Sulfur Dioxide

Crops

Identification of Petitioned Substance

Chemical Names:
Sulfur dioxide

Other Name:
Sulfur (IV) oxide
Sulfur superoxide
Sulfurous acid anhydride
Sulfurous anhydride

Trade Names:
Sulfurous oxide

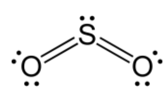
CAS Numbers:
7446-09-5

Other Codes:
EINECS 231-195-2
U.S. EPA Pesticide Chemical Code 077601
CA DPR Chemical Code 561
UN 1079

Characterization of Petitioned Substance

Composition of the Substance:

Sulfur dioxide (SO_2) is an angular molecule containing a sulfur atom and two oxygen atoms and can be produced naturally or as a result of combustion of sulfur-containing substances such as petroleum or coal. The sulfur atom has a formal charge of 0 and an oxidation state of +4 and is surrounded by 5 electron pairs. The chemical structure of sulfur dioxide is shown below:



Properties of the Substance:

Sulfur dioxide is a colorless gas with a strong, pungent odor. It is nonflammable and very soluble in water. Sulfur dioxide is a strong reducing agent and is highly reactive.

Due to its high vapor pressure, sulfur dioxide is primarily present in the gaseous phase and can move unchanged to other natural surfaces, including water, soil, and vegetation, following release to the atmosphere (ATSDR, 1998). Because of the high water solubility of sulfur dioxide, oceans can serve as sink (ATSDR, 1998). Sulfur dioxide can be absorbed by soil if pH and moisture content are suitable (ATSDR, 1998).

Chemical Properties (Source: U.S. EPA, 2007b)

Physical State	Gas
Appearance	Colorless
Odor	Strong odor, suffocating
Molecular Weight	64.06
Boiling Point	10° C
Melting Point	-72.7° C
Solubility	11.3 g/100 mL (water at 20° C) 0.58 g/100 mL (water at 90° C)
Vapor Pressure	300 mm Hg at 20°C
Relative Density	1.4 at -10° C (water = 1)
Specific Gravity	2.26

Specific Uses of the Substance:

According to the U.S. EPA Registration Eligibility Document (RED) for inorganic sulfites, sulfur dioxide is registered for use as a fungicide and is typically used to treat for *Boitrytis cinerea*, which causes gray mold disease on grapes. Sulfur dioxide fumigation products are formulated as a compressed liquid that becomes a gas upon release. Compressed liquid fumigation is used in cold-storage facilities and for fumigation of vehicles used to transport post-harvest grape products. In addition, sulfur dioxide products are used to prevent spoilage and oxidation in wine; to sanitize equipment used in wineries, to treat, in combination with carbon dioxide, for black widow spiders on grapes in storage settings; and to preserve and maintain the appearance of fruit products (e.g. dried fruits) by preventing rotting. Another common use of sulfur dioxide is as a bleaching agent in food. In addition, sulfur dioxide is sometimes added as a warning marker and fire retardant to liquid grain fumigants. As discussed further below, the U.S. Department of Agriculture (USDA) National Organic Program (NOP) and the Canada Food Inspection Agency both approve the use of sulfur dioxide as a rodenticide in smoke bombs that are released underground.

Sulfur dioxide is also used in a wide variety of industrial applications, including the manufacture of hydrosulfites and by the petroleum industry (ATSDR, 1998). It is also used to dechlorinate wastewaters before release (U.S. EPA, 2007b). Specifically, free and combined chlorine are reduced to chloride upon reaction with sulfur dioxide. Because of its reduction properties, sulfur dioxide also acts as a bleaching agent for paper and clothing (ATSDR, 1998).

Sulfur dioxide emissions are produced by industries, vehicles, and equipment that combust sulfur-containing fossil fuels, as well as from various industrial processes (U.S. EPA, 2010a). When fossil fuel combustion occurs at power plants, sulfur dioxide is released to the atmosphere (U.S. EPA, 2010a). Atmospheric sulfur dioxide then reacts with water, oxygen, and other chemicals to produce acid rain (U.S. EPA, 2007a). Acid rain is defined as the mixture of wet and dry deposition from the atmosphere that contains high amounts of sulfuric and nitric acids (U.S. EPA, 2007a).

Approved Legal Uses of the Substance:

Sulfur dioxide is currently included in the National List as a synthetic substance allowed for use in organic crop production (7 CFR 205.601). In particular, sulfur dioxide is approved for use as an underground rodent control only, specifically in the form of smoke bombs.

