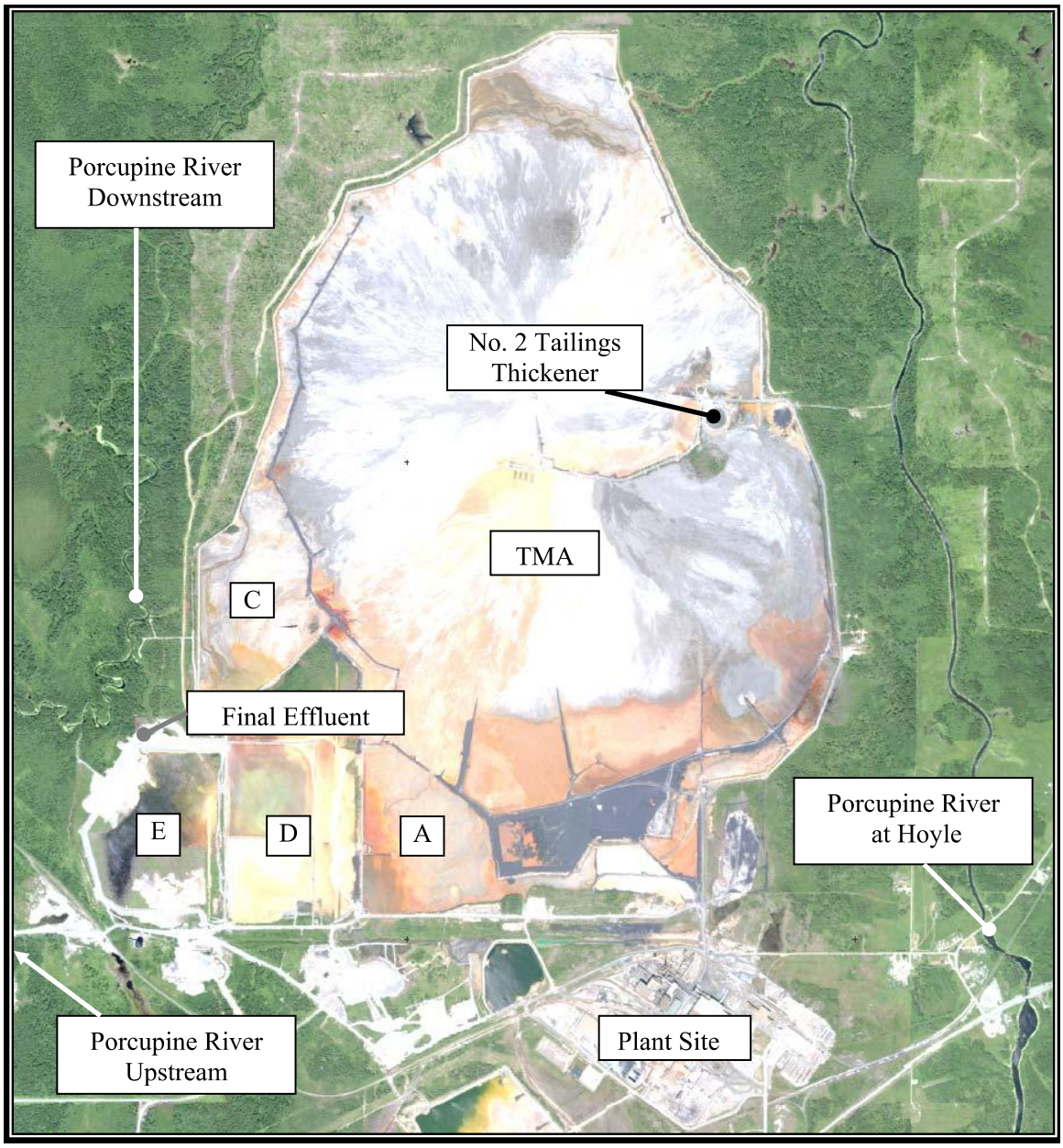



**Figure 9: Layout of Kidd metallurgical site TMA**

Source: Kuyucak and Yaschyshyn, 2007.

## 4.2 Thiosalts concentrations in effluents

The average overflow from the thickener unit to treatment ponds A and C is 44,000 $m^3$/day and the average thiosalt concentration entering treatment ponds A and C is about 217 mg/L. Thiosalt concentrations from the thickener overflow and their concentrations

in the final effluent are shown in Figure 10. Thiosalt concentrations data shown in Figure 10 are from the year 2009 to 2010; the data are obtained by analysis of a laboratory sample of the effluent. Figure 11 (a) and (b) show the distribution of thiosalt speciation in thickener overflow and in the final effluent post treatment. Figure 12 presents the final effluent data and the thiosalt speciation in the effluent prior to April 2009.

