Chlorine/Bleach

Crops

Identification of Petitioned Substance

Chemical Names:
Calcium Hypochlorite
Sodium Hypochlorite
Chlorine Dioxide

Other Names:
Calcium hypochlorite and sodium hypochlorite also are known as bleach; synonyms are listed below in Table 1.

Trade Names:
Trade names are listed below in Table 1.

CAS Numbers:
Calcium Hypochlorite: 7778-54-3
Sodium Hypochlorite: 7681-52-9
Chlorine Dioxide: 10049-04-4

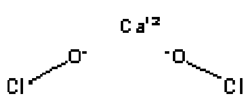
Other Codes:
Calcium Hypochlorite: 014701 (EPA/OPP Chemical Code)
Sodium Hypochlorite: 014703 (EPA/OPP Chemical Code); NH3486300 (RTEC number)

Characterization of Petitioned Substance

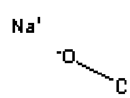
<u>Composition of the Substance</u>:

Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials not found in nature. Calcium hypochlorite and sodium hypochlorite are commonly known as bleach. The molecular formulas and structures of these compounds are shown below.[1]

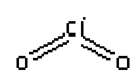
Calcium Hypochlorite ($CaCl_2O_2$)



Sodium Hypochlorite ($ClNaO$)



Chlorine Dioxide (ClO_2)



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

Calcium hypochlorite is a white solid that readily decomposes in water, releasing oxygen and chlorine. Sodium hypochlorite is a colorless, transparent liquid (DCC, Undated) that is generally used dissolved in water at various concentrations. Sodium hypochlorite solutions are clear, greenish to yellow liquids. Calcium hypochlorite and sodium hypochlorite solutions both have an odor of chlorine.

[1] Source: www.chemfinder.com

Chlorine dioxide is a yellow-green to orange gas or liquid. Production of chlorine dioxide liquid uses acids and sodium chlorite solutions to generate the chlorine dioxide. To produce chlorine dioxide gas, hydrochloric acid (HCl) or chlorine is brought together with sodium chlorite.

Additional names and chemical properties of calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are listed below in Table 1.

Table 1. Synonyms and Chemical Properties of Calcium Hypochlorite, Sodium Hypochlorite, and Chlorine Dioxide[2]

	Calcium Hypochlorite	Sodium Hypochlorite	Chlorine Dioxide
Synonym	BK Powder; Calcium hypochloride; Calcium hypochlorite; Calcium hypochlorite, dry; Calcium oxychloride; Chloride of lime; Chlorinated lime; HTH; Hy-Chlor; Hypochlorous Acid, Calcium Salt; Lime chloride; Lo-Bax; Losantin; Mildew remover X-14; Perchloron; Pittchlor	Antiformin; B-K; bleach; Carrel-dakin solution; Chloros; Chlorox; Clorox; Dakin's solution; Hychlorite; Javelle water; Javex; Liquid bleach; Mera industries 2MOM3B; Milton; Modified dakin's solution; Piochlor; Showchlon; Sodium hypochlorite; Sodium hypochlorite, 13% active chlorine; Sodium oxychloride	Alcide; Anthium dioxcide; Chlorine(IV) oxide; Chlorine oxide; Chlorine peroxide; Chloroperoxide; Chloriperoxyl; Chloryl radical; Caswell No. 179A; Doxcide 50
Trade Names	Perchloron, Clorox™, Purex, CPE00345 Pro Pure Calcium Hypochlorite, Kem Tek SHOCK	Clorox™, Purex, Javel water	---
Molecular Weight	142.9848	74.44217	67.4518
Boiling Point (˚C)	---	40	-59
Melting Point (˚C)	100	18	11
Density	2.35 (25˚C)	1.209 (25˚C)	1.642 (0˚C)
Vapor Pressure (25˚C)	7.22E-13 mmHg	---	---
Water Solubility (25˚C)	2.14E+05 mg/L	---	3.01 g/L

Reaction products of calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are listed below in Table 2. The reaction products produced in water (highlighted) are those that are produced during the disinfection process.