Sulfur dioxide is considered by the U.S. Food and Drug Administration (FDA) as generally recognized as safe (GRAS) when used in accordance with good manufacturing practice, except that it is not used in meats; in food recognized as a source of vitamin B1; on fruits or vegetables intended to be served raw to consumers or sold raw to consumers, or to be presented to consumers as fresh (21 CFR 182.3766). Dried fruits (excluding dark raisins and prunes), lemon and lime juices, wine, molasses, and sauerkraut juice are allowed to contain sulfur dioxide concentrations of less than 100 ppm (U.S. EPA, 2007b). Concentrations of sulfur dioxide between 50 and 100 ppm are allowed for grape juice, wine vinegar, fruit topping, gravies, dried potatoes, and maraschino cherries (U.S. EPA, 2007b). Pectin, corn syrup, corn starch, fresh shrimp, sauerkraut, pickled foods, hominy, frozen potatoes, maple syrup, imported jams and jellies, and fresh mushrooms may contain concentrations of sulfur dioxide between 10 ppm and 50 ppm (U.S. EPA, 2007b). Proper labeling is required on foods containing levels of sulfur dioxide that exceed 10 ppm (U.S. EPA, 2007b).

Under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), U.S. EPA provides a tolerance for sulfur dioxide residues in or on post harvest grapes (40 CFR 180.444). The tolerance is listed as 10.0 ppm when sulfur dioxide is used as a fungicide. Fumigation may occur indoors or in trailers or other transport devices (U.S. EPA, 2007b). Grapes may be fumigated up to twenty times and on a seven to ten day interval (U.S. EPA, 2007b). If fumigation area concentrations exceed 2.0 ppm, a NIOSH/MSHA approved respirator must be used for short exposures of limited duration (U.S. EPA, 2007b). Labels on fumigation products containing sulfur dioxide must include information on the appropriate personal protective equipment (eye protection, gloves, boots, and protective clothing) (U.S. EPA, 2007b). When sulfur dioxide is used to treat for black widow spider, the U.S. EPA approves a concentration of up to 10,000 ppm and an exposure period of approximately thirty minutes (U.S. EPA, 2007b). During the aeration phase of treatment, the approved sulfur dioxide release concentration is one below 30 ppm (U.S. EPA, 2007b).

The U.S. EPA has proposed label revisions for sulfur dioxide end-use products (fumigants) in their May, 2007 document titled the 'Reregistration Eligibility Decision- Inorganic Sulfites' (U.S. EPA, 2007b). The proposed revisions are as follows:

- When treating grapes for *Botrytis cinerea* (bunch rot/gray mold) or black widow spider in a warehouse fumigation chamber, do not release treated air into the atmosphere containing concentrations of sulfur dioxide in excess of 30 ppm (as determined by a Sensidyne or Kitagawa syringe sampler, or a Draeger handpump);

- When treating grapes in a truck, trailer or other transport vehicle, do not release treated air into the atmosphere containing concentrations of sulfur dioxide in excess of 2 ppm (as determined by a Sensidyne or Kitagawa syringe sampler, or a Draeger handpump);

- Sulfur dioxide concentration in transport vehicles must be below 2 ppm before moving over public roads or highways;

- Before moving or using sulfur dioxide fumigant products, handlers must be trained how to appropriately use respirators which conform to OSHA requirements (described in 29 CFR 1910.124) and how to appropriately handle and use sulfur dioxide;

- When making gas applications or checking connections handlers must wear a NIOSH/MSHA approved full face respirator with an organic-vapor removing cartridge, in addition to sulfur dioxide impervious gloves, boots and coveralls over long-sleeved shirt and long pants;

- If a sulfur dioxide concentration of 2 ppm is exceeded at any time, all persons working in the fumigation area must wear a NIOSH/MSHA approved full face respirator with an organic-vapor removing cartridge. If sulfur dioxide concentrations of 10 ppm are exceeded, or when concentrations are unknown, an approved self-contained breathing mask (SCBA) or combination air supplied SCBA respirator must be used by all persons working in the fumigation area; and

- Sulfur dioxide aerations must not be performed concurrently from multiple chambers.

The U.S. EPA has not registered sulfur dioxide for use as a rodenticide. However, U.S. EPA has registered rodent control smoke bombs with the active ingredients sulfur, charcoal carbon, and sodium nitrate or potassium nitrate (saltpeter). The action of these smoke bomb products is described below.

<u>Action of the Substance</u>:

As indicated by its current inclusion on the National List, sulfur dioxide is used as a rodenticide in the form of smoke bombs that are applied underground. Elemental sulfur, which produces sulfur dioxide gas when burned, is an active ingredient in rodent control smoke bomb products registered by U.S. EPA under FIFRA. Ignition of the smoke bomb generates a mixture of gases that may include sulfur dioxide. The composition of the gases will vary depending on specific product formulations (e.g., the use of sodium nitrate or potassium nitrate) and use conditions. However, the fumes may be toxic or irritating if inhaled. Smoke bombs also consume oxygen needed by animals for respiration.

According to Mason and Littin (2003), when sulfur dioxide comes in contact with the mucous membranes of the nasal cavities of rodents, the following effects may occur: irritation to the nasal cavity, damage to the airways and lungs, structural changes to the epithelium, bronchoconstriction, hemorrhage, laryngeal spasm, edema, collapsed lungs, emphysema, and respiratory arrest. When a lethal dose is received, death is generally due to asphyxia (Mason and Littin, 2003). Although some marketing information [1] for sulfur-based rodenticide smoke bombs identifies asphyxiation due to oxygen depletion as the cause of death, the product labels do not indicate this mode of action and note that the product produces toxic fumes.