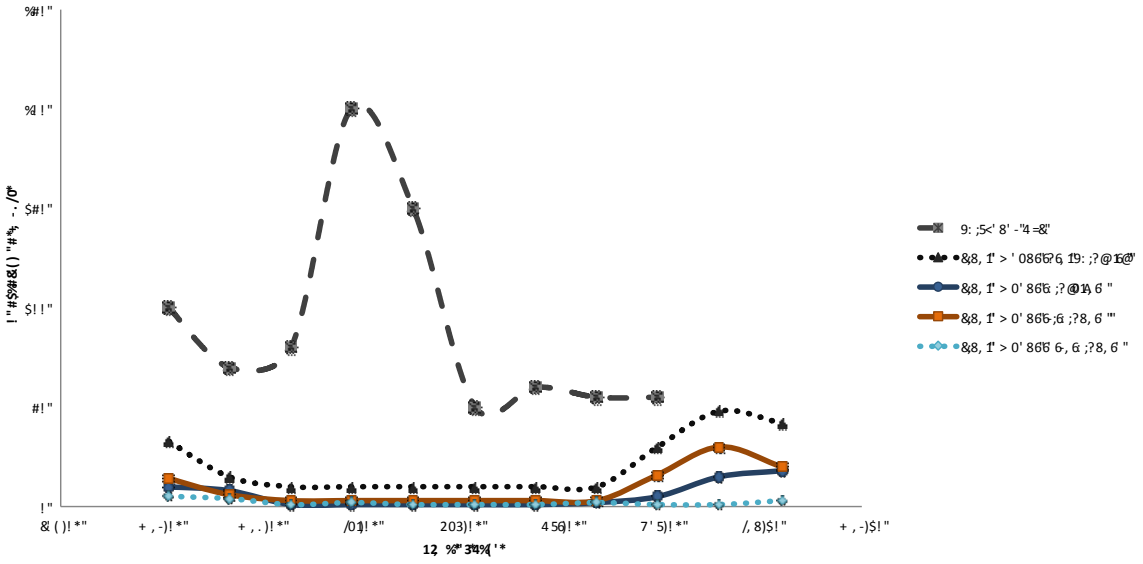
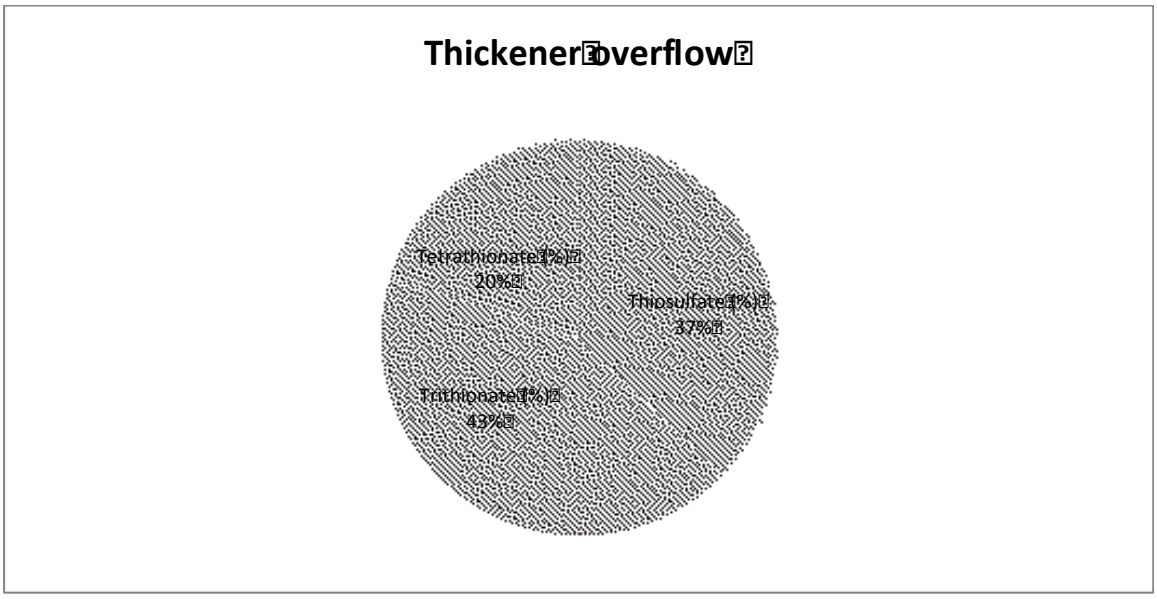
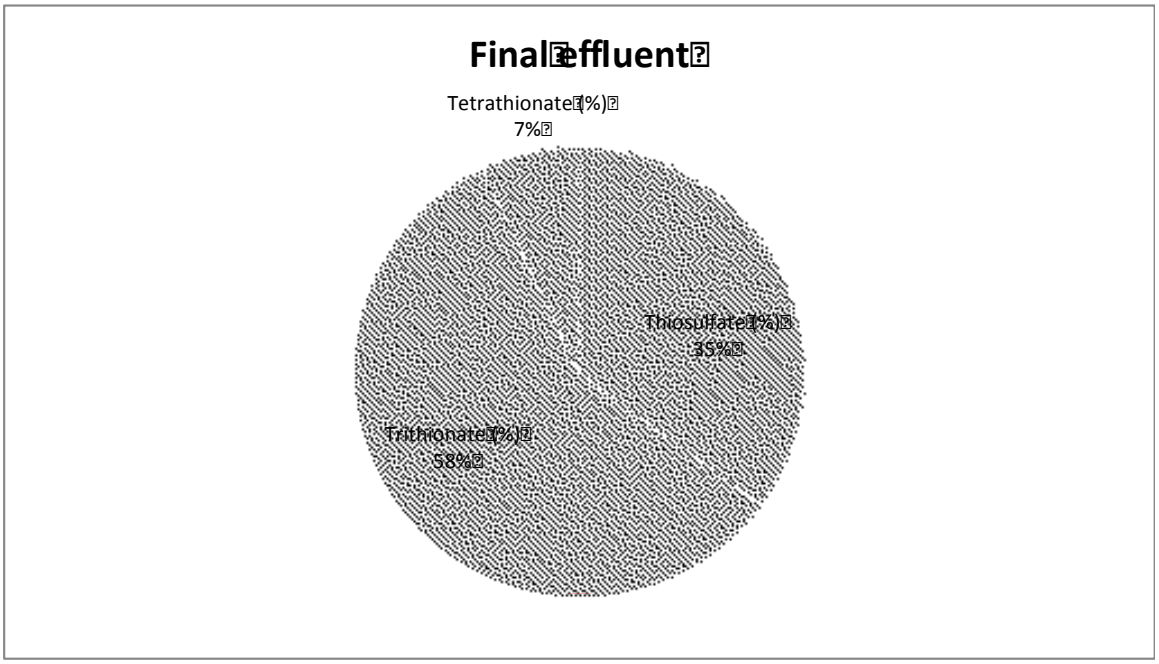



**Figure 10: Average thiosalt concentrations in thickener and final effluent (2009-2010)**




(a)




(b)

**Figure 11: Thiosalt speciation in effluent before entering and before leaving TMA**

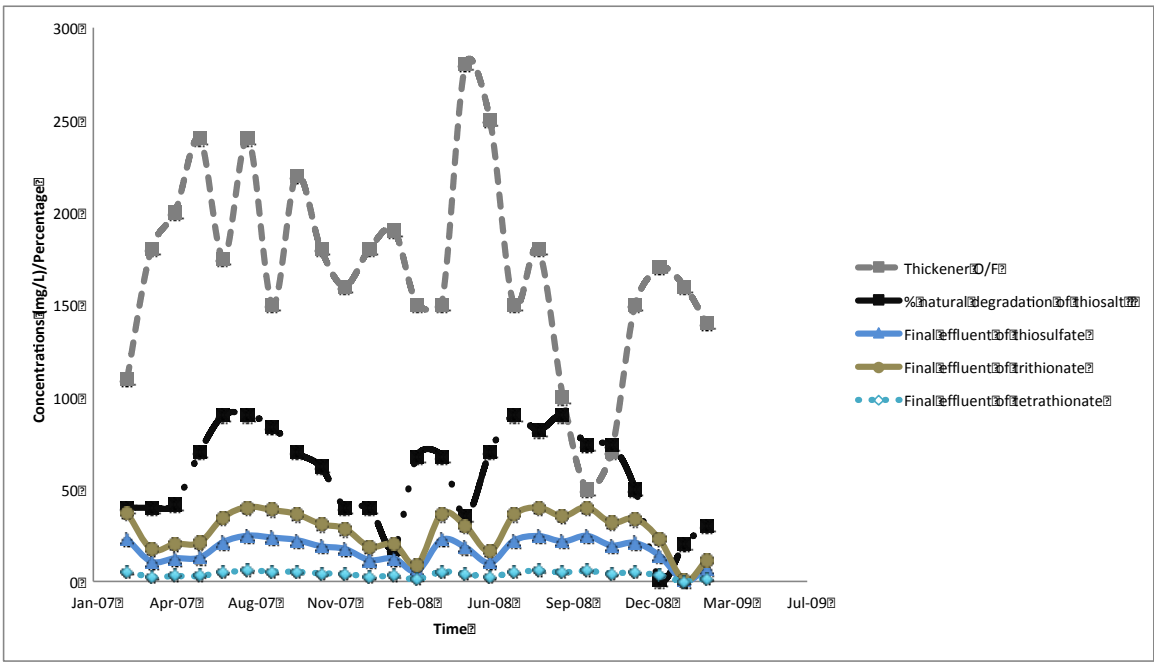



**Figure 12: Thiosalt concentrations in thickener overflow and final effluent for the years 2007-2009**

Natural degradation of thiosalts during the course of 2007 to 2009 is shown in Figure 12. The natural degradation values were based on observation at the Kidd Metsite TMA. From the available data of thiosalts concentrations from Kidd Metsite, concentrations are selected to present the risk assessment methodology and are presented in Table 9. The concentrations shown in Table 9 are selected based on the thiosalt effluent concentration between 2007 and 2009 as shown in Figure 12.

**Table 9: Thiosalt downstream concentrations considered for the study**

| Input Parameters | Value |
|---|---|
| Initial pH | 9.2 |
| Thiosulfate | 25 mg/L |
| Trithionate | 40 mg/L |
| Tetrathionate | 6 mg/L |

# Chapter 5 Results and Discussion

## 5.1 Determination of NOEC

Considering the methodology to derive NOEC values as described in chapter 3, the available toxicity data is subjected to the bootstrapping technique and results are presented as follows:

***Threshold of toxicity/ NOEC***

The procedure mentioned in Figure 6 and section 3.2.4 is followed to generate the missing toxicity data and subsequently distributions are fitted to the toxicity data. Distributions that fit the generated toxicity data are shown in Table 10. The normal, weibull and logistic distributions were fitted and the subsequent SSDs developed are presented in Appendix Figures A.7 to A.12. They are ranked in accordance to their goodness of fit tests. The R-squared value for Logistic, Normal and Weibull distributions are calculated and are 0.992, 0.997 and 0.953 respectively.