Table 2: Reaction Products of Calcium Hypochlorite, Sodium Hypochlorite, and Chlorine Dioxide

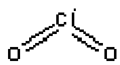
	Reaction Products Produced in Air	Reaction Products Produced in Water
Calcium Hypochlorite	Compounds commonly found in the air	Calcium, hypochlorite ions[3], and hypochlorous acid
Sodium Hypochlorite	Compounds commonly found in the air	Sodium, hypochlorite ions, and hypochlorous acid
Chlorine Dioxide	Chlorine gas and oxygen	Chlorite (50-70%) and chlorate ions

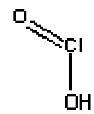
[2] Sources: www.chemfinder.com; ChemIDplus; Hazardous Substance Data Base; ATSDR

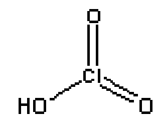
[3] An ion is an electrically charged atom or molecule.

As noted above in Table 2, chlorine dioxide forms chlorite ($ClHO_2$) and chlorate ($ClHO_3$) ions when added to water. Differences in the chemical structure of chlorine dioxide, chlorite, and chlorate are presented below.[4]

Chlorine Dioxide (ClO_2) **Chlorite** ($ClHO_2$) **Chlorate** ($ClHO_3$)







<u>Specific Uses of the Substance</u>:

Sodium and Calcium Hypochlorite

Sodium and calcium hypochlorite are chlorinated inorganic disinfectants used to control bacteria, fungi, and slime-forming algae that can cause diseases in people and animals (EPA, 1991, 1992). These disinfectants also are used in cleaning irrigation, drinking water, and other water and wastewater systems.

Chlorine Dioxide

Chlorine dioxide is an antimicrobial disinfectant and pesticide used to control harmful microorganisms including bacteria, viruses, and fungi on inanimate objects and surfaces primarily in indoor environments. It is used in cleaning water systems and disinfecting public drinking water supplies (ATSDR, 2004a). It also is used as a bleaching agent in paper and textile manufacturing, as a food disinfectant (e.g., for fruit, vegetables, meat, and poultry), for disinfecting food processing equipment, and treating medical wastes, among other uses (EPA, 2003a).

<u>Approved Legal Uses of the Substance</u>:

Chlorine materials, including calcium hypochlorite, sodium hypochlorite, and chlorine dioxide, are currently listed as synthetic substances allowed for use in organic crop production (7 CFR 205.601(a)(2)), except that residual chlorine levels in the water shall not exceed the maximum residual disinfectant limit under the Safe Drinking Water Act. EPA has set a maximum residual disinfectant level of 4 mg/L for chlorine in drinking water (EPA, 2002).

Additional legal approved uses of the substances are discussed below.

Sodium and Calcium Hypochlorite

Calcium hypochlorite and sodium hypochlorite are EPA-registered pesticides (OPP Nos. 014701 and 014703, respectively) that are used in controlling bacteria, fungi, and slime-forming algae (EPA, 1991, 1992). A Registration Standard for sodium and calcium hypochlorite was issued in February 1986 by EPA. EPA concluded that no additional scientific data were needed to register or reregister products that contain 5.25

[4] Source: www.chemfinder.com

percent to 12.5 percent sodium hypochlorite or 65 percent to 70 percent calcium hypochlorite, as long as the products contain no other active ingredients, contain no inert ingredients other than water, and bear Toxicity Category I labeling (indicating the highest degree of acute toxicity) (EPA, 1991).

Calcium hypochlorite and sodium hypochlorite are both "indirect" food additives[5] approved by FDA (http://www.cfsan.fda.gov/~dms/opa-indt.html). Sodium hypochlorite is a generally recognized as safe (GRAS) substance (40 CFR 180.2), and calcium hypochlorite is exempt from the tolerance requirement under FFDCA section 408 (40 CFR 180.1054). Calcium hypochlorite and sodium hypochlorite may be used as a final sanitizing rinse on food processing equipment (21 CFR 178.1010); sodium hypochlorite may be used in washing and lye peeling of fruits and vegetables (21 CFR 173.315). These hypochlorites also can be used in postharvest, seed, or soil treatment on various fruit and vegetable crops (EPA, 1991).