Combinations of the Substance:

Compressed sulfur dioxide gas in U.S. EPA-registered fumigant generally is not used in combination with other substances. When used to treat for black widow spiders on grapes in storage settings, sulfur dioxide gas may be used in combination with carbon dioxide. A combination of sulfur dioxide, water, and citric acid is used as an effective sanitizing agent in wineries and is used to clean equipment and storage areas.

Sulfur-based rodenticide smoke bombs contain sulfur, charcoal carbon, and either potassium nitrate or sodium nitrate as active ingredients. Combustion of these chemicals produces smoke containing sulfurous oxides other chemicals.

Status

Historic Use:

The high reactivity and acidic properties of sulfur dioxide make for its common use in commercial processes (ATSDR, 1998). Sulfur dioxide has been used in the paper and pulp industry as a bleaching agent (ATSDR, 1998). Other common uses of sulfur dioxide include use as a steeping agent for grain in food processing, as a catalyst or extraction solvent in the petroleum industry, as an intermediate for bleach production, and as a flotation depressant for sulfide ores in the mining industry (IARC, 1992).

In food preparation, historical uses of sulfur dioxide include fumigation of commodities. Ancient Greeks are reported to have used sulfur dioxide, produced by burning sulfur, to fumigate homes. Ancient Greek and Roman winemakers burned sulfur in order to capture sulfur dioxide for use as a wine preservative (Phillips, 2006).

OFPA, USDA National Organic Program Final Rule:

Since 2001, sulfur dioxide has been included on the National List of Allowed and Prohibited Substances for organic crop production. In particular, sulfur dioxide is allowed for use in underground rodent control only (as smoke bombs) (65 FR 80637; 7 CFR 205.601(g)(1)). Sulfur dioxide is also approved for use in organic handling and is permitted only in wine labeled 'made with organic grapes,' provided that the total concentration of sulfite does not exceed 100 ppm (7 CFR 205.605(b)).

International

The Canada Food Inspection Agency, Food and Drug Regulations – "Sulphur smoke bombs used for rodent control shall be used in conjunction with other methods and only when a full pest control program is maintained but temporarily overwhelmed." (Last modified in 2009)

The European Union (EU) – Annex VIII (EC 889/2008), Section A states that sulphur dioxide may be used in fruit wines without added sugar (including cider and perry) or in meads labeled as organic. This is the only allowed use of sulphur dioxide.

[1] For example: http://www.get-revenge.us/molecontrol.html; http://www.wholesale-garden-supplies.com/product.php?productid=22734&cat=0&page=1;

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

<u>Evaluation Question #1: What category in OFPA does this substance fall under:</u> (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?

(A) Sulfur dioxide contains an active ingredient in the following category: copper and sulfur compounds.

(B) The substance is not classified on the U.S. EPA's list of synthetic inert ingredients in pesticide products (List 4). Tolerance information is available from the U.S. EPA on sulfur dioxide. Sulfur dioxide is not classified as an inert substance but is considered as synthetic. In 2007, the U.S. EPA determined that sulfur dioxide was eligible for reregistration under the condition that labeling statements be required when the substance is used to treat for *Boitrytis cinerea*, which causes gray mold disease on grapes and when used for indoor applications to equipment and grapes used for wine making (U.S. EPA, 2007).

<u>Evaluation Question #2:</u> Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Sulfur dioxide is produced commercially from elemental sulfur, pyrites, sulfide ores of non-ferrous metals, gypsum and anhydrite, waste sulfuric acid and sulfates, hydrogen sulfide-containing waste gases, and flue gases from the combustion of sulfurous fossil fuels (IARC, 1992). The most common method of production occurs by burning sulfur, but sulfur dioxide can be produced by purifying and compressing sulfur dioxide gas from smelting operations (ATSDR, 1998). Sulfur dioxide has been produced by burning molten sulfur in a special burner with a controlled amount of air. The burner gas, free of dust and cooled, is dissolved in water in a series of two towers. In a third tower, the solution is sprayed at the top and flows down while steam is injected at the base. The gas issuing from the third tower is then cooled to remove most moisture and passed up a fourth tower against a countercurrent of sulfuric acid. The dried gas is liquefied by compression (IARC, 1992).

Below are examples of natural and synthetic processes that result in the formation of sulfur dioxide.

1. In sulfur based smoke bombs, sulfur dioxide can be produced by burning (i.e., oxidizing) elemental sulfur:

$$S_8 + 8\ O_2 \rightarrow 8\ SO_2$$

2. Sulfur dioxide can be produced following the combustion of hydrogen sulfide (H_2S):

$$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$$

Evaluation Question #3: Is the substance synthetic? Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21).

