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Reregistration Eligibility Decision for Inorganic Polysulfides

List D

Case No. 4054

Approved by: Debra Edwards — Date: 9/30/2005

Debra Edwards, Ph. D. September 30, 2005
Director
Special Review and Reregistration Division

Reregistration Eligibility Decision for

Inorganic Polysulfides

Special Review and Reregistration Division
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U.S. Environmental Protection Agency
1801 South Bell Street
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September 30, 2005

Background:

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) was amended in 1988 to accelerate the reregistration of products with active ingredients registered prior to November 1, 1984. The amended Act calls for the development and submission of data to support the reregistration of an active ingredient, as well as a review of all submitted data to the EPA. Reregistration involves a thorough review of the scientific database underlying a pesticide's registration. The purpose of the Agency's review is to reassess the potential risks arising from the currently registered uses of the pesticide; to determine the need for additional data on health and environmental effects; and to determine whether or not the pesticide meets the "no unreasonable adverse effects" criteria of FIFRA.

EPA has completed its Reregistration Eligibility Decision (RED) document for the inorganic polysulfides case, which includes one chemical, calcium polysulfide. In this document, EPA presents the results of its review of the potential human health effects of dietary, drinking water, occupational/residential exposure to calcium polysulfide, and ecological risks. Based on this assessment, the Agency has determined that products containing calcium polysulfide as the sole active ingredient are eligible for reregistration. Also, as a result of this assessment, one exemption from the requirement for a tolerance has been reassessed.

I. Executive Summary:

Calcium polysulfide is used as an active ingredient primarily in agricultural and residential use fungicides, but some products also have secondary insecticidal activity. There are sixteen products currently registered with calcium polysulfide as an active ingredient, with only three of these also containing other active ingredients. Calcium polysulfide is mildly irritating to the skin and can cause irreversible damage to the eye due to its high pH. The current calcium polysulfide product labels require personal protective equipment for all handlers and a Restricted Entry Interval for all post-application activities of 48 hours in accordance with the Worker Protection Standard. Products containing calcium polysulfide in addition to other active ingredients would need to be assessed separately. The Agency has determined that calcium polysulfide rapidly degrades to calcium hydroxide and sulfur in the environment and in the human body. Therefore, this assessment of calcium polysulfide is based, in part, on the Agency's 2002 Inert Ingredient Focus Group tolerance reassessment decision for calcium, ammonium, potassium, magnesium and sodium hydroxide and on the 1991 reregistration eligibility decision for sulfur. Calcium polysulfide has a tolerance exemption under 40CFR 180.1232. The current exemption from the requirement of a tolerance for calcium polysulfide (lime sulfur) under 40CFR 180.1232 is considered reassessed and meets the reasonable certainty of no harm as defined by FQPA.

Like calcium polysulfide, calcium hydroxide is irritating to skin and eyes. However, calcium hydroxide is a direct food substance affirmed as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA). A 1975 FDA assessment of calcium hydroxide states that the average daily intake of calcium hydroxide is 5 mg/kg for adults and ranges from 15 to 28 mg/kg for infants. Further, the Agency's 2002 TRED states that "Given the widespread occurrence of these hydroxides in the existing food supply, the amounts that can be applied to food as a result of a use in a pesticide product would not be expected to significantly increase the existing amounts in the food supply....EPA concludes that there is a reasonable certainty that no harm will result to the general population, and to infants and children, from aggregate exposure to residues of ammonium, sodium, potassium, calcium, and magnesium hydroxides."

According to the sulfur RED, "The human risks, if any, from both dietary and occupational exposures are considered to be very low because of the general knowledge of the chemical sulfur, its ubiquitous

occurrence, and its low toxicity, as well as its long history of use by humans, including some pharmaceutical applications." However, sulfur can cause eye and skin irritation and EPA has determined that a hazard exists for workers reentering fields following foliar application of sulfur dust (i.e., eye and skin irritation to people who handle sulfur dust or who come into contact with treated foliage during field work). Thus, a 24-hour restricted entry interval and protective clothing requirements are included on all current labeling of applicable sulfur products.

In the ecological assessment, risks for freshwater fish resulting from spray drift and acute risks for birds and mammals were identified. However, due to the rapid dissociation of calcium polysulfide to components with very low toxicity, no mitigation for freshwater fish, mammals or avian species is warranted at this time. Also, based on the dissociation of calcium polysulfide, as well as the findings in the calcium hydroxide TRED and the sulfur RED, it has been determined that the use of products containing calcium polysulfide as the sole active ingredient would not present a human health hazard to the general public.

II. Use Information:

Calcium Polysulfide

Calcium polysulfide (CAS Number 1344-81-6) has various synonyms, including calcium sulfide and lime sulfur. As mentioned above, calcium polysulfide is used as an active ingredient in insecticides and fungicides (PC Code 076702).

