Ammonium Thiosulfate (ATS)

$(NH_4)_2S_2O_3$
CAS Registry Number 7783-18-8 (Solution)
CAS Registry Number 7664-41-7 (Anhydrous)
PC Code: 080103

Thiosulfate   Ammonium Counter Cation
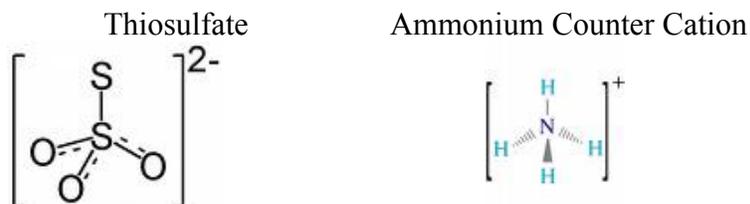
End-Use Product:	Oxalis/Spurge X
EPA Reg.No.	9499-1
Formulation:	Concentrate (55.5% ATS)
Uses:	Herbicide to control spurge and oxalis in dichondra lawns

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Date: 13 September 2007

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I.   Executive Summary

A.   Nature of the Chemical Stressor

Ammonium thiosulfate (CAS No. 7783-18-8), an inorganic compound, is the chemical stressor considered in this assessment. Ammonium thiosulfate dissociates completely in water. The dissociation products are the thiosulfate anion and its ammonium counter cation. This is the first step in the behavior of thiosulfate in the environment. Both thiosulfate and ammonium are considered in this risk assessment.

Thiosulfate is a metastable, moderately reducing oxyanion of sulfur. Chemical reactions (redox reactions) of thiosulfate generate chemical species of sulfur that differ in their oxidation state. The ammonium counter cation in ammonium thiosulfate is a source of "ammoniacal nitrogen." Its major chemical reaction in the environment is oxidation to nitrate nitrogen, which is known as nitrification. Ammonium also exists in equilibrium with ammonia gas.

Ammonium thiosulfate is registered to kill oxalis and spurge in dichondra lawns. The only end-use product is "Oxalis/Spurge X, Concentrate Foliar Spray" (USEPA Reg. No. 9499-1; Approval date of last label 9/30/2003). This product is a concentrate foliar spray containing 55.0% ammonium thiosulfate. Ammonium thiosulfate is also used as a fertilizer.

B.   Potential Risks to Non-target Organisms

This ecological risk assessment considers the limited use of ammonium thiosulfate as an herbicide on dichondra lawns in residential/homeowner settings in California. This assessment is qualitative in nature; that is, the risk quotient approach is not utilized. The nature of ammonium thiosulfate and its predicted behavior in the environment make it difficult to provide meaningful quantitative exposure estimates for aquatic and terrestrial systems. Since ammonium thiosulfate is being used as an herbicide, there is a possibility that non-target plants may be at risk; however, given that it is only used in residential/homeowner settings, the potential for adverse effects to non-target plants seems highly unlikely. Based on this qualitative assessment for the pesticidal use of ammonium thiosulfate, risk to non-target aquatic and terrestrial organisms (including Federally-listed species) is presumed to be negligible.

C.   Environmental Fate and Exposure

The thiosulfate anion is only stable in neutral or alkaline media. It is unstable in acid media. Thiosulfate acid cannot be generated by acidification in aqueous solutions of its salts because it decomposes to sulfuric acid and a mixture of elemental sulfur, hydrogen sulfide, polysulfide, and sulfur dioxide. In aqueous media, thiosulfate irreversibly disproportionates to sulfide and sulfate.

The chemistry of sulfur in soils (and in water) is complex because of its many oxidation states of sulfur, which not only involves oxysulfur species, but also species containing only sulfur (e.g., elemental sulfur, sulfide). The predominance of a given species is dependent on pH and redox potential of the media, as well as by the type of bacteria present in soils. The terminal, thermodynamically-favored reaction product of thiosulfate is sulfate, except in highly reduced soils. As an anion, sulfate is expected to be mobile in soils. Sulfate is ubiquitous and is present in most natural waters, where it is considered a permanent solute. Sources of sulfate in natural water are dissolution of naturally occurring sulfate salts, runoff of oxidized sulfide ores, acid rain deposition, industrial waste, and fertilizers. No aquatic exposure modeling was performed for sulfate, and risk was discussed qualitatively.

For the ammonium counter cation, its major chemical reaction in the environment is oxidation to nitrate. Ammonium is expected to be in equilibrium with ammonia gas in the soil air voids. The volatilization of ammonia is dependent on temperature and pH of the media and increase with increasing temperature and pH. As a cation, ammonium can adsorb to soil colloid or organic matter through electrostatic cation exchange. For ammonia, a screening-level aquatic exposure assessment using the GENEEC model (Version 2.0) was conducted to estimate surface water concentrations of ammonium from use of ammonium thiosulfate as a pesticide.

D.   Ecological Effects

There are no acceptable registrant-submitted ecotoxicity data available for fish, aquatic invertebrates, aquatic plants, birds, terrestrial invertebrates, or terrestrial plants for consideration in this risk assessment for ammonium thiosulfate. The aquatic assessment relies on the USEPA ambient water quality criteria for ammonia (1999 Update). The terrestrial assessment is qualitative in nature, but it does consider mammalian toxicity data provided by the Health Effects Division. Ammonium thiosulfate is practically non-toxic to mammals on an acute oral basis.

E.   Uncertainties and Data Gaps

No acceptable environmental fate or ecotoxicity guideline studies are available for ammonium thiosulfate. However, given the nature of the chemical and its predicted behavior in the environment, this was not an impediment to the risk assessment. At this time, the EFED is not requesting any environmental fate or ecotoxicity studies to be submitted for ammonium thiosulfate.