Sulfur dioxide occurs in the environment as a product of natural processes (e.g., volcanic eruptions). However, sulfur dioxide used in industrial and commercial applications is typically obtained from synthetic processes. For example, sulfur dioxide can be produced by burning molten sulfur in a fabricated burner with a controlled amount of air. The burner gas is cooled and then dissolved in water in two separate cooling towers. In a third tower, the solution is sprayed at the top and flows down while steam is injected at the base (IARC, 1992). The gas from the third tower is cooled to remove most moisture and passed up a fourth tower against a countercurrent of sulfuric acid. The dried gas is liquefied by compression so that it can be transported (IARC, 1992).

Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. § 6518 (m) (2)).

Because of the high vapor pressure of sulfur dioxide, the substance typically occurs as a gas and when released to the air, may move unchanged to various surfaces, such as soil, water, vegetation, and grass (ATSDR, 1998). While in the air, sulfur dioxide can also react to form sulfates, sulfur trioxide, and sulfuric acid (ATSDR, 1998). Because of the high level of solubility, sulfur dioxide dissolves in water and forms sulfurous acid (ATSDR, 1998). While it has been determined that sulfur dioxide is absorbed by soil, little is known about its movement in soil (ATSDR, 1998).

The U.S. EPA regulates sulfur dioxide as a criteria air pollutant, and the one-hour standard is air is 75 ppb (U.S. EPA, 2010b). Sulfur dioxide is oxidized rapidly by both homogeneous and heterogeneous reactions and is removed from the atmosphere by precipitation and by dry deposition on surfaces, mainly as sulfuric acid. The atmospheric lifetime of sulfur dioxide is about 10 days (IARC, 1992). Sulfur dioxide emissions are regulated by U.S. EPA in part because they serve as a precursor to acid rain.

In addition to wet and dry deposition, atmospheric sulfur dioxide can be transferred to soil by diffusion (ATSDR, 1998). Sulfur dioxide uptake by soil is dependent upon soil pH and moisture content (ATSDR, 1998). One estimate of the uptake of sulfur dioxide by soil and vegetation is 52 x 10^6 tons per year (ATSDR, 1998). The presence of sulfur dioxide can degrade soil systems by acidification and impact future plant growth. In addition, acidification of soil can inhibit microbial activity, such as nitrification and soil respiration, and cause the leaching of essential nutrients. An increase in soil acidity can also increase the amount of available iron, manganese, and aluminum, which are toxic to plants (Agrawal et al., 1984). Agrawal et al. observed the affects of sulfur dioxide on *Vicia faba* and determined that sulfur dioxide can affect plant growth directly when it is absorbed by plants and indirectly through significant changes to the soil system. Agrawal et al. (1984) concluded that the long-term effects of industrial pollution, with respect to altered physico-chemical properties of soil, are critical.

Oceans are generally considered to be a sink for sulfur dioxide due to the high solubility of the substance (ATSDR, 1998). It is also possible that oceans can be a source of sulfur dioxide if the equilibrium pressure of sulfur dioxide in surface water exceeds the partial pressure of sulfur dioxide in the air immediately above it.

Hill (1971) and Garland et al. (1973) reported that vegetation could be an important sink for sulfur dioxide and several other air pollutants. Plants can absorb sulfur dioxide from air. Siebke et al. (1990) developed a model for simulating uptake and metabolism of sulfur dioxide by different leaf cell compartments.

<u>Evaluation Question #5:</u> Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants. Describe the persistence and areas of concentration in the environment of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)).

When used as a rodenticide, elemental sulfur is ignited with sodium or potassium nitrate and carbon to produce fumes that contain a mixture of chemicals. These fumes may contain sulfur dioxide gas, which if inhaled by rodents may come in contact with the mucous membranes. When sulfur dioxide comes into contact with the mucous membranes of the nasal cavity, irritation occurs (Mason and Littin, 2003). Sulfur dioxide causes a range of damage to the airways and lungs, including changes to the structure of the epithelium, laryngeal spasm, bronchoconstriction, hemorrhage, edema and accumulation of blood and fluid in the airways and lungs, collapsed lungs, emphysema, and eventually respiratory arrest (Mason and Littin, 2003). Therefore, asphyxia is the probable cause of death.

Sulfur dioxide has been reported to have toxic effects on humans. Respiratory effects are common following acute (i.e., short-term) exposures and include bronchoconstriction. Inhalation exposure is of particular concern for asthmatic individuals. In a study conducted by Bethel et al. (1984), the authors reported that, because of the severity of the pulmonary response, exposures to sulfur dioxide had to be terminated for some of the asthmatic subjects while other subjects required medical attention. Two out of seven asthmatics required a bronchodilator after exposure to cold air and 0.5 ppm sulfur dioxide.

Rabinovitch et al. (1989) reported a case study describing a sulfide dust explosion in a copper mine that liberated large amounts of sulfur dioxide. Analysis of the gas sample obtained at the time of rescue indicated that the sulfur dioxide concentrations were greater than 40 ppm. Effects resulting from the exposure consisted of burning of the nose and throat, dyspnea, and severe airway obstruction that was only partially reversed two years after the exposure.