Calcium polysulfide has fungicidal and secondary acaricidal activity, and is used to control powdery mildews, anthracnose, scab, and other diseases, as well as spider mites. Based on current labels, calcium polysulfide is registered for feed and food uses on the following sites: alfalfa, almonds, apples, beef, blackberries, blueberries, boysenberries, caneberries, cherries (sweet), cherries (tart), citrus, clover, currants, dairy cattle, deciduous fruit trees, gooseberries, grapes, hazelnuts (filberts), hogs, nectarines, oranges, peaches, pears, pecans, pistachio nuts, plums, prunes, quinces, raspberries, rye, sheep, stone fruits, tangerines, and walnuts. The non-food/non-feed use sites include the following: cherry (dormant), horses, ornamentals, residential lawns, and sheep. Products are applied as liquid sprays (ground, air blast, and hand-held equipment, with no labels specifically prohibiting aerial). The end use products include soluble concentrates (SL/C) and emulsifiable concentrates (EC) formulation. The Agency database, OPPIN Query, indicates that all of the current products are formulated ranging from 5% to 29% calcium polysulfide as the active ingredient. All but three of the current products list calcium polysulfide as the sole active ingredient, with the others listing aliphatic hydrocarbons (4-166 and 239-2528) or calcium thiosulfate (8660-67) as the additional active ingredients (Table 1).

Table 1. Registered Products Being Reassessed Containing Calcium Polysulfide

Registration Number	Registration Name	Percent Calcium Polysulfide	Other Active Ingredients	Formulation Type	Date first registered
33955-420	Acme Lime Sulfur Spray	29%	none	soluble concentrate	2 Feb, 1974
5887-143	Black Leaf Lime Sulfur Spray	29%	none	soluble concentrate	30 July, 1982

Table 1. Registered Products Being Reassessed Containing Calcium Polysulfide					
Registration Number	Registration Name	Percent Calcium Polysulfide	Other Active Ingredients	Formulation Type	Date first registered
4-166	Bonide Oil and Lime Sulfur Spray	5%	80% aliphatic petroleum hydrocarbons	emulsifiable concentrate	7 May, 1971
4-402	Bonide Lime Sulfur Spray	30%	none	soluble concentrate	4 May, 1966
66196-3	BSP Sulforix	27.5%	none	emulsifiable concentrate	29 May, 1953
802-73	Lilly/Miller Polysul Summer & Dormant Spray Concentrate	28.7%	none	soluble concentrate	7 April, 1950
51036-226	Lime-Sulfur	29%	none	soluble concentrate	13 May, 1988
66196-2	Lime-Sulfur Solution	29%	none	soluble concentrate	2 March, 1975
8660-67	Liquid Lime-Sulfur 32 Degrees Baume	28%	2% calcium thiosulfate	soluble concentrate	6 Dec., 1972
239-2391	Ortho Dormant Disease Control	26%	none	soluble concentrate	15 April, 1972
239-2528	Ortho Dormant Insect & Disease Control	16.66%	34.84% aliphatic petroleum hydrocarbons	emulsifiable concentrate	11 July, 1986
239-309	Orthorix Spray	26%	none	emulsifiable concentrate	24 Sept, 1948
11656-51	Poly-Sul Fungicide Insecticide Miticide	29%	none	emulsifiable concentrate	20 Oct, 1976
71096-6	Rex Lime Sulphur Solution	28%	none	soluble concentrate	26 June, 1948
769-558	Suregard Lime Sulphur Solution 32 BE	29%	none	soluble concentrate	17 Nov, 1981
71096-11	Tetrasul 4S5	27%	none	soluble concentrate	15 Aug, 2002

The Biological and Economic Analysis Division (BEAD) Screening Level Usage Analysis (SLUA) in Appendix A indicates that the crops receiving the greatest amounts of pounds ai of total applied calcium polysulfides include grapes and apples, with pears, peaches, and cherries also receiving substantial amounts, on a national basis, followed by blackberries, raspberries, and blueberries. The states where the greatest amounts are used include California, Washington, and Oregon. Based on the information reviewed in the BEAD assessment of current labels, the highest application rates are for blueberries (66.58

lb ai/A) and cherries and grapes (61.48 lb ai/A), although the BEAD Revised Usage assessment indicates that "average" or "typical" rates actually applied to these crops are substantially lower, 17.31, 14.96, and 9.38 lb ai/A to blueberries, cherries, and grapes, respectively.

Calcium polysulfide is produced by reacting lime with sulfur in boiling water. The resultant solution is highly alkaline (pH 11.5-11.8) and corrosive. Upon application to agricultural crops, calcium polysulfides or its dissociation products reach foliage and soils and can enter water bodies via spray drift and later via run-off and erosion. Calcium polysulfide present in moist soils and/or on moist foliage is expected to dissociate rapidly; therefore, run-off and erosion into surface water, as parent calcium polysulfide, should be negligible. Calcium polysulfide dissociates to form calcium cations and sulfur (S), and therefore the fate of this pesticide is dependent on the fate of its dissociation products. The EFED Environmental Science Chapter states two important conclusions regarding fate: 1) the expected change in environmental background levels of calcium cations and elemental sulfur due to application of the pesticide would be expected to be low compared with the relative presence of these chemicals already appearing in the environment; and 2) the fate and transport characteristics of these dissociation products suggest that applications of calcium sulfide to targeted foliage/soils would result in minimal movement to water bodies by drift, likely resulting in low concentrations in these aquatic systems.