Chlorine Dioxide

EPA has registered the liquid form of chlorine dioxide for use as a disinfectant and sanitizer. The Agency also has registered chlorine dioxide gas as a sterilant. According to EPA's website, chorine dioxide was due for pesticide reregistration in 2005.

Chlorine dioxide is added to drinking water as a disinfectant in some municipal water-treatment systems in the United States. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (chlorine dioxide's oxidation product) (EPA, 2002).

According to FDA, chlorine dioxide is a direct food additive permitted in food for human consumption when it used in an amount not to exceed 3 ppm residual chlorine dioxide as an antimicrobial agent in water used in poultry processing and to wash fruits and vegetables (21 CFR 173.300).

Action of the Substance:

In water and soil, sodium and calcium hypochlorite separate into sodium, calcium, hypochlorite ions, and hydrochlorous acid molecules. Hypochlorous acid molecules are neutral and small in size. As a result, when hypochlorous acid molecules exist in equilibrium with the hypochlorite ions, they easily diffuse through the cell walls of bacteria. This changes the oxidation-reduction potential of the cell and inactivates triosephosphate dehydrogenase, an enzyme which is essential for the digestion of glucose. Inactivation of this enzyme effectively destroys the microorganism's ability to function.

Chlorine dioxide kills microorganisms directly by disrupting transport of nutrients across the cell wall.

Status

International:

Canada - Canadian General Standards Board - http://www.pwgsc.gc.ca/cgsb/032_310/32.310epat.pdf

Bleach (not exceeding 10 percent) is permitted in packaging and sanitation. Additionally, it is an acceptable agent for cleaning equipment when used in the production and processing of maple syrup.

European Economic Community (EEC) Council Regulation 2092/91 –
http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991R2092_do_001.pdf

Sodium hypochlorite (e.g., as liquid bleach) is authorized for the clearing and disinfecting of livestock buildings and installations.

[5] Indirect food additives are substances used in food-contact articles, and include adhesives and components of coatings (21 CFR Part 175), paper and paperboard components (21 CFR Part 176), polymers (21 CFR Part 177), and adjuvants and production aids (21 CFR Part 178).

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

Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical process? (From 7 U.S.C. § 6502 (21))

Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are manufactured by chemical processes. The chemical manufacturing processes for calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are described below.

Calcium Hypochlorite[6]

Calcium hypochlorite is produced by passing chlorine gas over slaked lime.[7] It is then separated from the coproduct, calcium chloride, and air dried or vacuumed.

Sodium Hypochlorite[8]

Generally, sodium hypochlorite is produced by reacting chlorine with a solution of sodium hydroxide (NaOH, also called lye or caustic soda). This method is used for most commercial productions of sodium hypochlorite. A more active, but less stable formulation of sodium hypochlorite can be produced by chlorinating a solution of soda ash (Na_2CO_3).

Chlorine Dioxide[9]

To form chlorine dioxide, sodium chlorate ($NaClO_3$) and sulfuric acid (H_2SO_4) are reacted with sulfur dioxide (SO_2), or chloric acid is reacted with methanol (CH_3OH) (HSDB, 2005). Alternatively, chlorine dioxide can be formed with chlorine (Cl_2) and sodium chlorite; sodium hypochlorite with hydrochloric acid; potassium chlorate with sulfuric acid; or by passing nitrogen dioxide through a column of sodium chlorate.

Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources? (From 7 U.S.C. § 6502 (21).)

No. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are manufactured by chemical processes. They are not extracted from naturally occurring sources.

Evaluation Question #3: Is the petitioned substance created by naturally occurring biological processes? (From 7 U.S.C. § 6502 (21).)

No. Calcium hypochlorite, sodium hypochlorite, and chlorine dioxide are all synthetic materials that are not found in nature.