**Table 10: Goodness of fit test rankings**

| Goodness test | Logistic | Normal | Weibull |
|---|---|---|---|
| A-D test | 4 | 2 | 3 |
| Chi-Square test | 4 | 3 | 2 |
| K-S test | 1 | 3 | 4 |
| Final rank | Second | First | Second |

All the distributions have a good fit index; the distributions and SSD also seem to fit data well as shown in Figures A.7 to A.12. The 5-percentile concentrations for all the distributions do not differ much. As a result, they can be safely assumed to be the normal distribution for the toxicity data generated for thiosalts. The 5-percentile concentrations established for thiosulfate and tetrathionate are shown in Table 11. The SSDs developed based on the toxicity data from which the 5 percentile concentrations are obtained are shown in Figures A.7 to A. 12 in the Appendix.

**Table 11: 5-percentile concentrations**

| | |
|---|---|
| Thiosulfate | 552.86 mg/L |
| Tetrathionate | 745.88 mg/L |

## 5.2 Exposure to thiosalts

Mine effluent data is selected from the Kidd metallurgical mine site in Canada as described by Kuyucak and Yaschyshyn (2007) and in Chapter 4 of this document; 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 9 in Chapter 4.

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 (2A) and (3A).

Of these two reactions, reaction 2A, a zero order reaction, 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 the pH from 9.2 to 7 were

calculated based on reaction rates and stoichiometry. Judging by the reaction rate of equation (2A), effluent pH changed from 9.2 to 7 within an hour. The thiosalt concentrations present originally in the discharged effluent underwent no significant change within this period. The Figures 13 and 14 illustrates the decrease in thiosalt concentration over the assessed duration as mentioned above.

Trithionate hydrolysis (reaction 4) at near neutral conditions decreased the effluent pH from 7 to 5.6 within an hour of effluent discharge. However, the loss of trithionate in that hour was very small as well (Fig 13 and 14). The active reactions in the pH range of 5.6 - 4 are reactions (4A) and (5A); both of the reactions alter the pH of the water body. Depending upon their corresponding reaction rates, final thiosalt concentrations and pH are estimated (Table 12). The final concentration of trithionate is estimated to be 13.04 mg/L. Thiosulfate is completely degraded into $HSO_3^-$ and $SO_3^{2-}$ ions and elemental sulfur after 60 hours from the time of discharge. The final pH of the effluent was estimated to be pH 4 after 77 hours from time of discharge.

**Table 12: Final results from exposure assessment model**

| Time after effluent discharge (hours) | 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 | 4 | 0 | 13.04 | 5.9 |