<u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).

As shown under Evaluation Question #2, sulfur dioxide can be prepared by burning elemental sulfur and through combustion of hydrogen sulfide and organosulfur compounds. If gases escape to the atmosphere during manufacture, sulfur dioxide is likely to be oxidized and removed from the atmosphere by wet and dry deposition on surfaces, mainly as sulfuric acid. Sulfur dioxide is considered the principal gas that leads to acid rain (U.S. EPA, 2007a). Runoff containing wet and dry acid deposition may impact farming environments and ecosystems. Many lakes and streams examined in a National Surface Water Survey suffer from chronic acidity, a condition in which water has a constant low pH level (U.S. EPA, 2007a). Runoff may combine with existing sources of irrigation and cause contamination on farms (U.S. EPA, 2007a). Acid rain causes a large number of effects that harm or kill individual fish, reduce fish population numbers, completely eliminate fish species from a waterbody, and decrease biodiversity (U.S. EPA, 2007a). As lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters decrease due to the interdependence of the entire ecosystem (U.S. EPA, 2007a).

Sulfur dioxide is listed as a toxic substance under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) under Title III of the Super-fund Amendments and Reauthorization Act (SARA). Disposal of wastes containing sulfur dioxide is controlled by a number of federal regulations. However, releases of sulfur dioxide to the environment from large processing facilities are not required to be reported to the Toxics Release Inventory (ATSDR, 1998).

An excess of sulfur dioxide can have degradative effects on soil systems and impact future plant growth by altering the pH and moisture content of the soil (Ophardt, 2003). Therefore, if used excessively as a rodenticide in smoke bombs, sulfur dioxide may potentially cause acidification of the soil as well as impact microbial activity and nitrification. Although empirical data or studies on these potential impacts are not available, any adverse effects of misuse of sulfur dioxide rodenticide products would likely be limited to the immediate area of use.

Evaluation Question #7: Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

Based on the available information, no interactions between sulfur dioxide released from underground smoke bombs and other substances used in organic crop or livestock production or handling have been identified. Because sulfur dioxide is only included on the National List for release underground in the form of smoke bombs, there would be no predicted chemical interaction with other substances used in organic livestock production or handling. However, because sulfur dioxide is potentially mobile in the soil environment (e.g., by gaseous diffusion or dissolving in water), it may conceivably interact with soil amendments or other substances applied to crop soils. No such reactions or consequent environmental or human health impacts are known, and no information is available to characterize the likelihood that sulfur dioxide released from underground smoke bombs would affect non-target species.

Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil) crops, and livestock (7 U.S.C. § 6518 (m) (5)).

The petitioned substance is proposed for use in underground smoke bombs, and would be released following use. The smoke bombs essentially cause asphyxia in rodents that may be exposed underground (e.g. in burrows) (Mason and Littin, 2003). When in contact with the mucous membranes of the nasal cavity, sulfur dioxide is converted to sulfuric and sulfurous acid (Mason and Littin, 2003). The nasal cavity becomes irritated and effects in the airways and lungs (e.g. bronchoconstriction, edema, accumulation of fluid in the airways and lungs, respiratory arrest, hemorrhaging, etc.) can lead to respiratory arrest in rodents (Mason and Littin, 2003). The effects of the sulfur dioxide gas are felt simultaneously by any target mammals in the burrows, so both adults and dependent young are killed by the rodenticide (Mason and Littin, 2003). In regard to secondary poisoning, Mason and Littin (2003) stated that if target mammals surface, there is a risk that predators may ingest sub-lethal levels of sulfur dioxide with effects such as irritation of the nasal cavity, lesions, and accumulation of fluids in the airways and lungs. Non-target animals also may dwell underground and be exposed to sulfur dioxide gas following release. Examples of potentially affected non-target animals include reptiles, amphibians, and invertebrates such as earthworms, mollusks, nematodes, protozoa, and insects. Little is known about the effects of sulfur dioxide based rodenticides on non-target species.

If the release of sulfur dioxide underground exceeds the threshold for soil absorption and the pH and moisture content of the soil are adequate, the soil may absorb sulfur dioxide and become acidic, thereby forming sulfurous acid (Ophardt, 2003). Sulfurous acid is on the National List as an approved soil amendment (7 CFR 205.601(j). Deeper soils have a higher capacity to retain sulfur dioxide and acidification of the soil may mobilize iron, manganese, and aluminum ions (Ophardt, 2003; Agrawal et al., 1984). Soil bacteria break down decaying plant matter, which releases nutrients such as calcium, magnesium, phosphate, nitrate, and others. A low soil pH and high aluminum ion concentration inhibits this process (Ophardt, 2003). Less calcium in the soil effects how well snails can form shells (Science Encyclopedia, 2010). Acidification of soil can cause leaching, which involves the removal of ions from the top soil or settling to the sub-soil. Leaching plays a significant role in tree growth if ions have been washed too far from roots (Ophardt, 2003). An excess in aluminum ions would occur, which adversely affect the growth of trees, as well as mosses, algae, fungi, and earthworms (Ophardt, 2003). Research has also found a decrease in carbohydrate production in the photosynthesis process of some plants exposed to acidic conditions (Ophardt, 2003). Hill (1971) and Garland et al. (1973) reported that vegetation could be an important sink for sulfur dioxide. Siebke et al. (1990) developed a model for simulating the uptake and metabolism of sulfur dioxide by different leaf cell compartments. Wet and dry deposition can cause leafy plants, such as lettuce, to hold increased amounts of potentially toxic substances (Science Encyclopedia, 2010).