Evaluation Question #4: Is there environmental contamination during the petitioned substance's manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)

Sodium and Calcium Hypochlorite

There is no information available from EPA or FDA to suggest that environmental contamination results from the proper manufacture, use, or disposal of calcium hypochlorite or sodium hypochlorite. Calcium hypochlorite and sodium hypochlorite are registered pesticides, implying that there is a potential for

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[6] Source: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
[7] Slaked lime is calcium hydroxide, a colorless crystal or white powder created when lime (calcium oxide) is reacted with water.
[8] Source: http://www.oxy.com/OXYCHEM/Products/sodium_hypochlorite/sodium_hypochlorite.htm
[9] Source: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB; Simpson et al., Unknown Date

misuse or improper disposal. However, these compounds are highly reactive and are broken down by sunlight to compounds commonly found in the air. In water and soil, sodium and calcium hypochlorite separate into sodium, calcium, hypochlorite ions, and hypochlorous acid molecules. Calcium hypochlorite and sodium hypochlorite are not bioaccumulative. Environmental effects are discussed in Evaluation Question #5.

Chlorine Dioxide

Information on chlorine dioxide available from EPA and FDA does not indicate that environmental contamination results from its proper manufacture, use, or disposal. However, during the "activation" of chlorine dioxide (i.e., activating dilute aqueous solutions of sodium chlorite with an acid to produce chlorine dioxide), the release of gas to the air or "off gassing" can be a safety hazard to users.

According to ATSDR (2004b), chlorine dioxide has not been found at any of the 1,647 current or former National Priorities List (NPL) sites that are targeted by EPA for long-term federal clean-up activities.

No information was found in the literature on concentrations of chlorine dioxide in air, sediments, or soil. In sediments and soil, concentrations of chlorine dioxide are expected to be small or not detectable due to its high reactivity (ATSDR, 2004b).

Chlorine dioxide contamination in water is difficult to identify because it is intentionally added to drinking water as a disinfectant in some municipal water-treatment systems. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (EPA, 2002). Levels of chlorite ion were sampled from drinking water distribution systems of publicly owned treatment works (POTW) facilities that utilized chlorine dioxide in the United States as part of the Information Collection Rule (ICR) in 1998; approximately 16 percent had levels of chlorite ion over the MCL of 1 mg/L (ATSDR, 2004b). Environmental effects of chlorine dioxide are listed in Evaluation Question #5.

Evaluation Question #5: Is the petitioned substance harmful to the environment? (From 7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i).)

Sodium and Calcium Hypochlorite

Although sodium and calcium hypochlorite are low in toxicity to avian wildlife, they are highly toxic to freshwater fish and invertebrates. Discharges of hypochlorite-containing wastes from facilities (i.e., point sources) are regulated through issuance of site-specific wastewater discharge permits intended to ensure that the amount of hypochlorites discharged will not pose a significant adverse effect to wildlife (EPA, 1991). Additionally, current NOSB approval is conditioned on residual chlorine levels in the water not exceeding the limit set by the Safe Drinking Water Act (4 mg/L).

When released to water or soil, one of the reaction products of sodium and calcium hypochlorite is hypochlorite ions. When mixed with organic materials (e.g., dirt), hypochlorite produces trihalomethanes (THMs)[10], which are carcinogenic (http://www.epa.gov/safewater/hfacts.html). Currently, the maximum contaminant level (MCL) for total THMs is 0.080 mg/L (http://www.epa.gov/safewater/hfacts.html).

Because sodium hypochlorite has the potential to raise soil pH and add sodium to the soil, it should not be used as an herbicide. Additionally, an experimental application of sodium hypochlorite directly to the leaves of eight species of foliage plants caused severe necrosis, chlorosis, and leaf abscission following a single application (HSDB, 2005).

[10] Trihalomethanes (THMs) are a group of four chemicals (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) that are formed along with other disinfection reaction products when chlorine or other disinfectants used to control microbial contaminants in drinking water react with naturally occurring organic and inorganic matter in water.

Chlorine Dioxide

Chlorine dioxide is a very reactive compound and breaks down quickly in the environment (ATSDR, 2004a). In air, sunlight rapidly causes chlorine dioxide to break down into chlorine gas and oxygen. When used as a disinfecting agent, however, the product of chlorine dioxide is primarily chlorite. Although chlorite in water may move into groundwater, reactions with soil and sediments may reduce the amount of chlorite reaching groundwater. The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Toxic reaction products are not known to occur when chlorite is mixed with organic materials. EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (EPA, 2002).

Evaluation Question #6: Is there potential for the petitioned substance to cause detrimental chemical interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518 (m) (1).)