II.   Problem Formulation

The purpose of this problem formulation is to provide the foundation for the ecological risk assessment being conducted for ammonium thiosulfate (ATS). As such, it articulates the purpose and objectives of the risk assessment, evaluates the nature of the problem, and provides a plan for analyzing the data and characterizing the risk (EPA, 1998).

A.   Nature of Regulatory Action

This ecological risk assessment is in support of the Reregistration Eligibility Decision (RED) for ammonium thiosulfate use as an herbicide. There is one end-use product considered in this assessment, Oxalis/Spurge (55.0% active ingredient ammonium thiosulfate), which is used to kill oxalis and spurge in dichondra lawns in California.

B.   Stressor Source and Distribution

1.   Nature of the Chemical Stressor

Ammonium thiosulfate (CAS No. 7783-18-8) is the chemical stressor considered in this assessment. Ammonium thiosulfate is an inorganic compound. Both ammonium and thiosulfate are considered in the assessment.

Ammonium thiosulfate is not listed as a High Production Volume (HPV) chemical or in the Toxic Release Inventory (TRI), but it is listed in the Toxic Substance Control Act (TSCA) (8b) Inventory of Chemical Substances (Substance of Commerce).

2.   Identification of the Chemical Stressor; Physical and Chemical Properties

The first step in the environmental fate of ammonium thiosulfate will be dissociation into ammonium and thiosulfate. Thiosulfate is one of the oxyanions of sulfur. The chemical reactions of thiosulfate in the environment are mostly controlled by the redox potential of the media, as well as pH. The mode of action of ammonium thiosulfate as an herbicide to control oxalis and spurge is presumably via fertilizer burn (salt injury).

Identification and information on ammonium thiosulfate/thiosulfate anion is summarized in Table II-1. Figure II.1 presents the ammonium counter cation and its equilibrium with ammonia. Sulfur compounds have an extensive and often ambiguous nomenclature, and the chemical names for sulfur chemical species relevant to thiosulfate are summarized in **Appendix A**.

Table II.1   Chemical Identification and General Information on Ammonium Thiosulfate (ATS) and the Thiosulfate anion

| Type of Information	Information
Common Name(s)	Ammonium Thiosulfate; ATS
Chemical Name-Synonyms	Ammonium Thiosulfate (sometimes the $S_2O_3^{2-}$ anion is referred as thiosulfites or hyposulfites) Thiosulfuric acid, diammonium salt Diammonium Thiosulfate Ammonium thiosulfate solution (60% or less) As per US EPA Substance Registry System
CAS Registry Number EPA PC Code No.	7783-18-8 (Solution) 7664-41-7 (Anhydrous) 080103
Empirical Formula	$(NH_4)_2S_2O_3$
Molecular Weight	148.21 (Anhydrous)
Molecular Structure of the anion	 Note the S-S bond (disulfide linkage) Note: The purple symbol stands for Na^+ or K+ cations. See below for ammonium Crystal Structure: S. T. TENG, H. FUESS AND J. W. BATS. 1979. *Acta Cryst.* B35, 1682-1684 The structure consists of NH$_4$ and S$_2$O$_3$ tetrahedra interconnected by hydrogen bonds. All but two H atoms were located by different methods. One of the NH$_4$ groups is possibly disordered at room temperature.
Oxidation state of sulfur in thiosulfate Smiles Notation	The two different S atoms in thiosulfate have charge densities corresponding to V and -I oxidation states [NH4+].[S-]S(=O)(=O)[O-].[NH4+]
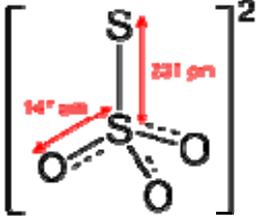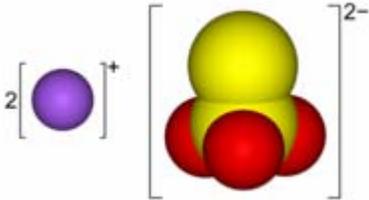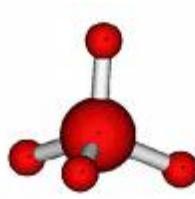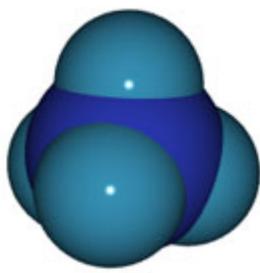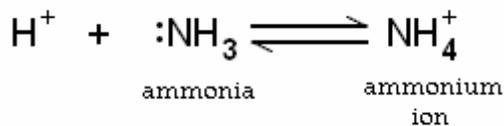
Ammonium ion

Figure II.1   Equilibrium Between Ammonium Cation and Ammonia
$NH_3(g) + H^+ \leftrightarrow [NH_4^+]$; Log $K^o=11.04$, where K^o is the equilibrium constant expressed in terms of activity.

The ammonium ion has a tetrahedral structure. The formal oxidation state of nitrogen in ammonia and ammonium cation is –III. Ammonia-based fertilizers serve as a source of nitrogen.

Physical and Chemical Properties

The physical and chemical properties of ammonium thiosulfate are shown in **Table II.2**.

Table II.2 Physical and Chemical Properties of Ammonium Thiosulfate

Property	Value
Melting Point Boiling Point	Decomposes at 160 C
Vapor Pressure Henry's Law Constant	Reported as 0 mmHg at 25C Not applicable
Solubility in Water (Thiosulfate is not stable under acidic pHs)	103.3 g/100 ml water @ 100 deg. C. Complete dissociation
Solubility in Non-aqueous Solvents	Easily soluble in cold water, hot water. Slightly soluble in acetone. Insoluble in diethyl ether. Insoluble in alcohol Unstable in acid pH

Behavior of Ammonium Thiosulfate, Thiosulfate and Ammonium in the Environment

Ammonium thiosulfate dissociates completely in water. The dissociation products are the thiosulfate anion and the ammonium cation. This is the first step in the behavior of thiosulfate in the environment.