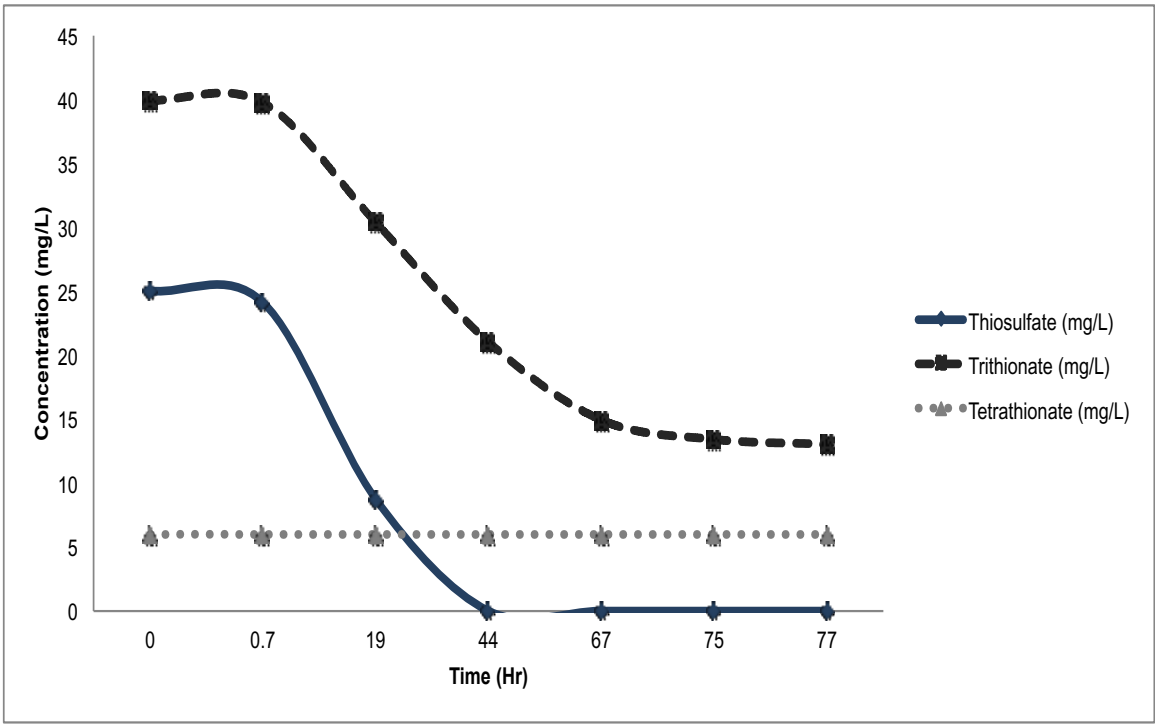



**Figure 13: Thiosalts concentration profile as assessed by the exposure model**

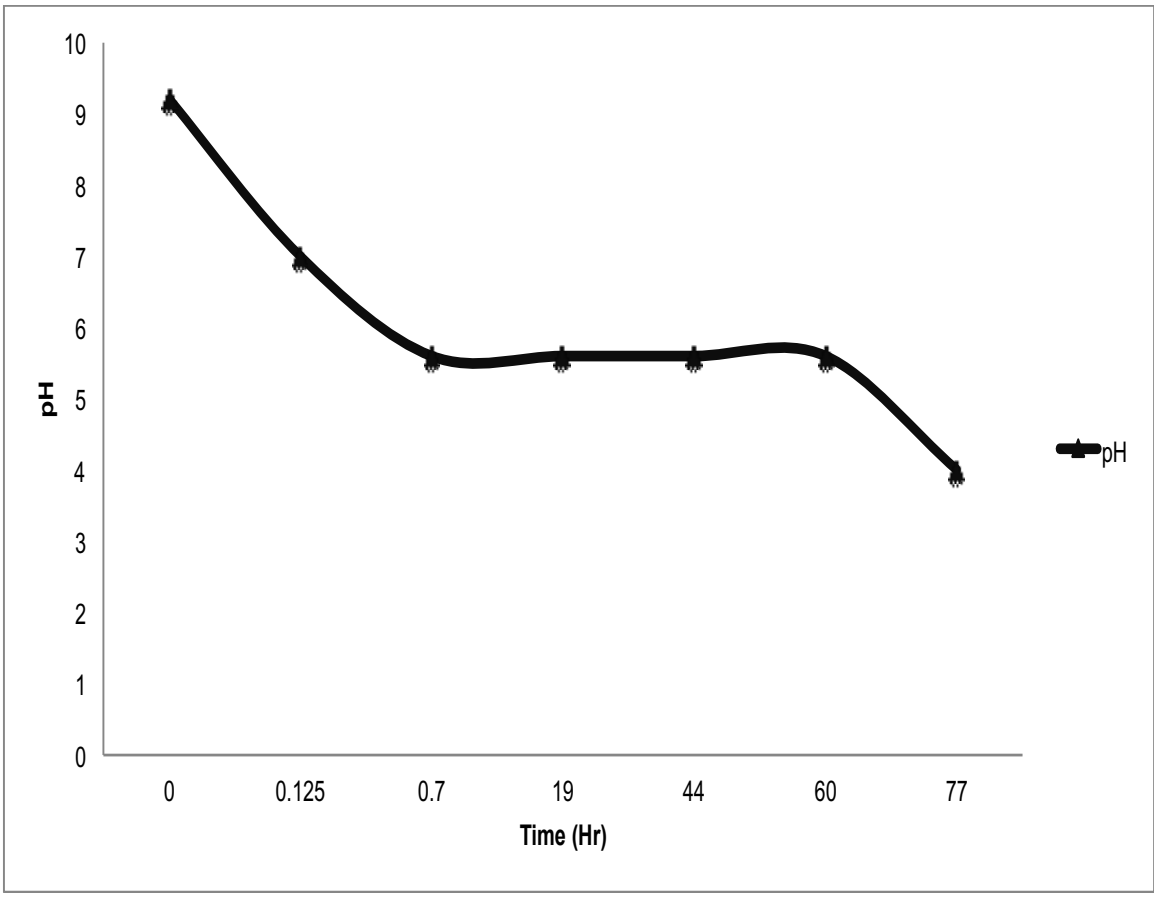



**Figure 14: pH profile of the effluent as assessed by the exposure model**

Hydrolysis of one mole of trithionate (Reaction 4A) produces 1 mole of thiosulfate and two mole $H^+$ ions, while reaction involving thiosulfate (reaction 5A) consumes the $H^+$ ions. Both of the reactions occur simultaneously. The rate of trithionate hydrolysis is far slower than the thiosulfate disproportionation reaction. Thus for the concentrations considered in the case study, pH of the effluent remains at about 5.6 until 60 hours after discharge as shown in Figure 14. 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 a 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 (Figure 14) and water body's continued acidic conditions over the next 77 hours can be a source of toxicity in the aquatic organisms. A sharp drop in pH of a solution could have many implications, especially for aquatic toxicity, as acclimation by the species to the changing conditions is limited. It is evident from the literature (Rolia et al. 1982; Frosberg 2011) that more severe acidic conditions prevailed in the fresh water 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). The effluent receiving water body for Kidd metallurgical site is Porcupine River; downstream of Porcupine River (near field) was monitored for water quality. It was observed that the pH downstream reached a lowest pH of 6 and mostly varied between a 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 14. This proposed exposure model is robust as it may include thiosalt reactions when they are established, thus making it a viable tool for exposure assessment of thiosalts to aquatic organisms.

## 5.3 Hazard indices from thiosalts

The thiosalt concentrations present in mining effluents from the case study (Table 9) were much lower than the maximum allowable concentrations determined by the bootstrapping technique. The Hazard Indices calculated are presented in Table 13. The results discussed are for a worst-case scenario considering no dilution of the effluent in the receiving waters. However, incorporating dilution factors in accordance with Environment Canada (2000), the results for the acidity of the receiving water are shown in Table 14.

**Table 13: Hazard indices**

| Target species | TTC of thiosulfate (mg/L) | TTC of tetrathionate (mg/L) | Exposed concentration (mg/L) | Hazard Index @ thiosulfate (Unitless) |
|---|---|---|---|---|
| Oncorhynchus mykiss | 552.86 | 745.88 | 54.56 | 0.098 |
| Daphnia magna | 552.86 | 745.88 | 54.56 | 0.098 |

**Table 14: Effect of dilution factors on effluent pH**

| Dilution Factor | Thiosulfate (mg/L) | Trithionate (mg/L) | Tetrathionate (mg/L) | Duration in hours for pH to reach 5.5 | 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 |

## 5.4 Conclusions

In the present study, a novel methodology for ecological risk assessment of thiosalts is developed. The bootstrapping technique is adopted and applied to determine the toxicity threshold concentration of thiosalts species. This technique helps to generate important missing toxicity data, thereby decreasing the uncertainty in the final assessment. A new exposure assessment methodology based on the relationship between acid producing and

consuming pathways of thiosalts species is developed. The new methodology assists to estimate the final concentration of thiosalts species in the water body; which in turn predicts the resulted pH. The results from exposure model matched with the observed results after considering dilution effects in the stream. 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 the 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 very toxic. However, their presence develops an indirect toxic environment for ecological species.

## 5.5 Novelty in this research

1. The available toxicity data of thiosalts is very limited. Comparing these toxicity data with the exposed thiosalt concentration may lead to a very conservative risk assessment approach. Using a target concentration that affects no more than 5 percentile of the species leads to more apt assessment. However, data on the concentration affecting 5 percentile is not available in the literature. The bootstrap technique is used to randomly generate missing toxicity data based on limited available data.
2. An aquatic exposure model is developed linking fluctuating pH of the water body with risk to its aquatic species. The exposure model estimates the residual thiosalt concentrations and pH for an exposure period under given conditions of temperature and initial pH. Using the maximum allowable decrease in pH, the

concentrations of thiosalts are back calculated and a thiosalt effluent standard is established.

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# Chapter 6: Appendix

## 6.1 Check for convergence of data

Two data sets are generated as mentioned in section 3.2.4, 'simultion generation' and also in Figure 6. Both the simulations are fitted with logistic, normal and weibull distributions as shown in the Figures A.1 – A.6.