Sodium and Calcium Hypochlorite

There is insufficient data to determine whether calcium hypochlorite or sodium hypochlorite have detrimental chemical interactions with other substances used in organic crop or livestock production. In water and soil, one reaction product of sodium and calcium is hypochlorite ions. These ions may react with other substances found in the water and soil. For example, hypochlorite when mixed with organic materials (e.g., dirt), creates THMs, which are carcinogenic. Currently, the maximum contaminant level (MCL) is 0.080 mg/L for total THMs (http://www.epa.gov/safewater/hfacts.html).

However, the potential for these chemical interactions to detrimentally affect other substances used in organic crop or livestock production depends on the concentrations of the chemicals and their breakdown products in irrigation water discharged from treated systems. No information is currently available on the post-treatment concentrations of these chemicals. The amount of calcium hypochlorite or sodium hypochlorite must be limited, however, so that flush water from cleaning irrigation systems does not exceed the maximum residual disinfectant limit of chlorine under the Safe Drinking Water Act (i.e., 4 mg of chlorine/L).

Chlorine Dioxide

Data are not sufficient to determine whether detrimental chemical interactions involving chlorine dioxide in organic crop or livestock production result from the proposed use as a cleaner for irrigation systems. When used as a disinfecting agent, chlorine dioxide reacts with organic and inorganic compounds in water, and 50-70% is converted to chlorite (EPA, 1999a). The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Toxic reaction products are not known to occur when chlorite is mixed with organic materials. Additionally, EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L of chlorite (EPA, 2002). Consequently, if the oxidant demand is greater than about 1.4 mg/L, chlorine dioxide may not be used as a disinfectant because the chlorite/chlorate ions reaction product might exceed the maximum level allowed, unless inorganic reaction products (e.g., chlorite) are subsequently removed (EPA, 1999a).

Evaluation Question #7: Are there adverse biological or chemical interactions in the agro-ecosystem by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

Calcium Hypochlorite or Sodium Hypochlorite

There is insufficient data to determine whether the proposed use of calcium hypochlorite or sodium hypochlorite causes chemical or biological interactions in the agro-ecosystem. Although calcium hypochlorite and sodium hypochlorite have the potential to kill soil microbes, as well as react with chemicals in the soil, there is not enough information on the concentration of the chemicals or the reaction products coming from the treated system to quantify the impact. One reaction product of sodium or calcium hypochlorite, when dissolved water or soil, is the hypochlorite ion. Hypochlorite ions may react with other substances found in the water and soil. For example, hypochlorite mixed with organic materials (e.g., dirt), creates THMs, which are carcinogenic (http://www.epa.gov/safewater/hfacts.html). However, the amount of calcium hypochlorite or sodium hypochlorite should be limited so that flush water from cleaning irrigation systems does not exceed 4 mg of chlorine/L, thereby limiting the level of trihalomethanes. Currently, the maximum contaminant level (MCL) for total THMs is 0.080 mg/L (http://www.epa.gov/safewater/hfacts.html).

Chlorine Dioxide

Data are not sufficient to determine whether adverse chemical or biological interactions in the agro-ecosystem result from the proposed use of chlorine dioxide in organic crop production. When used as a disinfecting agent, chlorine dioxide reacts with organic and inorganic compounds in water, and 50-70% of chlorine dioxide is converted to chlorite (EPA, 1999a). Although chlorite in water may move into groundwater, reactions with soil and sediments may reduce the amount of chlorite reaching groundwater. The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Toxic reaction products are not known to occur when chlorite is mixed with organic materials. Additionally, EPA has set a maximum contaminant level (MCL) of 0.8 mg/L for chlorine dioxide in drinking water and 1 mg/L for chlorite (EPA, 2002). Consequently, if the oxidant demand is greater than about 1.4 mg/L, chlorine dioxide may not be used as a disinfectant because the chlorite/chlorate ions reaction product might exceed the maximum level allowed, unless inorganic reaction products (e.g., chlorite) are subsequently removed (EPA, 1999a).