Thiosulfate is a metastable, moderately reducing oxyanion of sulfur. Chemical reactions (redox reactions) of thiosulfate generate chemical species of sulfur that differ in their oxidation state.

The main types of chemical reactions of thiosulfate relevant in the environment are:

1   Disproportionation (chemical and microbially mediated)
2   Chemical and microbially mediated redox reactions
3   Complexation with metal ions
4   Bimolecular nucleophilic substitution reactions (SN2 mechanisms); dihalogenation

The ammonium counter cation in ammonium thiosulfate is a source of "ammoniacal nitrogen". Its major chemical reaction in the environment is oxidation to nitrate nitrogen, that is $N(-III) \rightarrow N(V)$, which is known as nitrification.

3.   Overview of Pesticide Usage

Ammonium thiosulfate (ATS) is registered to kill oxalis and spurge in dichondra lawns. The only end-use product is "Oxalis/Spurge X, Concentrate Foliar Spray" (USEPA Reg. No. 9499-1; Approval date of last label 9/30/2003). This product is a concentrate foliar spray containing 55.0% ATS.

The major use of ammonium thiosulfate is not as a pesticide, but rather as a fertilizer (soil nutrient and amendment). In 2005, over 700 million pounds (350,580 short tons) of ammonium thiosulfate was used as a fertilizer (USDA/NASS). Compared to its use as a pesticide, less than 6500 pounds of ammonium thiosulfate is used annually.

In minerals processing, ATS is increasingly used as a leaching agent for gold and silver extraction from auriferous ores. It is increasingly used as an alternative for conventional cyanide leaching.

C.   Receptors

1.   Aquatic and Terrestrial Effects

The receptor is the biological entity that is exposed to the stressor (EPA, 1998). In general, the receptors considered in ecological risk assessments for pesticides are aquatic organisms, such as fish (surrogate for aquatic-phase amphibians), invertebrates, and plants (non-vascular and vascular), and terrestrial organisms, such as birds (surrogate for reptiles and terrestrial-phase amphibians), mammals, invertebrates, and plants.

D.   Analysis Plan

Available Data

No environmental fate guideline studies (Subdivision N) are available for ammonium thiosulfate; thus, the environmental fate and exposure assessment will be based on open literature data. EPISuite Version 3.2, a tool commonly used in the ecological risk assessment process when environmental fate data are unavailable, cannot be used to estimate the environmental fate and transport of ammonium thiosulfate because it is not an appropriate model for inorganic chemicals.

There are no acceptable registrant-submitted ecotoxicity data available for fish, aquatic invertebrates, aquatic plants, birds, terrestrial invertebrates, or terrestrial plants for consideration in this risk assessment for ammonium thiosulfate. The aquatic assessment will rely on the U.S.E.P.A. ambient water quality criteria for ammonia (1999 Update).[1] The terrestrial assessment will rely on the mammalian toxicity data provided by the Health Effects Division.

Aquatic Risk

For sulfate, the most likely sulfur species in water, the Agency has established a Secondary Maximum Contaminant Level (SMCL) of 250 mg/L. It is highly unlikely that the aquatic exposures of sulfate would approach that level as a result of its limited use as an herbicide to control spurge and oxalis in dichondra lawns. Therefore, no aquatic exposure modeling will be performed for sulfate.

For ammonium, aquatic exposure estimates will be generated using the Tier I GENEEC model (GENeric Estimated Exposure Concentrations, Version 2.0). Assumptions will be made to select the environmental fate input parameters. Further, since the label does not specify an application rate in terms of pounds of ATS per acre, assumptions must be made to estimate the application rates in terms of pounds per acre. Given that the product is applied in residential/homeowner settings, assumptions will be made to estimate the percent of treated area, which will be used to correct the model-generated aquatic exposure estimates. It is recognized that these assumptions will result in highly conservative aquatic exposure estimates.

Given the multiple assumptions and the complexity of the sulfur and nitrogen systems (multiple chemical species in different oxidation states), the aquatic exposure assessment carries a very high degree of uncertainty. Despite this uncertainty, the model estimates will be compared to the U.S.E.P.A. ambient water quality criteria for ammonia to determine if there is a potential risk to aquatic animals as a result of the pesticidal use of ammonium thiosulfate.

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[1] http://www.epa.gov/waterscience/criteria/ammonia/99update.pdf

Terrestrial Risk

Given the expected behavior of ammonium thiosulfate in the environment, it is inappropriate to use the Tier 1 T-REX model (Version 1.3.1) to estimate terrestrial dietary exposures. The potential risk of ammonium thiosulfate (when used as a pesticide) to terrestrial organisms will be discussed qualitatively.

III.   Analysis

A.   Use Characterization

Ammonium thiosulfate (CAS No. 7783-18-8) is the chemical stressor considered in this assessment. The end-use product, Oxalis/Spurge X (55.0% active ingredient ammonium thiosulfate), is used to kill oxalis and spurge in dichondra lawns in California.

Dichondra (*Dichondra repens;* kidney weed dichondra) is a low growing, creeping perennial that spreads by underground runners. The leaves are kidney-shaped and dark green in color. The overall appearance is that of a flat cover. It has a neat rich velvety appearance throughout the year and needs no mowing.

According to the product label, the dichondra lawn is to be watered the day before applying the ATS product, but the foliage must be dry at the time of application. The range of temperature at which Oxalis/Spurge X is to be applied is between 72 and 80° F (22 to 26.7° C). Above 80° F., it could cause severe, temporary damage to the dichondra foliage. The product can be used on young dichondra.