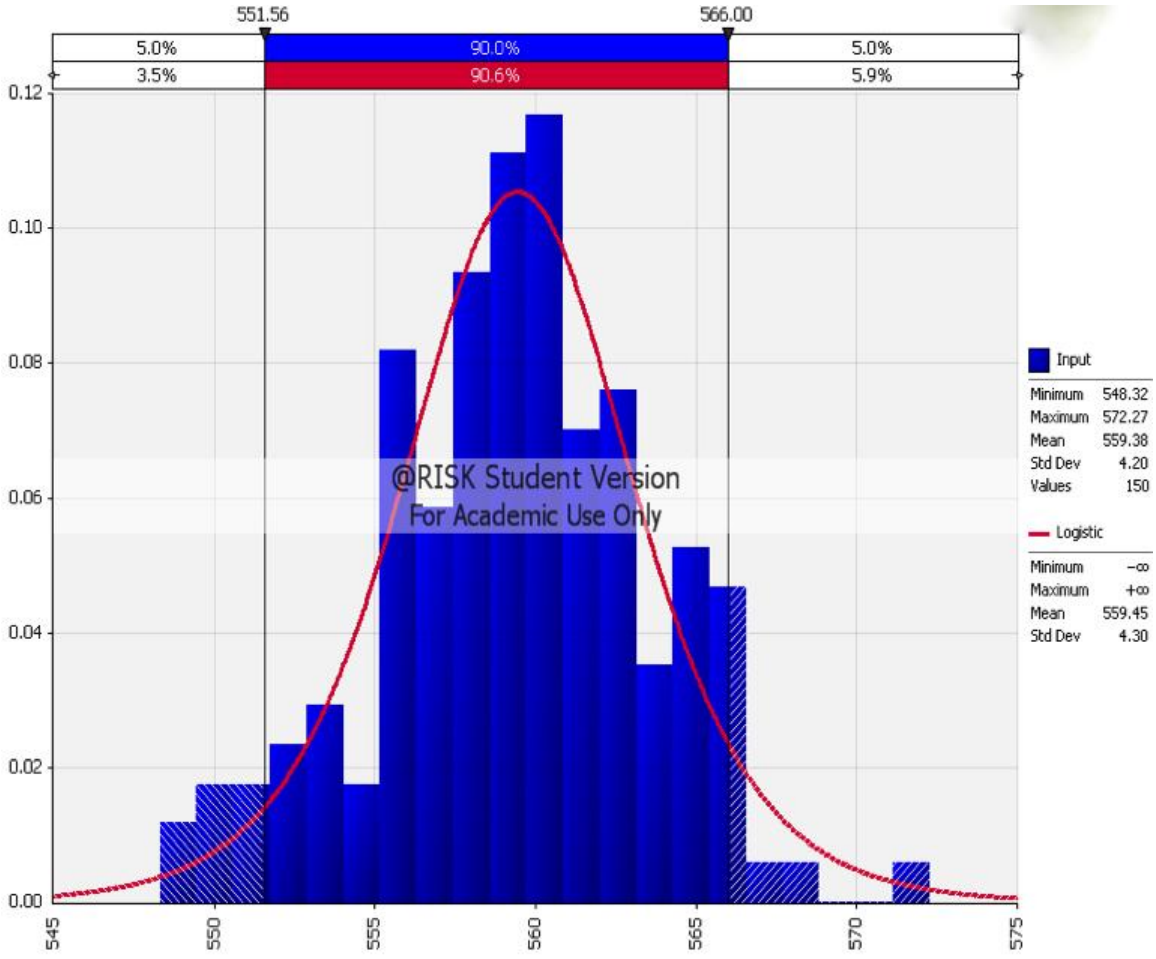


Figure A.1: Logistic distribution fitted to dataset 1/simulation 1

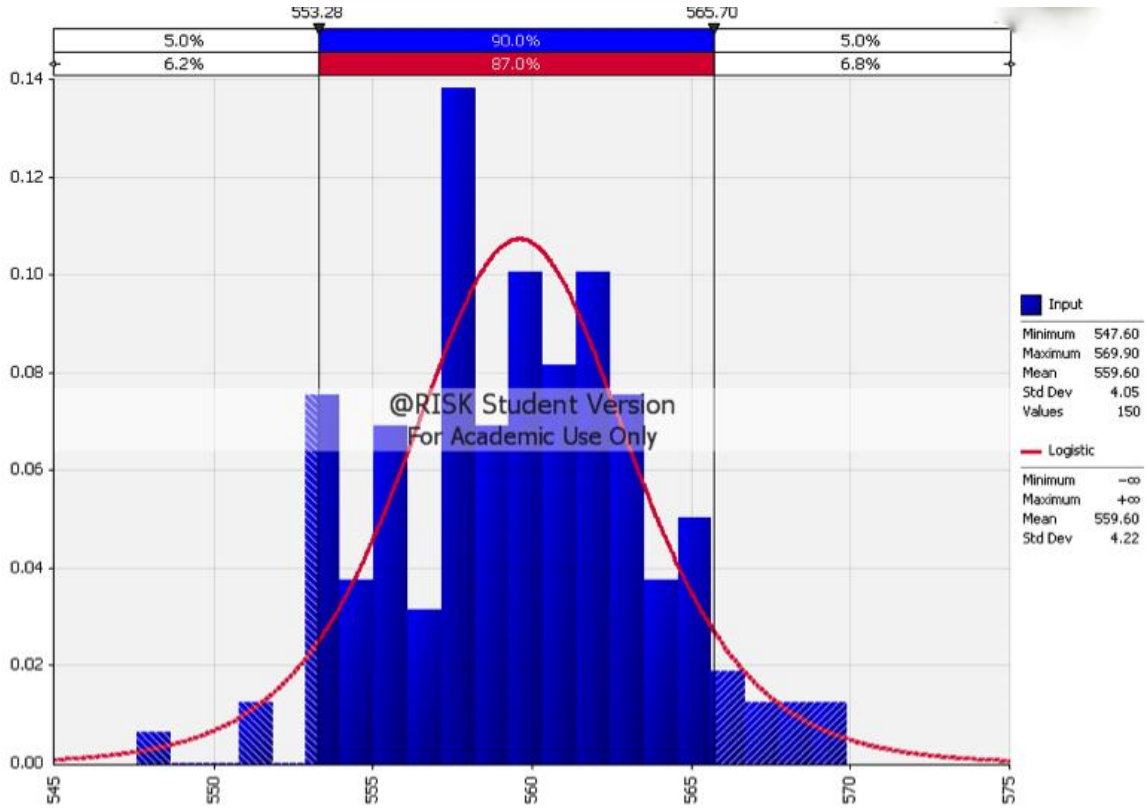


Figure A.2: Logistic distribution fitted to dataset 2/simulation 2

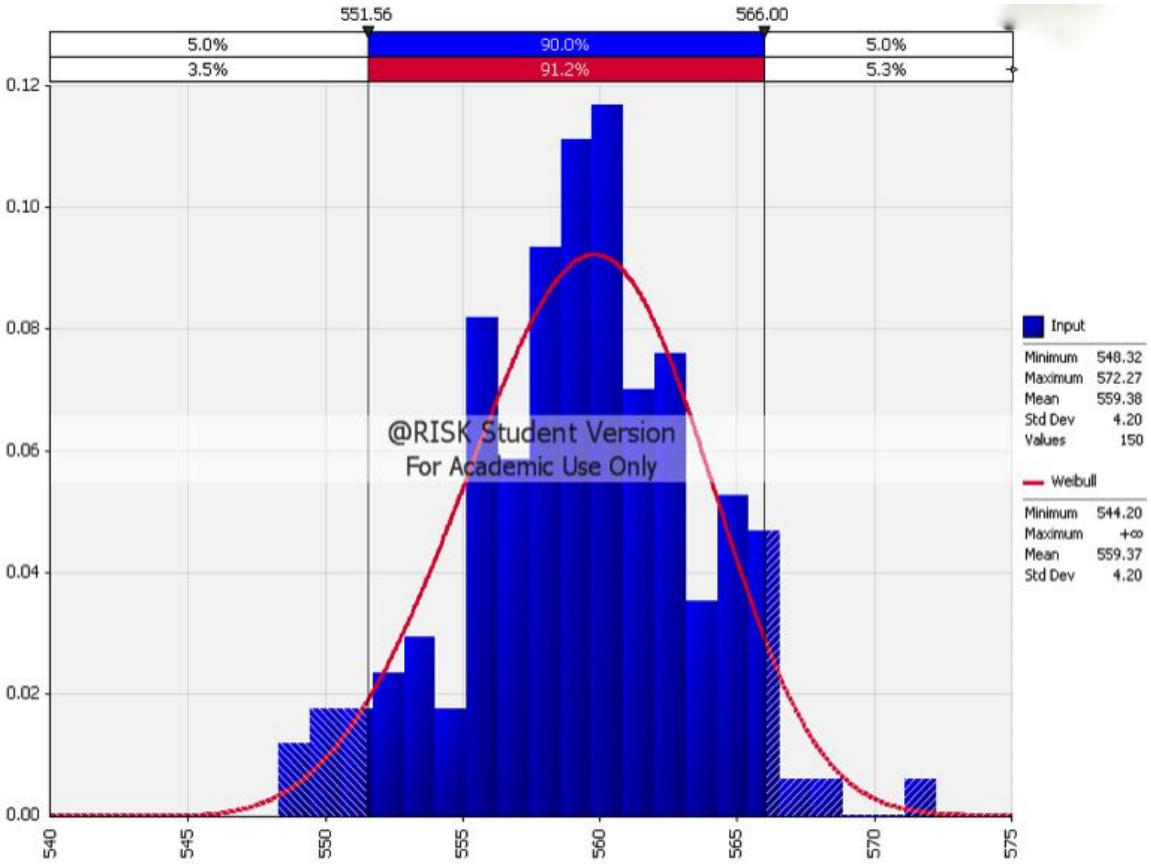


Figure A.3: Weibull distribution fitted to dataset 1/simulation 1

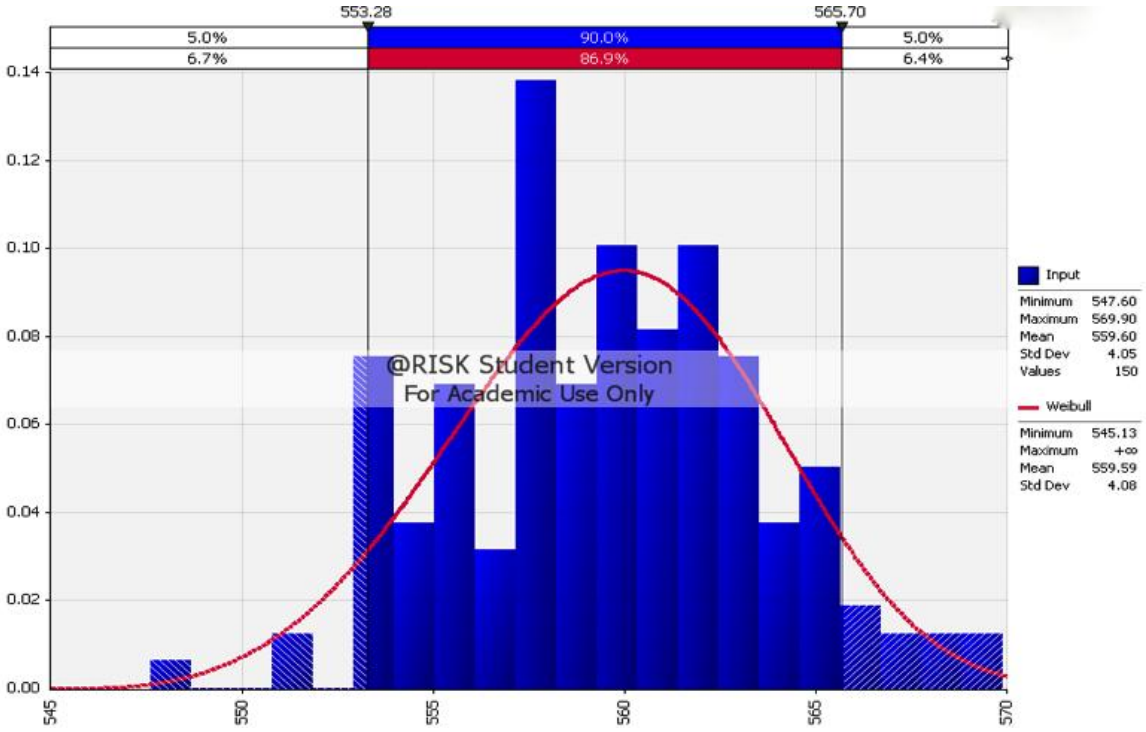


Figure A.4: Weibull distribution fitted to dataset 2/simulation 2

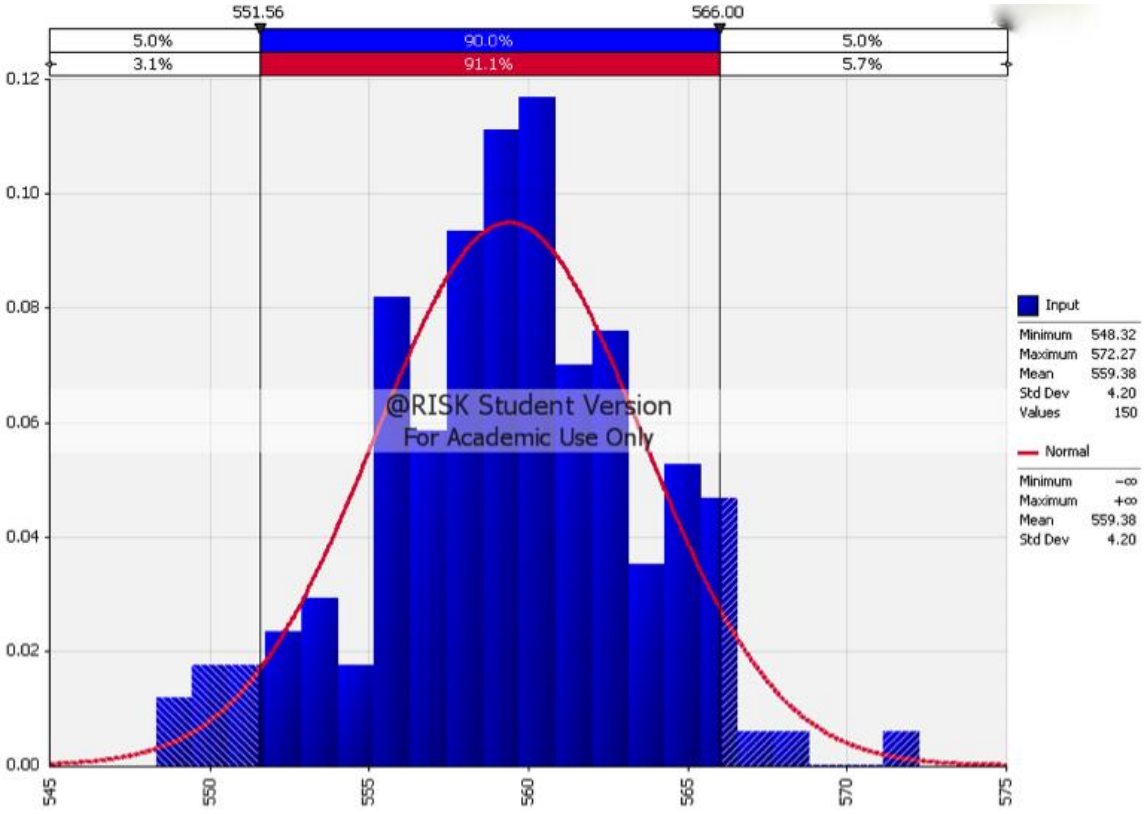


Figure A.5: Normal distribution fitted to dataset 1/simulation 1

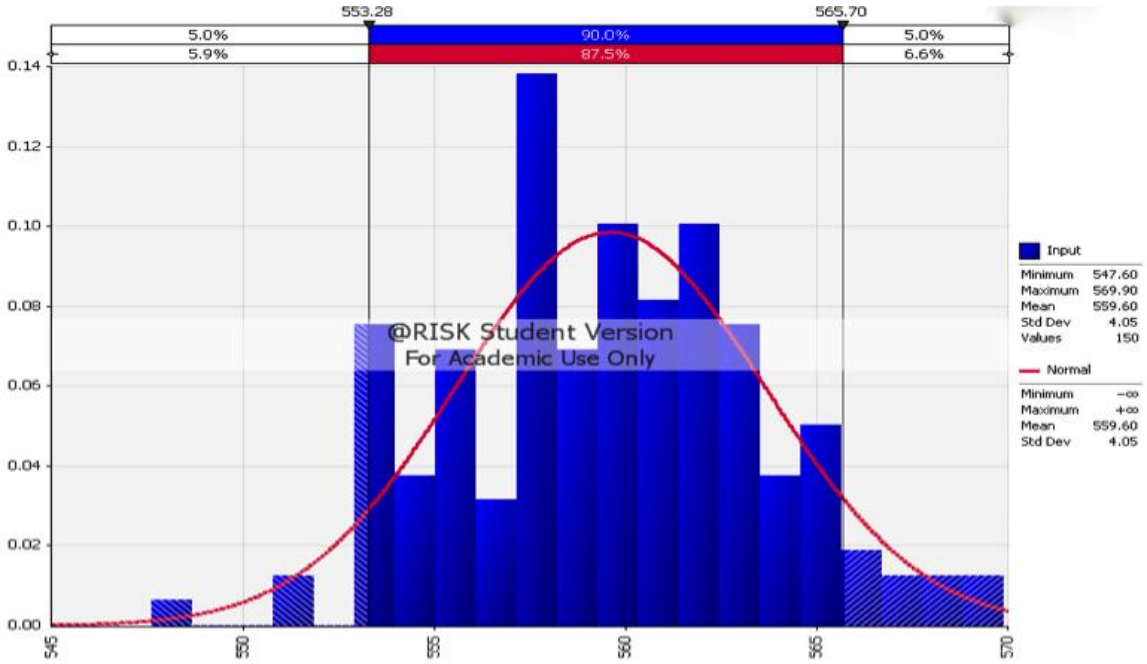


Figure A.6: Normal distribution fitted to dataset 2/simulation 2

Two distributions from a randomly selected data are said to be converged when the distribution parameters lie in close proximity. Proof of convergence for the randomly generated toxicity data in this research is presented in Table A.1.

Table A.1: Check for convergence

| **Distribution** | **Simulation 1 (parameters)** | **Simulation 2 (parameters)** |
|---|---|---|
| Weibull | 4.05 (**β**), 16.7 (**θ**) | 3.98 (**β**), 15.964 (**θ**) |
| Normal | 559.37(**μ**), 4.20(s) | 559.60(**μ**), 4.04 (s) |
| Logistic | 559.43(**μ**), 2.37 (s) | 559.60 (**μ**),2.328 (s) |

## 6.2 Determining 5-percentile concentrations

Thiosulfate toxicity data generated using the bootstrapping technique is fitted to normal, logistic and weibull distributions. The R square values for various distributions were already mentioned in section 5.1. The various distributions and SSDs developed for the thiosulfate toxicity data are presented in Figures A. 7 to A. 12; note that the all the distributions fit well with the toxicity data.