Calcium Hydroxide

Calcium hydroxide is used in pesticide products as both an inert ingredient and an active ingredient. As an inert ingredient, it is used primarily as a solid diluent and/or carrier, and has been placed on the Agency's pesticide inert ingredient list 4B. This classification indicates that the Agency has concluded that calcium hydroxide will not adversely affect the public health or the environment under current use patterns. As an active ingredient, there is currently only one manufacturing use product registered with calcium hydroxide. Calcium hydroxide is listed as an FDA GRAS chemical under 21CFR 184.1205, with no limitations specified as to its use in food except good manufacturing use practice.

The tolerance exemptions reassessed for calcium hydroxide, with the respective citation in the Code of Federal Regulations (CFR), and the use pattern as an inert ingredient are listed in Table 2.

Table 2. Tolerance Exemptions Reassessed in the 2002 Calcium Hydroxide TRED

Tolerance Exemption Expression	CAS No.	40 CFR	PC Code	Use Pattern
calcium hydroxide	1305-62-0	**Active Ingredient**		
		Not Applicable	075601	Microbiocide/Microbiostat
		Inert Ingredient		
		180.910	875601	solid diluent, carrier

Sulfur

As an active ingredient in pesticides, sulfur is an insecticide and fungicide used on terrestrial food and feed crops, non-food crops, aquatic food crops, greenhouse food and non-food crops, indoor food and non-food, and indoor/outdoor residential premises. Non-pesticidal uses include use as a fertilizer or as a soil amendment for reclaiming alkaline soils.

III. Physical/Chemical Properties:

The physical and chemical properties of calcium polysulfide are provided in Table 3. This information was obtained from the profiles in TOXNET (Hazardous Substances Data Bank (HSDB) and CambridgeSoft (ChemFinder), as well as various MSDS sheets for calcium polysulfide.

Table 3. Physical/Chemical Properties

		References
Molecular formula	Ca (Sx)	ChemFinder, 2005
Color/Form	Deep orange liquid	HSDB, 2005
Odor	unpleasant smell of hydrogen sulfide; rotten egg odor	HSDB, 2005
Density/Specific Gravity	1.28 @ 15.6°C	HSDB, 2005
pH	10.9-11.2	MSDS, 2005a
	11.5 - 11.9	MSDS, 2005c
	11.8 - 11.9	MSDS, 2005d
Water Solubility	Soluble in water	HSDB, 2005
	"Very soluble"	MSDS, 2005c
	"soluble"	MSDS, 2005d

IV. Hazard Characterization:

A. Toxicity

Tables 4 and 5 list the acute toxicity data for calcium polysulfide and sulfur, respectively.

Table 4. Acute Toxicity Profile for Calcium Polysulfides

Study Type	Category	Results	Reference
Acute Oral (LD_{50})	III	820 mg/kg (male) 820 mg/kg (female)	MSDS, 2005b
Acute Dermal (LD_{50})	III	>2000 mg/kg	
Acute Inhalation (LC_{50})	IV	3.9 mg/L (male) 3.1 mg/L (female)	
Primary Eye Irritation	I	Irreversible damage due to high pH	
Primary Skin Irritation	III	Mildly irritating	

Table 5. Acute Toxicity Profile for Sulfur			
Study Type	Category	Value	Reference
Acute Oral (LD_{50})	IV	> 5 mg/kg	Sulfur RED
Acute Dermal (LD_{50})	III	> 2 mg/kg	
Acute Inhalation (LC_{50})	III	> 2.56 mg/L	
Primary Eye Irritation	III	n/a	
Primary Skin Irritation	IV	n/a	

Based on the current product labels for calcium polysulfides, personal protective equipment (PPE) is required for all handlers. This includes coveralls over long-sleeved shirts and long pants, waterproof gloves, chemical resistant footwear plus socks, protective eyewear, chemical resistant headgear for overhead exposure, chemical resistant apron when cleaning equipment, mixing, or loading, and a MSHA/NIOSH approved dust/mist filtering respirator. In addition, the Restricted Entry Interval for all postapplication activities is 48 hours, in accordance with the Worker Protection Standard 40 CFR part 170.

According to the calcium hydroxide TRED (EPA, 2002), acute toxicity studies were obtained from Toxnet for calcium hydroxide; however, these studies were not reviewed by the Agency. An oral LD_{50} of 7340 mg/kg (rats) was reported for calcium hydroxide. The NIOSH International Chemical Safety Card states that calcium hydroxide irritates the respiratory tract, and is corrosive to the eyes and skin. Repeated or prolonged exposure can cause dermatitis, and may also affect the lungs due to exposure to dust particles (NIOSH, 2005).