The label also indicates that the product can be used in bladegrass lawns. Bladegrass can tolerate temperatures up to 95° F (35° C), but it is not to be used until a minimum of three mowings. The product should not be applied immediately after mowing. Weeds should be killed before they go to seed.

The product is claimed to work best in sunlight.

The label recommends mixing 4 oz/gallon of water per 100 feet of area to be treated. It is recommended the addition of a "good spreader-sticker" and use of pressure type tank sprayer because hose-end garden sprayers and water cans are ineffective. Leaves must be thoroughly saturated. According to the label, application can be repeated every 10 days or two weeks, but the number of applications per year (maximum total application rate) is not specified in the label.

B.   Exposure Characterization

1.   Environmental Fate and Transport

The first step in the environmental fate of ammonium thiosulfate, $(NH_4)_2S_2O_3$, will be dissociation [i.e., $(NH_4)_2S_2O_3 \leftrightarrow 2\ NH_4^+ + S_2O_3^{2-}$]. Because $(NH_4)_2S_2O_3$ is a salt, dissociation will be controlled by the water solubility of $(NH_4)_2S_2O_3$ (i.e., 103.3 g/100

mls of H_2O @ $100^{\circ}C$ or 1,033,000 mg/L; 1,033 g/L). Concentrations of $(NH_4)_2S_2O_3$ below the water solubility will cause complete dissociation to $2NH_4^+$ and $S_2O_3^{2-}$. As a first approximation, $(NH_4)_2S_2O_3$ concentrations in soil solution based on the maximum application rate and different depths of soil incorporation are not expected to exceed the water solubility of $(NH_4)_2S_2O_3$ (Table II.2). Therefore, $(NH_4)_2S_2O_3$ is not expected to exist as the $(NH_4)_2S_2O_3$ salt (i.e., as a discrete, non-dissociated entity) when applied because it will completely dissociate to $2 NH_4^+$ and $S_2O_3^{2-}$ ions.

The thiosulfate anion is only stable in neutral or alkaline media. It is unstable in acid media. Thiosulfate acid cannot be generated by acidification in aqueous solutions of its salts because it decomposes to sulfuric acid and a mixture of elemental sulfur, hydrogen sulfide, polysulfide, and sulfur dioxide. In aqueous media, thiosulfate irreversibly disproportionates to sulfide and sulfate[2]. The rate of disproportionation is pH-dependent, with the rate of disproportionation being directly proportional to the hydrogen ion concentration (i.e, with decreasing pH). Sulfite is a transient intermediate in this reaction Another reaction intermediate of thiosulfate is tetrathionate $(S_4O_6^{2-})$, which undergoes further reactions to sulfate, the thermodynamically stable sulfur species.

Chemical and microbial reactions are involved in the transformation of thiosulfate (and of other sulfur species) in the environment. Both sulfide and thiosulfate are the most abundant reduced species of sulfur in the environment and both are converted to sulfate in the oxidative half of the sulfur cycle.

Redox and disproportionation reactions of thiosulfate (chemical; bacterial) are involved in the sulfur cycle in the environment. For example, disproportionation has been identified as an important pathway in bacterial energy metabolism in anoxic marine sediments. In the environment, sulfur (elemental sulfur, S°) is cycled between S(VI)-Sulfate and S(-II)-sulfide soluble and insoluble sulfur species, such as thiosulfate. Because thiosulfate, sulfite, and sulfate are chemical species relevant to the natural sulfur cycling, it would be difficult to distinguish between these reactions from those arising from the addition of thiosulfate as an herbicide. In any case, added thiosulfate would be incorporated into the natural sulfur cycle, where the thermodynamically-stable end product is sulfate.

Among the types of enzymes involved in the oxidation-reduction of thiosulfate and other sulfur species are rhodanese (thiosulfate cleaving) and sulfite oxidase (plus electron transfer). Several *Thiobacillus* species are known to be involved in the formation or transformation of thiosulfate[3]. The enzymatic reaction products are dependent on the

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[2] Disproportionation reactions apply to reactions in which an element in one of the reaction products is in a lower oxidation state and the other is of a higher oxidation than the oxidation state of the parent species. For example, $2U(V) \rightarrow U(IV) + U(VI)$ in water.

[3] Another important *Thiobacillus* species is *Thiobacillus ferroxidans*. It not only oxidizes sulfide to sulfate, but above pH 3 it also oxidizes Fe(II) to Fe(III), mostly from pyrite and/or marcasite. As the pH increase, Fe(III) generates a series of hydrolytic reactions hydroxyoxides, with the concomitant formation of hydronium ions (H_3O^+). These reactions are responsible for acid mine drainage, which has negative impact on the environment. *Thiobacillus thiooxidans* oxidizes sulfur only.

conditions of the media (e.g., presence of absence of oxygen). An important *Thiobacillus* species involved in the oxidation of thiosulfate is *Thiobacillus thiooxidans*.

Besides enzymatic reactions, thiosulfate can coordinate with several metals (i.e., thiosulfate is a ligand; thiosulfate complexes). These metal complexes serve as catalysts to the oxidation of thiosulfate (e.g., Co(III)-thiosulfate complexes). In leaching of gold from auriferous ores using ammonium thiosulfate, Cu(II)-amine complexes can catalyze the undesirable conversion of thiosulfate (oxidation) to polythionates instead of the desirable of thiosulfate with gold and prevent the desirable complexation of thiosulfate with gold. The photoreduction of thiosulfate in semiconductor dispersions (TiO_2) reduce the efficiency of thiosulfate conversion to sulfide and sulfite/sulfate. However, the extent of complexation and surface reactions of thiosulfate in the environment is not well documented.