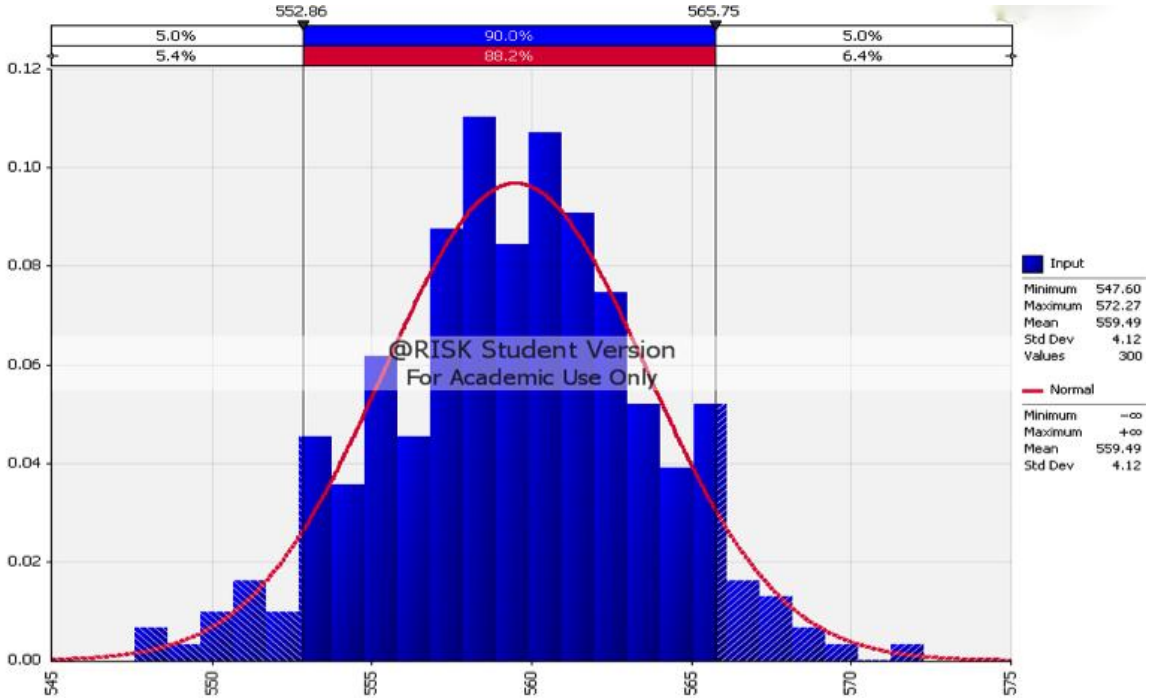


Figure A. 7: Normal distribution fitted to the generated thiosulfate toxicity data

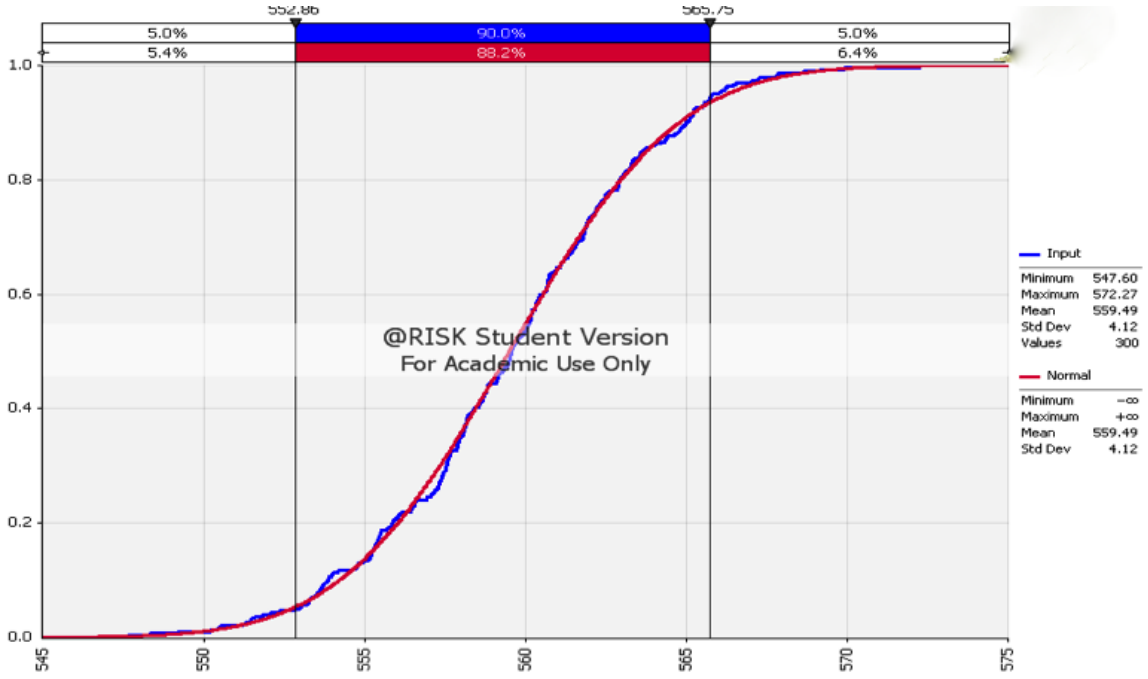


Figure A. 8: SSD of the generated thiosulfate toxicity data using normal distribution

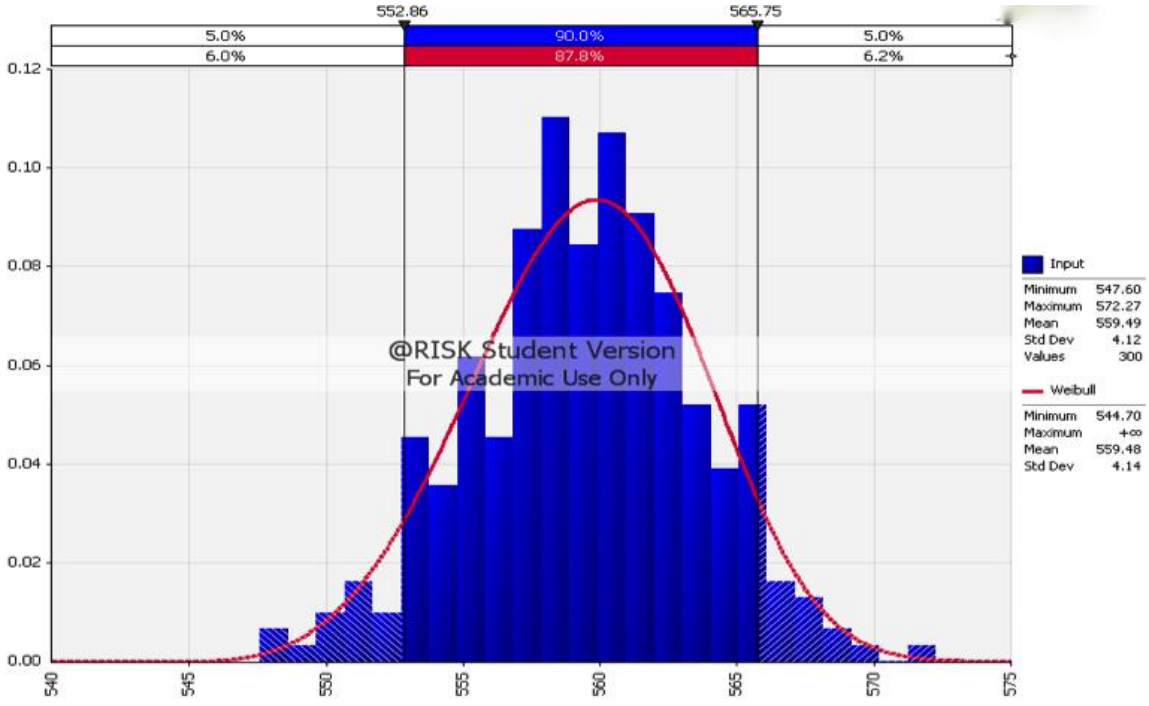


Figure A. 9: Weibull distribution fitted to the generated thiosulfate toxicity data