From the sulfur RED, chronic exposure at low levels is generally considered safe, with no known risks of oncogenic, teratogenic, or reproductive effects associated with its use. In addition, sulfur has been shown to be non-mutagenic in microorganisms (EPA, 1991).

For calcium polysulfide, the Agency waived the data requirements for acute inhalation and dermal sensitization, because "calcium polysulfide, upon dissolution in water, is converted rapidly to calcium hydroxide and colloidal elemental sulfur" (Tox Branch II, HED, 1991). In addition, the Agency also determined the all the subchronic and chronic toxicity testing requirements to be waived, based on the availability of adequate toxicity data in the literature for the degradation products. Based on that determination, the toxicity of calcium polysulfide is due to the degradation products and "exposure to human[s] is self-limiting and can be regulated through [product] labeling" (Tox Branch I, HED, 1993).

B. Metabolism

The Agency has determined that calcium polysulfide rapidly degrades to calcium hydroxide and sulfur in the human body. Thus, the data requirements for the higher tier toxicity studies have been waived by the Agency, and there are no repeated dose toxicity studies available for calcium polysulfide (Tox Branch I, HED, 1993).

C. Special Considerations for Infants and Children

Based on the toxicity data reviewed in this document for calcium polysulfides, calcium hydroxide, and sulfur, there is no information which indicates increased sensitivity to calcium polysulfide for infants and children. Although calcium polysulfide and its degradates can cause skin and eye irritation, once incorporated into the food supply, there is a low potential for risk to these groups of the population.

V. Exposure Assessment:

The Agency has determined that calcium polysulfide readily breaks down into calcium hydroxide and sulfur in the human body. Since the risks have already been assessed for both of these other chemicals and use patterns are similar, it is not necessary to generate a separate risk assessment for calcium polysulfide. The conclusions of the RED document for sulfur and the TRED document for calcium hydroxide indicate that these chemicals have been determined to not present unacceptable risks to humans.

VI. Dietary Exposure:

Based on the rapid dissociation of calcium polysulfide in the environment, as well as in the human body, to calcium hydroxide and sulfur, the Agency has determined that only a qualitative dietary assessment is needed, based on the results of the RED and TRED for these constituent products. Thus, the Agency has determined that there are no dietary risk concerns, whether from the ingestion of food or water or both, for calcium polysulfide.

VII. Aggregate Assessment:

In examining aggregate exposure, FFDCA section 408 directs EPA to consider available information concerning exposures from the pesticide residue in food and all other non-occupational exposures, including drinking water from ground water or surface water and exposure through pesticide use in gardens, lawns, or buildings (residential and other indoor uses). In developing this assessment document for calcium polysulfide, a qualitative assessment for all pathways of human exposure (food, drinking water, and residential) is deemed appropriate given the lack of human health concerns associated with exposure to this chemical, as well as its constituent products (calcium hydroxide and sulfur). Thus, the Agency has determined that there are no aggregate risk concerns resulting from exposure to calcium polysulfide through food, drinking water and/or residential uses.

VIII. Cumulative Exposure:

Section 408(b)(2)(D)(v) of the FFDCA requires that, when considering whether to establish, modify, or revoke a tolerance, the Agency consider "available information" concerning the cumulative effects of a particular pesticide's residues and "other substances that have a common mechanism of toxicity." If chemicals are structurally related and all are low toxicity chemicals, then the risks either separately or combined should also be low. Unlike other pesticides for which EPA has followed a cumulative risk approach based on a common mechanism of toxicity, EPA has not made a common mechanism of toxicity finding as to calcium polysulfide and any other substances.

For the purposes of this action, EPA has assumed that calcium polysulfide does not share a common mechanism of toxicity with other substances. For information regarding the Agency's efforts to determine which chemicals have a common mechanism of toxicity and to evaluate the cumulative effects of such

chemicals, see the policy statements released by EPA's Office of Pesticide Programs concerning common mechanism determinations and procedures for cumulating effects from substances found to have a common mechanism on EPA's website at http://www.epa.gov/pesticides/cumulative/.

IX. Risk Characterization:

As mentioned above, the Agency has determined that calcium polysulfide readily breaks down into calcium hydroxide and sulfur in the environment and in the human body. Assessments performed on both these substituent compounds indicate a reasonable certainty of no harm to human health. Therefore, it has been determined that the use of products containing calcium polysulfide (as the sole active ingredient) also would not present a human health hazard to the general public. Furthermore, the current exemption from the requirement of a tolerance for calcium polysulfide (lime sulfur) under 40CFR 180.1232 is considered reassessed, and meets the reasonable certainty of no harm standard as defined by FQPA.