In summary, the chemistry of sulfur in soils (and in water) is complex because of its many oxidation states, which not only involve oxysulfur species, but also species containing only sulfur. The predominance of a given species is dependent on pH and redox potential of the media, as well as by the type of bacteria present in soils (see the "Ammonium Thiosulfate Behavior in Soils" section). The terminal, thermodynamically favored reaction product of thiosulfate is sulfate, except in highly reduced soils. Sulfate would form insoluble compounds by precipitation with cations such as Ba^{2+} and Ca^{2+} if the concentrations of sulfate and cation exceed the solubility product. Other sulfur species formed from thiosulfate, such as sulfide and polysulfide(s)[4], may be transient and unstable products under most environmental conditions.

In addition, oxidation of thiosulfate to sulfate is involved in the degradation of volatile, halogenated hydrocarbons fumigants by dehalogenation through a bimolecular nucleophilic substitution (SN2) mechanism. Thiosulfate dehalogenation reactions have been reported for methyl bromide; methyl iodide, and chloroacetanilide herbicides, for example:

$$CH_3Br + S_2O_3{}^{2-} \rightarrow CH_3S_2O_3 + Br^-$$
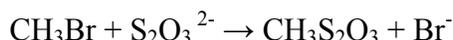
Although the chemical reactions of thiosulfate are independent of the nature of the counter cation, the use of ATS as a sulfur and nitrogen fertilizer/soil amendment appears to present several advantages. Both thiosulfate and its intermediate tetrathionate have been found to inhibit nitrification (oxidation reaction) of ammonia and hydrolysis of urea, thus increasing nitrogen efficiency.

For the ammonium counter cation, its major chemical reaction in the environment is oxidation to nitrate. Ammonium is expected to be in equilibrium with ammonia gas in the soil air voids. The volatilization of ammonia is dependent on temperature and pH of the

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[4] S^{2-} may polymerize to polysulfides ($S_n{}^{2-}$). In aqueous media, the polysulfide with the highest number of sulfurs is $S_4{}^{2-}$. Polysulfide can also oxidize to oxyanions of sulfur (oxic condition) or breakdown polysulfides with a lower number of sulfurs, including S^{2-}.

media and increases with increasing temperature and pH. As a cation, ammonium can adsorb to soil colloid or organic matter through electrostatic cation exchange.

2. Aquatic Exposure Assessment

For sulfate, the most likely sulfur species in water, the Agency has established a Secondary Maximum Contaminant Level (non-enforceable), SMCL of 250 mg/L for drinking water. Ambient surface water concentrations of sulfate range from 0.1 to 12,000 mg/L (USGS NWIS, March 21, 2005). The maximum sulfate concentration was detected at sites in Montana, Wyoming, and Arizona. These sites were generally associated with mining activities. It is very unlikely the concentration of sulfate from ammonium thiosulfate would approach the maximum concentration sulfate in surface water or the SMCL as a result of its limited use as an herbicide to control spurge and oxalis in dichondra lawns. No aquatic exposure modeling will be performed for sulfate, and risk will be discussed qualitatively.

For ammonia, a screening-level aquatic exposure assessment using the GENEEC model (Version 2.0) was conducted to estimate surface water concentrations of ammonium from use of ammonium thiosulfate as a pesticide. Ammonium concentrations in surface water were used to estimate ammonia concentrations using chemical equilibria. Additionally, the Henry's constant was used to estimate the partitioning of ammonia between water and air. It is important to note that the GENEEC model is not designed to address environmental behavior of inorganic compounds. Therefore, the Tier I modeling required conservative assumptions for input parameters (**Table III.1**). This exposure assessment is conservative because it assumes 100% of ammonium from ammonium thiosulfate is available for runoff. Competing environmental fate processes for ammonium fixation (sorption on sediment and soil) and transformation (nitrification, denitrification, etc.) are not considered in the assessment.

The Tier 1 aquatic exposure modeling scenario assumes a 10-hectare field is 100% treated with ammonium thiosulfate at 74.31 lbs/A. Because the registered pesticidal use of ammonium thiosulfate is in residential/homeowner settings, it is highly conservative to assume 100% of the area is treated. According to the U.S. Census data, a typical house (residence) area is 1000 sq-foot (0.023 acre) located within a 0.25 acre plot. It is then assumed that the area in the plot not occupied by the house is a dichondra lawn and that all of the lawn is treated with ATS at the estimated application rate. With these assumptions, the percent treated area is 91%. This percent treated area correction is used as a refinement in the exposure assessment.

Table III.1. Environmental fate, physical/chemical, and use information input parameters selected GENEEC model to estimate ammonia concentrations in surface water resulting from ammonium thiosulfate application to dichondra lawns.

Input parameter	Value	Source	Comments
Hydrolysis half-life (days)	0	Assumed	pH-dependence of redox reactions are not taken into account
Photolysis in Water half-life (days)	0	Assumed	Photooxidation reactions not taken into account
Aerobic Soil Metabolism half-life (days)	0	Assumed	Microbial nitrification not considered
Anaerobic Aquatic Metabolism half-life (days)	0	Assumed	Microbial nitrification not considered
Solubility in Water, mg/L	1030	Open literature	This solubility is based on the solubility of ATS, which is mostly reported as "very soluble"; "totally soluble". The value used to run GENEEC is the reported solubility of ATS at 100°C. The solubility would be lower at 25°C.
K_{oc}	0	Assumed	Ammonium is known to sorb onto clay surfaces. For screening level purposes, a K_{oc} of zero was assumed
Method of Application	Ground, Broadcast	Assumed from the available label	Spot applications are probably more typical for this product
Frequency of Application	4 times per year	Assumed	The label does not specify an upper limit of number of applications per year
Interval between applications (days)	10	Shorter interval specified in the label	N/A
Application Rate, lb Ammonium/A	18.09	Estimated	The application rate for ammonium was based on an estimate of the application rate of ATS in terms of lb ATS/A

The GENEEC estimated environmental concentrations (EECs) for the ammonium cation are summarized in **Table III.2.** It includes uncorrected concentrations corrected for percent treated area. The concentrations appear to remain stable as a result of the environmental fate assumptions used for model input parameters. The GENEEC model output is provided in **Appendix B**.