Evaluation Question #8: Are there detrimental physiological effects on soil organisms, crops, or livestock by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

When used as an irrigation system cleanser, calcium hypochlorite, sodium hypochlorite, and chlorine dioxide would not be expected to have any detrimental physiological effects on soil organisms, crops, or livestock. If used properly, bleach materials will have little contact with soil organisms, crops, or livestock. Additionally, these bleach materials are highly reactive and break down very quickly. Current NOSB approval is conditioned on residual chlorine levels in the water not exceeding the limit set by the Safe Drinking Water Act (4 mg/L). If misused, however, sodium hypochlorite may possibly raise soil pH and add sodium to the soil. Additionally, sodium hypochlorite may also be phytotoxic; an experimental application of sodium hypochlorite directly to the leaves of eight species of foliage plants caused severe necrosis, chlorosis, and leaf abscission following a single application (HSDB, 2005). Other detrimental effects of misuse include the killing of beneficial microorganisms.

Evaluation Question #9: Is there a toxic or other adverse action of the petitioned substance or its breakdown products? (From 7 U.S.C. § 6518 (m) (2).)

Calcium Hypochlorite or Sodium Hypochlorite

Based on acute exposure studies, the oral LD_{50} value (i.e., the concentration at which at least 50 percent of the test organisms die) of sodium hypochlorite in rats is 8,910 mg/kg, and the oral LD_{50} value in mice is 5,800 mg/kg (HSDB, 2005). The oral LD_{50} value of calcium hypochlorite in rats is 850 mg/kg (HSDB, 2005). Hypochlorous acid and hypochlorite ions are highly toxic and corrosive, and EPA has placed them in Toxicity Category I (indicating the highest degree of acute toxicity) for oral, dermal, eye, and inhalation effects (EPA, 1999b).

As stated in sections above, hypochlorite, a breakdown product of calcium hypochlorite and sodium hypochlorite, when mixed with organic materials (e.g., dirt), forms trihalomethanes, which are carcinogenic (http://www.epa.gov/safewater/hfacts.html). There is a slightly increased risk of developing bladder or colorectal cancer over a lifetime if trihalomethanes are ingested in excess of the current drinking water limits over an extended period of time. EPA has ruled that concentrations of trihalomethanes in water should be less than 80 parts per billion (ppb).

Calcium hypochlorite and sodium hypochlorite are highly caustic and are a concern for occupational exposures. Acute exposure to high concentrations can cause eye and skin injury. These toxic effects are primarily due to the corrosive properties of hypochlorite. Ingestion of small quantities of household bleaches (3-6% hypochlorite) may lead to gastrointestinal irritation. Ingestion of more concentrated commercial bleach (10% or higher hypochlorite) or hypochlorite powder may result in corrosive injuries to the mouth, throat, esophagus, and stomach with bleeding, perforation, and eventually death. Permanent scars and narrowing of the esophagus may occur in survivors of severe intoxication (ATSDR, 2002; EPA, 1991).

Inhalation of chlorine gas released from concentrated hypochlorite solutions may cause nasal irritation, sore throat, and coughing. Contact with strong hypochlorite solutions may cause burning pain, inflammation, and blisters to the skin. Mild bleach solutions may cause slight transitory irritation if they come in contact with the eye, while more concentrated solutions may cause severe injuries. Long-term exposure to low levels of hypochlorite can cause dermal irritation (ATSDR, 2002).

There is no evidence that exposure to calcium hypochlorite or sodium hypochlorite causes reproductive effects (ATSDR, 2002).

Chlorine Dioxide

Chlorine dioxide is a severe respiratory and eye irritant in experimental animals. The oral LD_{50} value of chlorine dioxide in rats is 292 mg/kg (HSDB, 2005). Similar effects (as discussed below) are observed in humans. The reaction products of chlorine dioxide when used as a disinfectant are chlorite (50-70%) and chlorate. The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Additional toxic effects of chlorite include mild neurobehavioral effects observed in rat pups exposed to 5.6 mg/kg/day (INCHEM, 2002). The toxicity of chlorate is similar to that of chlorite, but chlorate is less effective at inducing oxidative damage (INCHEM, 2002).