X. Environmental Fate and Exposure Considerations:

Calcium Polysulfide

Lime sulfur is readily soluble in water, and solutions of lime sulfur have a highly alkaline pH, ranging from 10.9 to 11.9 (Table 3). In an agricultural setting, the end-use products containing this chemical are mixed in water and the solution applied to growing rain-fed and/or irrigated crops. In such environments, it can be assumed that moisture is abundant on/in targeted plants/soils. Calcium polysulfide is expected to rapidly dissociate in the presence of any moisture to form calcium cations (calcium hydroxide) and elemental sulfur. Upon application, most of the applied material reaches targeted crops/soils, while some reaches, as drift, non-targeted plants/soils. It is considered likely that "rapid dissociation" is initiated when water is added to the end-use product within the tank-mix, and much of the "active ingredient" reaching the treated crop is colloidal sulfur.

Any calcium polysulfide reaching targeted crops is expected to be washed off into the soil as parent and/or with time, with the dissociation products consisting mainly of elemental sulfur and calcium. These same dissociation products are expected to form from parent that reaches the soil directly from application. In the soil system, the modest amounts of calcium and sulfur that result from the use of calcium polysulfide are not believed to be significant when compared to their respective natural background levels.

Since calcium polysulfide dissociates quickly in the environment, runoff and/or leaching of the parent into nearby water bodies is assumed to be negligible; thus, aquatic exposure models which consider runoff and/or leaching, such as GENEEC2 and PRZM/EXAMS, are not used in this assessment. To estimate exposure of terrestrial organisms (mammals and birds), the terrestrial exposure model T-REX was used to estimate exposures resulting from single spray application of calcium polysulfide. As with the aquatic assessment, due to rapid breakdown, it is unlikely that repeated applications would result in the accumulation of calcium polysulfide on terrestrial forage materials. Accumulations on forage material, if any, would most likely be of sulfur and/or inert ingredients.

Calcium Hydroxide

Calcium hydroxide is commonly found in soil and water, suggesting that low levels would not pose adverse effects to wildlife or water resources. Large releases may cause direct effects, such as exceedances of toxicity thresholds, or indirect effects, such as disruption of ecosystems through altering of pH or increasing availability of algal nutrients. Calcium hydroxide is a medium to strong base, and as such, can cause varying degrees of pH change depending on the amount of material released and the buffering

capacity of the soil or water. Hydroxides are persistent in the environment, but they also tend to dissociate, react with organic and inorganic materials, and form complexes with ionic substances.

Sulfur
All environmental fate data requirements were waived in 1982, based on the fact that sulfur is a natural component of the environment (EPA, 1991). It is possible for sulfur to oxidize to sulfuric acid and acidify soils; however, this is not considered likely to be a deleterious effect. In addition, elemental sulfur added to the environment will become incorporated into the natural sulfur cycle. There is potential for non-target organisms to be exposed to sulfur due to its large annual usage and relatively high application rates. However, the risks associated with exposure to sulfur appear to be low.

XI. Ecotoxicity and Environmental Risk Considerations:

Calcium Polysulfide
Based on an extensive search of environmental toxicity data, the most sensitive aquatic species in each category was selected for detailed environmental risk analysis (Table 6). Note that in some cases, the study report had not clarified that the results were based on the active ingredient present in the test solution, so the EFED Science Chapter has corrected for the percent active ingredient (i.e., lowered the acute toxicity value reported in the study, based on the % ai).

Table 6. Calcium Polysulfide Toxicity Reference Values (mg active ingredient/L) for Aquatic Organisms.

Exposure Scenario	*Species*	*Scientific Name*	*Exposure Duration*	*Toxicity Reference Value (mg a.i./L)*	*Reference (Classification)*
Freshwater Fish					
Acute	Rainbow trout	*Oncorhynchus mykiss*	96 hours	LC_{50} = 0.97 mg a.i./L [a] (study value: 3.35 mg/L)	McCann 1976 (Acceptable)
Chronic	No Data Available				
Freshwater Invertebrates					
Acute	Water flea	*Daphnia pulex*	48 hours	LC_{50} = 2.9 mg a.i./L [a] (study value: 10 mg/L)	MRID 40098001 (Acceptable)
Chronic	No Data Available				
Estuarine/Marine Fish					
Acute	No Data Available				
Chronic	No Data Available				
Estuarine/Marine Invertebrates					
Acute	No Data Available				
Chronic	No Data Available				

Exposure Scenario	*Species*	*Scientific Name*	*Exposure Duration*	*Toxicity Reference Value (mg a.i./L)*	*Reference (Classification)*
Aquatic Plants					
Algae	green algae	*Selenastrum capricornutum*	120 hours	EC_{50} = 14.1 mg a.i./L [b] EC_{05} = 0.5 mg a.i./L [b]	MRID 43960801 (Acceptable)
Macrophytes	No Data Available				

[a] The study report did not specify if toxicity endpoints were expressed in terms of mg formulation/L or mg a.i./L. Taking the most conservative approach, it is assumed that toxicity endpoints were reported in terms of mg formulation/L. To calculate toxicity values in terms of mg a.i./L, values were multiplied by the % a.i. in the formulation tested. Details are provided in Appendix E of the EFED Science Chapter.
[b] The EC_{50} was used to assess risk to non-listed aquatic algae; the EC_{05} value was used to assess risk to listed algae. Also, the statistical methods used in the study were different than those used by EFED; therefore, the numbers used here are slightly different than those reported in the MRID (EC_{50} = 15 mg a.i./L, EC_{05} = 1.2 mg a.i./L).