Table III.2. Aquatic EECs (in mg/L) for Ammonium Cation in surface water (Source: Ammonium Thiosulfate; Uncorrected and corrected for percent of treated area, PTA, 0.91)

	Peak	Maximum 4 day-average	Maximum 21 day-average	Maximum 60 day-average	Maximum 90 day-average
Uncorrected	4.29	4.29	4.29	4.29	4.29
PTA Corrected	3.90	3.90	3.90	3.90	3.90

The relative concentration of the ammonium and ammonia gas depend on the pH of the media according to the equilibrium expression for the reaction,

$$NH_3(g) + H^+ \leftrightarrow [NH_4^+];$$
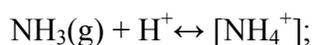
$$K^o = [NH_4^+]/ [NH_3(g)] [H^+],$$

where K^o is the equilibrium constant expressed in terms of activity

Assuming the activity coefficient (γ) to be 1 (i.e., ionic strength not considered), the equilibrium constant is then expressed in terms of molar concentration. That is, K^o becomes K and Log K^o=11.04 becomes Log K = 11.04 (Lindsay, 1979):

$$Log[NH_3(g)] = -11.04 + log[NH_4^+] + pH$$

This equation is used to estimate the relative concentrations of ammonium and ammonia gas in the receiving water body as controlled by the pH of the water. This equation indicates that theoretically, the concentration of dissolved ammonia gas increases with increasing pH.

Table III.3. GENEEC Environmental Exposure Concentration (EECs) of Ammonia in Surface Water (Corrected for percent of treated area, 0.91)

GENEEC EECS	Peak Ammonium EEC (mg/L)	Peak Ammonia EEC[1] (mg N/L)		
		pH 5	pH 7	pH 9
PCT Corrected	3.90	2.77E-6	2.79E-4	0.027

[1]Estimated using following equation: log(NH_3(g))=-11.04 + log (NH_4^+)+ pH

These are overall, upper bound concentrations resulting solely from the use of ammonium thiosulfate on dichondra lawns. These concentrations do not differentiate between solvated and ammonia gas. Ammonia has a Henry's Law Constant of ammonia at 25° C is 3.5 x 10^{-6} atm-m^3/mole (1.41 x 10^{-4}, unitless). Volatilization of ammonia is dependent on temperature and pH of the media and increase with increasing temperature and pH. In addition, these exposure estimates do not take into account assimilation (uptake by organisms), binding to humic acids and clays in soils, nitrification in soil/water body, atmospheric oxidation reactions of volatilized ammonia, or the contribution from ammonia fertilizers.

3.   Terrestrial Exposure Assessment

Based on basic physical-chemical principles, ammonium thiosulfate will dissociate to form ammonium (NH_4^+) and thiosulfate ($S_2O_3^{2-}$) ions when used as an herbicide application in a residential setting to control spurge and oxalis in dichondra lawns. Dissociation in water is the first step involved in the environmental fate of ammonium thiosulfate.

Given the environmental fate of ammonium thiosulfate in terrestrial systems (see Section III.B.1), it is not appropriate to model terrestrial dietary residues using the T-REX model. The potential terrestrial risks associated with using ammonium thiosulfate as a pesticide will be discussed qualitatively.

C. Effects Characterization

For ammonium thiosulfate, there are no acceptable registrant-submitted ecotoxicity data available for any receptors other than mammals. That is, there are no acceptable data for the following taxa: fish (surrogate for aquatic-phase amphibians), aquatic invertebrates, aquatic plants, birds (surrogate for reptiles and terrestrial-phase amphibians), terrestrial invertebrates, and terrestrial plants. A search of the publicly-accessible ECOTOX website (http://www.epa.gov/ecotox) revealed one aquatic toxicity study that is unacceptable for use in this risk assessment[5], and there were no terrestrial toxicity data for ammonium thiosulfate.

As described in the Exposure Characterization section above, the aquatic risk assessment for ammonium thiosulfate will focus on ammonia. Ammonia is known to exhibit aquatic toxicity and has been studied extensively in the open literature. The available evidence indicates that the toxicity of ammonia can depend on ionic composition, pH, and temperature. The Agency (Office of Water) has developed ambient water quality criteria for ammonia,[6] which will be used in this risk assessment for ammonium thiosulfate use as a pesticide.

The terrestrial risk assessment will be qualitative for ammonium thiosulfate due to its environmental fate properties and predicted behavior in the environment. For the sake of being complete, **Table III.4** summarizes the available toxicity data for mammals (provided by the Health Effects Division). Ammonium thiosulfate is practically non-toxic to mammals on an acute oral basis, and the acute dermal and inhalation toxicity studies revealed no mortalities.

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[5] Ecotox. Ref. No. 14566. Fathead minnow acute toxicity study. Substance purity and mortality data were not reported.
[6] For more information visit: http://www.epa.gov/waterscience/criteria/ammonia/99update.pdf

Table III.4. Toxicity of ammonium thiosulfate to mammals.