Because of the effects that sulfur dioxide has on soil chemistry, many non-target organisms living in the soil are likely to be affected. However, extensive testing has not been completed in the non-target species likely to be exposed to rodent control devices that use sulfur dioxide gas. Inhalation exposure studies in dogs and rabbits have shown that absorbed sulfur dioxide metabolites are taken up by the blood and readily distributed to the body (ATSDR, 1998).

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

Sulfur dioxide is identified as a toxic substance under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) under Title III of the Super-fund Amendments and Reauthorization Act (SARA). Disposal of wastes containing sulfur dioxide is controlled by a number of federal regulations (ATSDR, 1998). Improper disposal can lead to release into the air and soil and produce adverse effects, including acidification.

The presence of sulfur dioxide in the air and soil following manufacture or improper disposal may affect soil and water bodies by creating an acidic pH. The balance of pH and soil nutrients is sensitive and can be altered when an amount of sulfur dioxide that exceeds the diffusion threshold is introduced. Acidic soil conditions can cause leaching and inhibit the growth of vegetation and microorganisms. Acidified soil may affect vegetation and animal health as well as microorganisms that maintain a chemical balance. Surface waters that receive run off of acidified soil have the potential to be acidified, thereby potentially affecting aquatic organisms (Ophardt, 2003).

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

Following low level inhalation exposure, the respiratory system appears to be the primary target system for sulfur dioxide (ATSDR, 1998). Acute-duration inhalation exposure studies in humans indicate that sulfur dioxide, in concentrations as low as 0.1 ppm, causes effects to the respiratory system in sensitive populations (e.g. asthmatics and the elderly) (ATSDR, 1998). Acute exposure to high concentrations can result in irreversible effects, including airway obstruction and edema (ATSDR, 1998 cited as Charan et al. 1979).

The following human and animal health observations were described by studies summarized in the ATSDR Toxicological Profile for Sulfur Dioxide (ATSDR, 1998):

- Following acute-duration inhalation exposure, studies in healthy human populations showed an increase in pulse rate (ATSDR, 1998 cited as Amdur et al. 1953).

- Animal studies showed no evidence of histopathological or microscopic lesions following acute-duration inhalation exposure (ATSDR, 1998 cited as Alarie et al., 1975).

- Neurological effects have been reported in humans following acute-duration inhalation exposure to sulfur dioxide (ATSDR, 1998).

- Gastrointestinal effects, including vomiting and nausea, were reported in a human acute-duration inhalation exposure study (ATSDR, 1998 cited as Rabinovitch et al., 1989).

- Hematological effects were observed in workers exposed to sulfur dioxide via inhalation route. An increase in the level of methemoglobin was detected among the exposed workers (ATSDR, 1998 cited as Savic et al., 1987).

- Clastogenic effects (i.e., exhibiting chromosome breakage) have been observed following occupational exposure in humans. Increases in sister chromatid exchange and chromosome aberrations have been reported in various studies (ATSDR, 1998).

- Sulfur dioxide is considered as a severe irritant to the skin and eyes in humans (ATSDR, 1998).

- Adverse hepatic, renal, endocrine, reproductive, and body weight effects have not been reported in humans exposed to sulfur dioxide via inhalation route (ATSDR, 1998).

IARC (1992) determined that there is inadequate evidence for determining carcinogenicity in animal models exposed to sulfur dioxide and sulfites. Therefore, sulfur dioxide and sulfites are considered as Group 3: not classifiable as to their carcinogenicity in humans.

<u>Evaluation Question #11:</u> Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

Although several synthetic substances have been identified for use in rodent control applications, most of these chemical controls are generally not encouraged by the National Sustainable Agriculture Information Service (ATTRA, 2010). Anticoagulants are not approved by NOP for use in organic farming, but are generally considered as the most common means of rodent control (Mason and Littin, 2003). First-generation coumarins (a substance that is deadly with a larger single dose or smaller doses over multiple days) include D-Con, WARF 42, Rax, Dethmore, Rodex, Tox-Hid, Prolin, Ratron, etc. (Moschetti, 1998). Second-generation coumarins (a substance that is toxic with a single dose) include Havoc, Talon, Contrac, Maki, Ratimus, D-Con Mouse Pruf II, brodifacoum, bromadiolone, etc. (Moschetti, 1998). Indandiones (a substance that is toxic with a single dose) include diphacinone, chlorophacinone, valone, pindone, Promar, Diphacin, Ramik, Afnor, Caid, Drat, Quick, Raticide-Caid, Ramucide, Ratomet, Raviac, Pival, PMP, etc. (Moschetti, 1998). These substances all have the potential to poison non-target animals.