The spray drift model AGDRIFT (SDTF 2001) was used to estimate the fraction of calcium polysulfide that is released indirectly to a water body due to spray drift following a typical aerial or ground based application to a crop. Since calcium polysulfide reacts quickly in the environment, runoff and/or leaching into nearby water bodies were assumed to be negligible. Spray drift from both aerial and ground applications was assessed. Although the BEAD assessment of the calcium polysulfide labels did not identify any labels which indicate instructions for aerial applications, aerial applications were evaluated because none of the labels specifically prohibit aerial use. Initial average deposition to water bodies was reported to be 3.21% for aerial applications, and 0.02 % for ground applications, such as air blast applications to orchards. Thus, based on the maximum label rates, the initial concentrations in the standard pond range from less than 0.0007 ppm for grapes treated via orchard/air blast, to 0.110 ppm for grapes treated by aerial applications. The AgDrift Model was also run with typical use rates, and the resulting in EECs ranged from 0.0169 ppm to 0.0407 ppm, respectively.

Acute Risk Quotients (RQs) were then calculated based on the estimated environmental concentration (EEC) divided by the aquatic toxicity data. The acute RQs for freshwater fish were as high as 0.12 (for blueberries with aerial applications at the maximum label rate), but for typical applications rates, even with aerial applications, the highest RQ was 0.042, which does not exceed the acute endangered species LOCs. In addition, for freshwater invertebrates, all acute RQs are below the LOCs for acute restricted use (LOC 0.1) and acute endangered species (LOC 0.05). In addition, the LOC for acute risk to plants (LOC 1) is not exceeded for non-listed or listed algae under any of the modeled crop scenarios. While there are no data available for estuarine or marine species, this has been identified in the EFED Science Chapter as a data gap. However, there is no information available that would indicate that crops treated with calcium polysulfide are grown directly adjacent to estuarine and/or marine waters.

The terrestrial exposure model T-REX (T-REX Version 1.12, dated December 7, 2004) was used to estimate exposures and risks to avian and mammalian species for single spray applications of calcium polysulfide. Since calcium polysulfide breaks down rapidly, it is unlikely that repeated applications would result in the accumulation of calcium polysulfide on terrestrial forage materials. Accumulations on forage materials, if any, would most likely be of calcium, sulfur, and/or inert ingredients. Therefore, only acute risks from single applications of calcium polysulfide are considered in this assessment. The EECs for

residues on various forage categories (short grass, tall grass. broadleaf plants/small insects, fruits/pods/large insects, and seeds) were obtained from the Tier I model T-REX for five crop uses: blueberries, grapes, almonds, apples, and alfalfa. As with aquatic organisms, these EECs were compared with the available reported toxicity data for the most sensitive species. For birds, acute RQs were derived using dose-based and dietary-based acute toxicity values (but since those LC_{50} values were >5000 mg a.i./kg, no RQ values could be calculated); for mammals, acute RQs were derived using a dose-based acute toxicity value (Table 7).

Table 7. Calcium Polysulfide Toxicity Reference Values (TRVs) for Terrestrial Organisms.

Exposure Scenario	*Species*	*Exposure Duration*	*Toxicity Reference Value*	*Reference MRID (Classification)*
Mammals				
Acute (Dose-based)	rat	single oral dose	LD_{50} (_) = 86.63 mg a.i./body wt. [a]	00154738 (Acceptable)
Chronic	No Data Available			
Birds				
Acute (Dose-based)	bobwhite quail	single oral dose	LD_{50} = 560 mg a.i./kg body wt.	43945101 (Acceptable)
Acute (Dietary-based)	bobwhite quail and mallard duck	5-day dietary	LC_{50} >5000 mg a.i./kg diet (for both species)	43945103 quail (Acceptable) 43945104 duck (Acceptable)
Chronic	No Data Available			
Plants	No Data Available			

[a] The study report did not specify if toxicity endpoints were expressed in terms of mg formulation/L or mg a.i./L. Taking the most conservative approach, it is assumed that toxicity endpoints were reported in terms of mg formulation/L. To calculate toxicity values in terms of mg a.i./L, values were multiplied by the % a.i. in the formulations tested (16.66%). Details are provided in Appendix E of the EFED Science Chapter.