Test Type	Test Organism	Results	Toxicity Category	MRID
Acute oral	Rat (Sprague-Dawley)	5-day LD50 (both sexes) = 3824 mg/kg 5-day LD50 (males) = 4054 mg/kg 5-day LD50 (females) = 3500 mg/kg	Practically non-toxic	41647405
Acute dermal	Rabbit	3-day LD50 > 2000 mg/kg bw (Male and female rabbits were treated dermally with 2000 mg/kg bw ammonium thiosulfate. All rabbits survived the treatment. No abnormal clinical signs or gross findings were noted. Erythema was noted in 3 males and in all 5 females; however, there were no skin reactions after day 3.)	N/A	41647406
Acute inhalation	Rat (Sprague-Dawley)	Male and female Sprague-Dawley rats were exposed to ammonium thiosulfate aerosol (1.79 mg/L) for four hours. Signs included polypnea and dyspnea, languid behavior, hunched appearance, prostration and tremors, rhinorrhea, chromodacryorrhea, and salivation. There were no effects on body weights and all animals survived the treatment.	N/A	41647407

IV.   Risk Characterization

A.   Aquatic Risk

As described in the Exposure Characterization (Section III.B), ammonium thiosulfate will quickly dissociate in the environment into ammonium and thiosulfate, both of which are considered in this aquatic risk assessment. Thiosulfate would be incorporated into the natural sulfur cycle, where the thermodynamically-stable end product is sulfate. Since the Agency has established an SMCL of 250 mg/L for sulfate in drinking water, and it is highly unlikely that sulfate levels would approach this level (as a result of this ammonium thiosulfate use), no aquatic exposure modeling was performed for sulfate. The risk of sulfate to aquatic organisms via the pesticidal use of ammonium thiosulfate is presumed to be negligible.

For ammonium, aquatic exposures were estimated using the Tier 1 GENEEC model and adjusted for the percent of the area treated. Ammonium EECs were then adjusted using equilibrium equations to estimate ammonia concentrations at three pH levels (5, 7, and 9). Based on the Agency's national criterion for ammonia in fresh water[7], aquatic life should be protected if both of the following conditions are satisfied for the temperature, T, and pH of the waterbody:

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[7] http://www.epa.gov/waterscience/criteria/ammonia/99update.pdf

1. The one-hour average concentration of total ammonia nitrogen (in mg N/L) does not exceed, more than once every three years on the average, the CMC (acute criterion) calculated using the following equations:

Where salmonid fish are present:
$$CMC = (0.275 / (1 + 10^{\,7.204 - pH})) + (39.0 / (1 + 10^{\,pH - 7.204}))$$

Or, where salmonid fish are not present:
$$CMC = (0.411 / (1 + 10^{\,7.204 - pH})) + (58.4 / (1 + 10^{\,pH - 7.204}))$$

2. The thirty-day average concentration of total ammonia nitrogen (in mg N/L) does not exceed, more than once every three years on the average, the CCC (chronic criterion) calculated using the following equations.

When fish early life stages are present:
$$CCC = [(0.0577 / (1 + 10^{\,7.688 - pH})) + (2.487 / (1 + 10^{\,pH - 7.688}))]$$
$$* \ MIN(2.85, 1.45*10^{0.028 \, * \, (25\text{-}T)})$$

When fish early life stages are absent:
$$CCC = [(0.0577 / (1 + 10^{\,7.688 - pH})) + (2.487 / (1 + 10^{\,pH - 7.688}))]$$
$$* \ 1.45*10^{0.028 \, * \, (25\text{-MAX }(T,7))}$$

Using these equations, these criteria were calculated assuming a temperature of 25°C at pH 5, 7, and 9. As shown in **Table IV.1**, the highly conservative GENEEC model estimated aquatic EECs for ammonia are all below the national water criteria. It is important to keep in mind that the GENEEC modeled EECs are upper bound concentrations and do not take into account uptake by organisms, binding to humic acids and clays in soils, nitrification in soil/water body, or atmospheric oxidation reactions of volatilized ammonia. This analysis suggests that the pesticidal use of ammonium thiosulfate poses negligible risk to aquatic organisms.

Table IV.1. Comparison of GENEEC modeled aquatic EECs versus national water criteria for ammonia.

GENEEC EECS	Peak Ammonium Concentration (mg/L)	Peak Ammonia Concentration[1] (mg N/L)		
		pH 5	pH 7	pH 9
PTA Corrected	3.90	2.77E-6	2.79E-4	0.027
National Water Acute Criterion (Salmonid)[2]		38.759	24.103	0.885
National Water Acute Criterion (Non-Salmonid)[2]		58.039	36.093	1.324
National Water Chronic Criterion[2] (Fish early life stage-present)@ 25°C		3.599	3.000	0.233
National Water Chronic Criterion[2] (Fish early life stage-absent)@ 25°C		3.599	3.000	0.233

[1] Ammonia concentration estimated using following equation: $\log(NH_3(g)) = -11.04 + \log(NH_4^+) + pH$

B.   Terrestrial Risk

Terrestrial exposures of ammonium and thiosulfate were not quantitatively estimated in this assessment. As described in the Exposure Characterization (Section III.B), the environmental fate of thiosulfate will be dependent on soil redox potential. In suboxic and oxic environments (where oxygen, nitrogen and iron act as electron acceptors), thiosulfate will be oxidized to form sulfate. In anoxic environment, thiosulfate will be reduced to form sulfide. The environmental fate of ammonium is predominantly dependent on nitrification and sorption on soil colloids and organic matter. Ammonium may also form ammonia ($NH_3(g)$) in very alkaline and sodic soil environments (pH 9-10).

Sulfur and nitrogen are essential nutrients for plants and animals. Available mammalian data indicate that ammonium thiosulfate is practically non-toxic on an acute oral basis. There are no toxicity data available for birds, terrestrial invertebrates, or terrestrial plants. Since ammonium thiosulfate is being used as an herbicide, there is a possibility that non-target plants may be at risk. However, given that it is only used in residential/homeowner settings in California on dichondra lawns, the potential for adverse effects to non-target plants (including Federally-listed species) seems highly unlikely.