Currently, the National List allows for the use of the synthetic substance, Vitamin D_3 (Cholecalciferol) as a rodenticide. Cholecalciferol-containing rodenticides produce hypercalcemia (i.e., excessive levels of calcium in the blood). Following ingestion, rodents generally die within two days and have not been observed to exhibit bait shyness. However, ATTRA notes that care should be used when placing bait, particularly where pets are present, due to the potential for unintentional ingestion (ATTRA, 2010). The National List states that Vitamin D_3 cannot be the sole means of rodent control and requires alternative methods for rodent control are documented in the Organic System Plan. Growers must take precautions to prevent killing non-target animals (205.271(a),(b),(c),(d) & 205.601(g)(1),(2)).

According to OMRI (2004), currently manufactured products containing Vitamin D_3 include:

- Terad3Ag Pellets: Motomco, Inc., 3699 Kinsman Blvd., Madison, WI 53704
- True Grit Rampage: Motomco Inc., 3699 Kinsman Blvd., Madison, WI 53704
- Ortho Rat-B-Gone: The Scotts Company, 14111 Scottslawn Rd., Marysville, OH 43041

Castor bean oil is a synthetic substance that has been made into a pellet that can be used in smaller gardens to kill rodents. Disadvantages of this method include a high amount of labor required to upkeep the application of the pellets in the tunnels. These pellets can be dangerous because they can poison household pets. Castor oil can also be sprayed (ATTRA, 2010).

Currently manufactured products (OMRI, 2010) containing castor oil:

- Dr. T Whole Control Mole Repellent: Dr. T's Nature Products, P.O. Box 682, Pelham, GA 31779
- MoleMax Mole and Vole Repellent: Bonide Products Inc., 6301 Sutliff Rd., Oriskany, NY 13424

Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

Planting repellant vegetation has been utilized as a non-synthetic method for controlling gopher populations. These plants include: castor bean, daffodils, squill, and euphorbia. Plants, including *Cestrum diurnum* (day jessamine) and *Solanum malacoxylon*, act as a source of cholecalciferol (ATTRA, 2010). Rodents should be removed from the area prior to planting, which can be difficult to achieve. If all animals are not removed, the rodents will be trapped inside (ATTRA, 2010).

According to ATTRA (2010), a majority of organic farmers rely on trapping for some level of rodent control. In order to maintain efficacy, ATTRA recommends that trapping should be done on a daily basis and especially during critical times in the life cycle of the rodent and the cropping season (ATTRA, 2010). The removal of food sources and shelter can deter rodents from farms.

Traps and Barriers:
There are many types of traps and barriers that are commonly used for rodent control. The use of live traps is common for capturing ground squirrels. These traps include a model called a "repeating trap" that can catch a whole colony from one baiting. One advantage of using traps is that the level of precision is higher because the exact tunnels can be followed. A second advantage is cost as traps are less expensive. Disadvantages of traps include the necessity of handling the animals that are caught, whether alive or dead. Ground squirrels have been found to carry bubonic plague and rabies and cases have been reported after humans reported contact. Traps also require regular monitoring and additional skill to set them. Examples of barriers include fencing and "gopher cages" or wire baskets placed in a hole at planting time to keep gophers out of the root zone. Because of their burrowing nature, gophers and ground squirrels can defeat most fences and the caging idea is confined to use on small acreages with valuable perennial plants (ATTRA, 2010).

Other Methods:
Flooding out tunnels using large amounts of water has been used in some instances (ATTRA, 2010). This practice is not effective, however, on sloped ground or when rodents other than gophers have been the source of infestation. This practice also uses a large amount of water and can create soil erosion. It may also be unfeasible to transport water to the location.

An increased population of predators is an effective control option. The corn snake (*Elaphe guttata)* and the rat snake (*Elaphe obsoleta*) are two snakes on the United States mainland that feed on rodents, such as mice, rats, and squirrels (ATTRA, 2010). Both species also feed on small birds, so a disadvantage to this method is that chicks and eggs might be at risk as well. Domestic cats are another option and will provide long-term control, although they will also prey on some birds (ATTRA, 2010). More than 95 percent of the diet of barn owls usually consists of small mammals, including rodents. Each barn owl may consume about one or two rodents per night. Per year, a nesting pair and their young can eat more than 1,000 rodents. Barn owls will commonly use man-made nest boxes. This alternative would certainly not be as feasible as the use of sulfur dioxide smoke bombs, but could have effective results (ATTRA, 2010).