Thus, dietary-based RQs were calculated using EECs expressed in terms of residue concentration for the various forage categories, and toxicity values (LC_{50}) expressed in units of dietary concentration. Dose-based RQs were calculated using a body weight-adjusted LD_{50} and consumption-weighted equivalent dose sorted by food source and body size. For both birds and mammals, three weight categories (or sizes) were considered (20 g, 100 g, 1000 g for birds, and 15 g, 35 g, 1000 g for mammals). Nearly all dose-based acute RQs for birds exceed the LOCs for acute risk (LOC 0.5), acute restricted use (LOC 0.2), and acute endangered risk (LOC 0.1). For example, the highest RQs for birds were for application to blueberries at the maximum label rate, with dose-based RQs ranging from 0.52 to 45.95, exceeding all acute LOCs for all forage categories, and from 0.13 to 11.95, for typical application rates to blueberries.

Note that these RQs are based on an acute oral toxicity test in bobwhite quail, with an LD_{50} value of 560 mg a.i./kg body weight, which indicates that calcium polysulfide is slightly toxic to avian species on an

acute oral basis. This study was based on gavage dosing. Note also that avian toxicity data are quite different when the acute dietary toxicity of calcium polysulfide is based on feeding studies (not gavage-dosed). The acute dietary toxicity was evaluated in bobwhite quail and mallard ducks, with both studies yielding LC_{50} values >5,000 mg a.i./kg diet. Based on these results, calcium polysulfide is categorized as practically non-toxic to birds on an acute dietary basis. These LC_{50} values of >5,000 mg a.i./kg diet were not evaluated to assess dietary-based acute risk of birds to calcium polysulfide.

The risks to terrestrial mammals also used dose-based acute RQs for mammals, specifically gavage-dosed rats. As with avian risks, nearly all dose-based acute RQs for mammals exceed the LOCs for acute risk (LOC 0.5), acute restricted use (LOC 0.2), and acute endangered risk (LOC 0.1). For example, the highest RQs for mammals were also for application to blueberries, with dose-based RQs ranging from 0.45 to 79.73 at the maximum label rate, exceeding all acute LOCs for all forage categories, and from 0.04 to 7.55 for typical application rates to blueberries. [Note that these RQs are based on an acute toxicity value of 86.63 mg a.i./body wt., from the EFED Science Chapter, much lower than the Acute Oral (LD_{50}) value of 820 mg/kg, as reported in Table 4, for the Acute Toxicity Profile for Calcium Polysulfides.]

All RQ values for terrestrial species which exceed LOCs are based on toxicity data from studies in which animals were dosed by gavage. The pH of calcium polysulfide solutions is reported to range from 10.9 to 11.9, suggesting that it is likely that the observed mortality in gavage-dosed rats and birds was due to corrosive effects on the lining of the gastrointestinal tract. When birds are tested with food which has calcium polysulfide incorporated into the diet (the 5-day dietary feeding studies in Table 7), there was essentially no mortality, even at the highest doses. Since almost all products containing calcium polysulfide are mixed with water prior to application, it is likely that significant dissociation occurs within the mix tank. In fact, some labels have language to address the formation of crusts or crystals which may occur in the tank prior to application. These surface solids are very likely comprised of elemental sulfur resulting from product dissociation. Regarding risks for freshwater fish resulting from spray drift, it is expected that calcium polysulfide will dissociate to calcium cations and sulfur upon contact with natural water bodies. Thus, no mitigation for terrestrial species or freshwater fish is warranted at this time.

Endangered Species Considerations

The Agency has developed the Endangered Species Protection Program to carry out its responsibilities under FIFRA in compliance with the Endangered Species Act (ESA). The ESA requires Federal agencies to ensure that their actions are not likely to jeopardize listed species or adversely modify designated critical habitat, and requires Federal agencies to use their authorities to further the purposes of the Act by carrying out programs for the conservation of listed species. To analyze the potential of registered pesticide uses that may affect any particular species, EPA uses basic toxicity and exposure data and considers ecological parameters, pesticide use information, geographic relationship between specific pesticide uses and species locations, and biological requirements and behavioral aspects of the particular species.

In accordance with the agreement between the U.S. EPA Office of Pesticide Programs and the U.S. Fish and Wildlife Service and the National Marine Fisheries Service (Letter of Agreement, http://endangered.fws.gov/consultations/pesticides/evaluation.pdf), the Agency has provided in this risk assessment an interpretation of the listed species' LOCs in terms of the chance of an individual effect should organisms be exposed to a media concentration or dose corresponding to1/10 or 1/20 of the LC50, LD50, or EC50 used as the acute toxicity measurement endpoint for a particular taxonomic group. The Agency has reviewed the data and other information for calcium polysulfide and its degradates and concludes that this fungicide does not warrant action under the Endangered Species Act. Although EPA's

screening-level assessment shows that there are possible "effects" on listed species or their critical habitat (some RQ values were above the level of concern for endangered species), the Agency has determined that mitigation is not warranted at this time, based on the characterizations presented above in the respective sections for exposure scenarios and toxicity data for fish, birds, and mammals. Thus, this determination was derived by the Agency based on the evaluation and characterization of relevant exposure assessments and toxicity tests that were conducted on aquatic and terrestrial animals, as well as aquatic and terrestrial plants.