Given the nature of the chemical and its expected behavior in the environment, and because sulfur and nitrogen are essential nutrients for plants and animals, risk to terrestrial organisms is not expected as a result of ammonium thiosulfate use as an herbicide on dichondra lawns.

C.   Federally Threatened and Endangered (Listed) Species Concerns

This risk assessment suggests that Federally-listed threatened and endangered aquatic and terrestrial species are not at risk as a result of the limited use of ammonium thiosulfate as an herbicide on dichondra lawns.

D.   Discussion of Uncertainties, Limitations, and Data Gaps

1. Exposure For All Taxa

a. Maximum Use Scenario

The screening-level risk assessment focuses on qualitatively characterizing potential ecological risks resulting from a maximum use scenario, which is determined from labeled statements of maximum ammonium thiosulfate application rate and number of applications with the shortest time interval between applications. The frequency at which actual uses approach this maximum use scenario may be dependent on herbicide resistance, timing of applications, cultural practices, and market forces.

b. Additive and/or Synergistic Effects

It was assumed that aquatic and terrestrial organisms were exposed only to ammonium thiosulfate use as an herbicide. Ecological risks associated with exposure to a mixture of

ammonium thiosulfate and other pesticides, adjuvants, heavy metals, industrial chemicals, pharmaceuticals, etc. were not considered in this risk assessment.

2.   Exposure For Aquatic Species

The Tier I (screening) simulation model GENEEC was used to estimate the exposure concentrations (EECs) of thiosulfate and the ammonium cation. This model is not suitable for inorganic chemicals, particularly those that undergo extensive, pH-dependent redox reactions. Assumptions had to be made for the selection of environmental fate parameters (hydrolysis, photolysis, biotransformation). It was assumed that thiosulfate and ammonium were stable (i.e, half-lives = 0). Therefore, these EECs represent an upper bound concentration of thiosulfate and ammonium cation that do not consider any redox reaction products in soil and water.

The available product label does not provide clear information on application rates and frequency of application. Given that the product is only used in residential settings, an application rate had to be estimated from U.S. Census 2000 data for a typical residential plot and assumed treated area, which then was used to estimate the percent treated area (PTA). Since GENEEC estimates assume that all of the area gets treated, the PTA served to correct the aquatic EECs.

3.   Data Gaps

There were no acceptable registrant-submitted environmental fate or ecotoxicity data available for ammonium thiosulfate. However, given the nature of the chemical and its predicted behavior in the environment, this was not an impediment to the risk assessment. At this time, the EFED is not requesting any environmental fate or ecotoxicity studies to be submitted for ammonium thiosulfate.

V.   Cited Literature

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Appendix A. Sulfur chemical species (other than thiosulfate) of environmental significance

Name of Sulfur Species	Oxidation State of Sulfur	Chemical Name of the Acid Form	Compounds
Sulfide S^{2-}	-II	Hydrogen sulfide, H_2S Hydrosulfide, HS-	Metal Sulfides , mostly minerals such as: Galena (PbS) Sphalerite (ZnS)
Polysulfide S_n^{2-}	-II	Acid form is not stable	In aqueous solution only S_3^{2-} and S_4^{2-} are stable.
Sulfur (elemental sulfur)	0	No acid form The thermodynamically stable form is cyclooctasulfur (cyclo-S_8); orthorhombic	Not applicable
Sulfur Dioxide, SO_2	IV	Not applicable	Not applicable It can be generated from burning of S-fuels It is of environmental concern because it forms sulfuric acid
Hydrosulfite, sulfite, HSO_3^- Sulfite, SO_3^-	IV	Acid form not stable	As salts
Sulfate, SO_4^{2-}	VI	Sulfuric acid, H_2SO_4	Sulfate salts (sodium potassium) Naturally occurring sulfate minerals (e.g., barite)

Sulfur oxyanions containing 3 or more sulfurs:
Polythionates $(S_n)O_6^{2-}$, of which tetrathionate is an example, $S_4O_6^{2-}$

Appendix B. Aquatic Exposure Model Estimates (GENEEC Version 2.0)

RUN No. 1 FOR Ammonium Cation ON   Dichondra   * INPUT VALUES *

```
 ------------------------------------------------------------------
 RATE (#/AC)  No.APPS &  SOIL  SOLUBIL  APPL TYPE NO-SPRAY INCORP
  ONE(MULT)   INTERVAL   Koc  (PPM )   (%DRIFT)  (FT)   (IN)
 ------------------------------------------------------------------
18.090( 72.360)  4  10       .0 1030.0  GRHIFI( 6.6)   .0   .0
```

FIELD AND STANDARD POND HALFLIFE VALUES (DAYS)

```
 ------------------------------------------------------------------
 METABOLIC  DAYS UNTIL  HYDROLYSIS  PHOTOLYSIS  METABOLIC  COMBINED
  (FIELD)  RAIN/RUNOFF  (POND)    (POND-EFF)  (POND)    (POND)
 ------------------------------------------------------------------
   .00    2       N/A     .00-    .00     .00      .00
```

GENERIC EECs (IN MILLIGRAMS/LITER (PPM))   Version 2.0 Aug 1, 2001

```
 ------------------------------------------------------------------
   PEAK     MAX 4 DAY   MAX 21 DAY   MAX 60 DAY   MAX 90 DAY
   GEEC    AVG GEEC    AVG GEEC    AVG GEEC    AVG GEEC
 ------------------------------------------------------------------
   4.29     4.29        4.29        4.29        4.29
```