References

National Sustainable Agriculture Information Service (ATTRA), 2010. Retrieved Dec. 21, 2010 from http://attra.ncat.org/calendar/question.php/2006/03/20/what_rodenticides_are_acceptable_for_use

Agrawal, M., Nandi, P. K., and Rao, D. N., 1984. Effects of sulphur dioxide fumigation on soil system and growth behavior of *Vicia faba* plants. J. of Plant and Soil. 86: 69-78.

Bethel, R.A., Sheppard, D., Epstein, J., 1984. Interaction of sulfur dioxide and dry cold air in causing bronchoconstriction in asthmatic subjects. J. Appl Physiol: Respir Environ Exercise Physiol 57:4 19-423.

Canadian General Standards Board, Dec. 2009. Retrieved Dec. 21, 2010 from Organic Production Systems Permitted Substances List. http://www.tpsgc-pwgsc.gc.ca/cgsb/on_the_net/organic/index-e.html

European Union, 2008. Retrieved Dec. 21, 2010 from http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:250:0001:0084:EN:PDF

Garland, J.A., Clough, W.S., Fowler, D., 1973. Deposition of sulfur dioxide on grass. Nature 242:256-257.

Hill, A.C., 1971. Vegetation: a sink for atmospheric pollutants. J Air Pollut Control Assoc 21:341-346.

International Agency for Research on Cancer (IARC), 1992. IARC monographs on the evaluation of the carcinogenic risk of chemicals to man: Occupational exposures to mists and vapours from strong inorganic acids, and other industrial chemicals. Vol. 54. Lyon, France: World Health Organization, International Agency for Research on Cancer.

Kellogg, W.W., Cadel, R.D., Allen, E.R., 1972. The sulfur cycle: Man's contributions are compared to natural sources of sulfur compounds in the atmosphere and oceans. Science 175:587-596.

Mason, G. and Littin, K. E., 2003. The Humaneness of Rodent Pest Control. J. of Animal Welfare. 12: 000-000

Moschetti, R., 1998. Rodenticide Poisoning. Retrieved Dec. 21, 2010 from http://webcanine.com/2007/ rodenticide-poisoning/

National Institutes of Occupational Safety and Health (NIOSH), 2010. Pocket guide to chemical hazards: Sulfur Dioxide. Retrieved Dec. 15, 2010 from http://www.cdc.gov/niosh/npg/npgd0575.html

OMRI. 2004. Generic Materials List. Retrieved Dec. 21, 2010 from http://www.omri.org/simple-gml-search/results/sulfur%20dioxide

Ophardt, C., 2003. Acid Rain- soil interaction. Virtual Chem Book. Retrieved Dec. 15, 2010 from http://www.elmhurst.edu/~chm/vchembook/196soil.html

Phillips, C., 2006. The Chemistry and Measurement of SO_2. Wine Business Monthly. Retrieved Dec. 15, 2010 from http://www.winebusiness.com/wbm/?go=getArticle&dataId=44897

Rabinovitch, S., Greyson, N.D., Weiser, W., 1989. Clinical and laboratory features of acute sulfur dioxide inhalation poisoning: Two-year follow-up. Am Rev Respir Dis 139:556-558.

Siebke, K., Badeck, F.W., Kohlmaier, G.H., 1990. Modeling pollutant exchange between plant and environmental uptake and metabolism of sulfur dioxide by different leaf cell compartments. Developments in environmental modeling, 16: Modeling in Ecotoxicology. New York, NY: Elsevier Science Publishing Co., Inc.

U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Sulfur Dioxide. Dec. 1998. Retrieved Dec. 15, 2010 from http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=253&tid=46

U.S. Environmental Protection Agency, 2007a. Effects of Acid Rain. Retrieved Dec. 16, 2010 from http://www.epa.gov/acidrain/effects/

U.S. Environmental Protection Agency (U.S. EPA), 2007b. Reregistration Eligibility Decision – Inorganic Sulfites. Retrieved Dec. 14, 2010 from http://www.epa.gov/pesticides/reregistration/REDs/ inorganicsulfites.pdf

U.S. Environmental Protection Agency (U.S. EPA), 2004. Inert Ingredients Ordered by CAS Number-List 4B, Office of Pesticide Programs. Retrieved Dec. 14, 2010 from www.epa.gov/opprd001/inerts/inerts_list4Bcas.pdf

U.S. Environmental Protection Agency (U.S. EPA), 2010a. Sulfur Dioxide (Six Common Pollutants). Retrieved Dec. 15, 2010 from http://www.epa.gov/airquality/sulfurdioxide/index.html

U.S. Environmental Protection Agency (U.S. EPA), 2010b. Fact Sheet Revisions to the Primary National Ambient Air Quality Standard Monitoring Network and Data Reporting Requirements for Sulfur Dioxide. Retrieved Dec. 16, 2010 from http://www.epa.gov/airquality/sulfurdioxide/pdfs/20100602fs.pdf