The Endangered Species Protection Program as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989) is currently being implemented on an interim basis. As part of the interim program, the Agency has developed County Specific Pamphlets that articulate many of the specific measures outlined in the Biological Opinions issued to date. The Pamphlets are available for voluntary use by pesticide applicators on the EPA website at www.epa.gov/espp. A final Endangered Species Protection Program, which may be altered from the interim program, was proposed for public comment in the Federal Register on December 2, 2002.

XII. Drinking Water Considerations:

Since calcium polysulfide dissociates quickly in the environment, runoff and/or leaching into nearby water bodies is assumed to be negligible; thus, aquatic exposure models which consider runoff and/or leaching, such as GENEEC2 and PRZM/EXAMS, are not used in this assessment. In the receiving water systems, the modest amounts of calcium and sulfur that result from the use of calcium polysulfide is not believed to be significant when compared to their respective natural background levels.

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Appendix 1. BEAD Screening Level Usage Analysis for Calcium Polysulfide for Agricultural Uses and Other Information

Screening Level Usage Analysis for

(Inorganic polysulfides (PC code 076702))

2/07/05

What is a Screening Level Usage Analysis (SLUA)?

- Available estimates of pesticide usage data for a particular active ingredient that is used on **agricultural** crops in the United States.

What does it contain?

- Pesticide usage data for a **single** active ingredient only.
- Agricultural use sites (crops) that the pesticide is *reported* to be used on
- Pesticide usage information on the national level for the United States.
- Annual percent of crop treated **(average & maximum)** for each agricultural use site.
- Average annual pounds of the pesticide applied for each agricultural use site.

What assumptions can I make about the data reported?

- **Average pounds of active ingredient applied** - Values are calculated by merging pesticide usage data sources together; averaging by year, averaging across all years, & then rounding. ***Note:*** If the estimated value is less than 500, then that value is labeled <500. Estimated values between 500 & <1,000,000 are rounded to 1 significant digit. Estimated values of 1,000,000 or greater are rounded to 2 significant digits.)
- **Average percent of crop treated** - Values are calculated by merging data sources together; averaging by year, averaging across all years, & rounding to the nearest multiple of 5. ***Note:*** If the estimated value is less than 1, then the value is labeled <1.
- **Maximum percent of crop treated** - Value is the single maximum value reported across all data sources, across all years, & rounded up. ***Note:*** If the estimated value is less than 2.5, then the value is labeled <2.5.

What are the data sources used?

- **USDA-NASS** (United States Department of Agriculture's National Agricultural Statistics Service) – pesticide usage data from 1998 to 2003.
- **NCFAP** (National Center for Food and Agricultural Policy) – pesticide usage data from 1997 & is ***only*** used if data is not available from the other sources.
- **Private pesticide market research** – pesticide usage data from 1998 to 2003.

What are the limitations to the data?

- Registered/labeled uses may exist but **are not surveyed** by the available data sources.
- Lack of reported usage data for the pesticide on a crop **does not imply** zero usage.
- Usage data on a particular site may be noted in data sources, but **not quantified**. In these instances, no usage would be reported in the SLUA for that use site.

- Non-agricultural use sites (e.g., turf, post-harvest, mosquito control, etc.) are not reported in the SLUA. A separate request must be made to receive these estimates.

Who do I contact for further information and/or questions on this SLUA?

- (Jenna Carter, Botanist, BEAD)
- ((703)308-8370, carter.jenna@epa.gov)

Screening Level Estimates of Agricultural Uses of Inorganic polysulfides
Sorted Alphabetically

OBS	**Crop**	**Lbs. A.I.**	**Percent Crop Ttd.**	
			Avg.	Max.
1	Almonds	6,000	<1	<2.5
2	Apples	700,000	10	15
3	Apricots	10,000	5	10
4	Blackberries	70,000	65	75
5	Blueberries	20,000	5	5
6	Cherries	100,000	5	5
7	Grapefruit	<500	<1	<2.5
8	Grapes	600,000	5	10
9	Hazelnuts (Filberts)	10,000	<1	<2.5
10	Lemons	9,000	<1	5
11	Oranges	30,000	<1	<2.5
12	Peaches	40,000	<1	5
13	Pears	300,000	15	25
14	Prunes & Plums	7,000	<1	<2.5
15	Raspberries	60,000	50	70
16	Walnuts	10,000	<1	<2.5

All numbers rounded.
'<500' indicates less than 500 pounds of active ingredient.
'<2.5' indicates less than 2.5 percent of crop is treated.
(slua003k.sas a005a8n.sas Inorganic polysulfides)