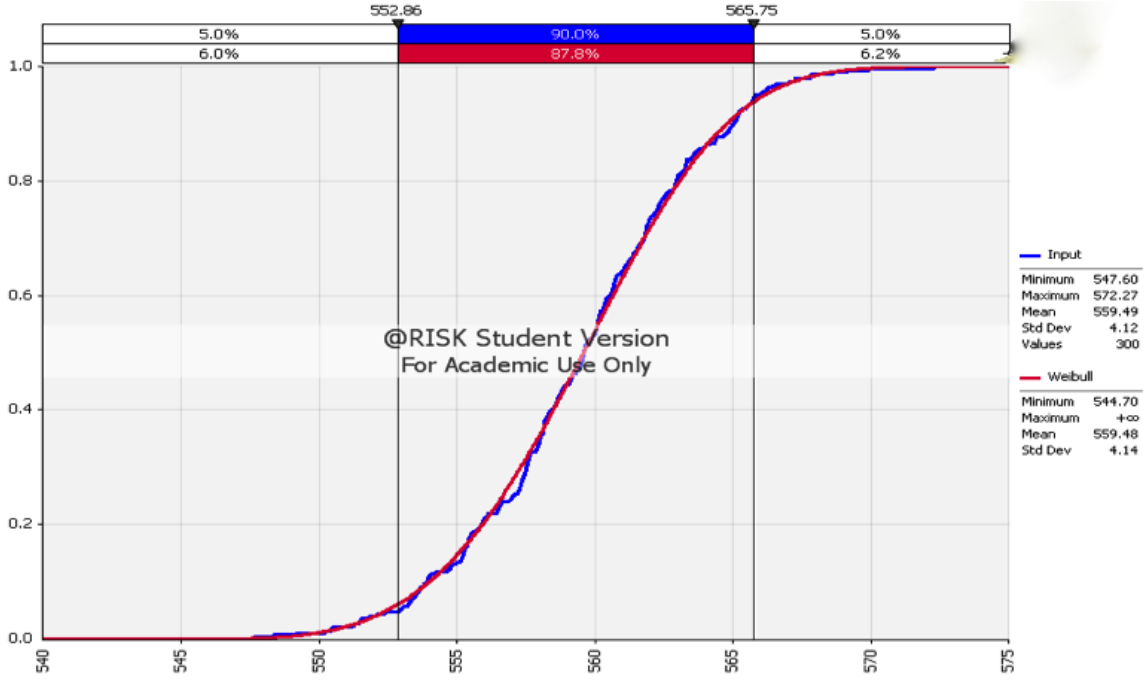


Figure A. 10: SSD of the generated thiosulfate toxicity data using weibull distribution

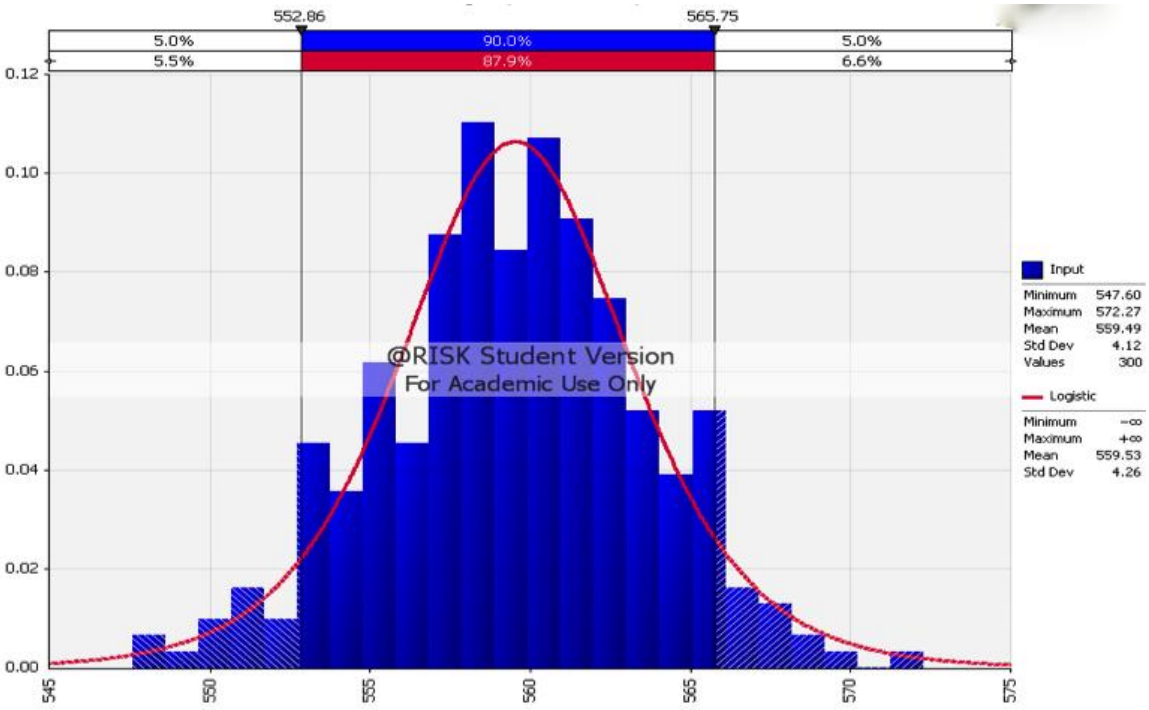


Figure A. 11: Logistic distribution fitted to the generated thiosulfate toxicity data

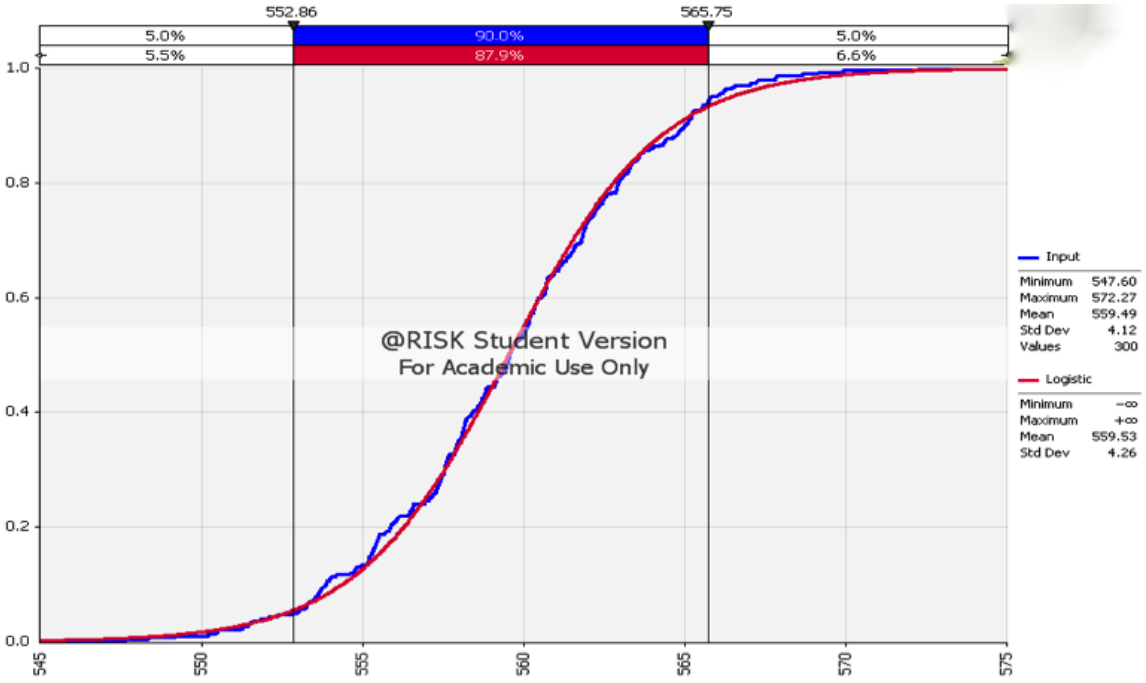


Figure A. 12: SSD of the generated thiosulfate toxicity data using logistic distribution