With regard to human toxicity, the RfD (reference dose[11]) for chlorine dioxide is 3×10^{-2} mg/kg-day. This value is based on two-generation reproductive toxicity study in rats exposed to chlorine dioxide via drinking water. The study was conducted by the Chemical Manufacturers Association. Results indicate that neurodevelopmental effects occurred at 3 mg/kg-day (i.e., 35 ppm sodium chlorite). An uncertainty factor of 100 was used in determining the RfD to account for uncertainties associated with interspecies extrapolation (i.e., differences between rats and humans) and intrahuman variability (i.e., differences between an average size adult male and sensitive subpopulations such as elderly, children, or immune compromised) (EPA, 2000).

The RfC (reference concentration[12]) for chlorine dioxide is 2×10^{-4} mg/m^3. This value is based on a 60-day rat inhalation study conducted by Paulet and Desbrousses in 1972. The critical effect observed in this study was vascular congestion and peribronchial edema, which occurred at concentrations as low as 2.76 mg/m^3 (human equivalent concentration of 0.64 mg/m^3). An uncertainty factor of 3,000 was applied to account for extrapolation from a subchronic study (i.e., less than lifetime), interspecies extrapolation (i.e., differences between rats and humans), intrahuman variability (i.e., differences between an average size adult male and

[11] RfD: "An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in EPA's noncancer health assessments." (EPA, 2005)

[12] RfC: "An estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark concentration, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in EPA's noncancer health assessments." (EPA, 2005)

sensitive subpopulations such as elderly, children, or immune compromised), and the overall small database of inhalation studies (such as the lack of inhalation developmental and reproductive toxicity studies) (EPA, 2000).

According to ATSDR, inhalation of chlorine dioxide gas may cause nose, throat, and lung irritation. There is no evidence that chlorine dioxide causes reproductive effects in humans (ATSDR, 2004a).

There are no studies on cancer in humans exposed to chlorine dioxide. Chlorine dioxide is currently classified by EPA as a Group D carcinogen, which means that there is inadequate data in humans and animals to determine whether it is a human carcinogen (EPA, 2000). Animal studies have shown mixed results. Concentrates prepared from drinking water treated with chlorine dioxide did not increase the incidence of lung tumors or skin tumors in mice or the incidence of precancerous changes in rat livers (Miller et al., 1986); however, chlorine dioxide did induce a hyperplastic response (an abnormal increase in the number of the cells) in mouse skin (Robinson et al., 1986). Additionally, tests designed to show whether chemicals interact with DNA or damage chromosomes (a sign that a chemical could cause cancer) have given both negative and positive results. The International Agency for Research on Cancer (IARC) also has determined that chlorine dioxide is not classifiable as to human carcinogenicity (ATSDR, 2004a).

Evaluation Question #10: **Is there undesirable persistence or concentration of the petitioned substance or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)**

Neither calcium hypochlorite nor sodium hypochlorite is persistent in the environment. When released to air, these substances are broken down by sunlight to compounds commonly found in the air. In water and soil, sodium and calcium hypochlorite separate into sodium, calcium, and hypochlorite ions (ATSDR, 2002). These ions may react with other substances found in the water. Due to the wide variety of compounds formed, it is difficult to make generalizations about the persistence of these breakdown products.

Chlorine dioxide is not persistent in the environment. Chlorine dioxide is a very reactive compound and breaks down quickly. In air, sunlight rapidly causes chlorine dioxide to break down into chlorine gas and oxygen (ATSDR, 2004a). When used as a disinfectant, chlorine dioxide primarily breaks down quickly and forms chlorite (50-70%) and chlorate (EPA, 1999a). Although chlorite in water may move into groundwater, reactions with soil and sediments may reduce the amount of chlorite reaching groundwater (ATSDR, 2004a). The toxic action of chlorite is primarily in the form of oxidative damage to red blood cells at doses as low as 10 mg/kg of body weight. Toxic reaction products are not known to occur when chlorite is mixed with organic materials. Neither chlorine dioxide nor chlorite builds up in the food chain (ATSDR, 2004a).

Evaluation Question #11: **Is there any harmful effect on human health by using the petitioned substance? (From 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).)**

Calcium Hypochlorite or Sodium Hypochlorite

Potential human health effects due to calcium hypochlorite or sodium hypochlorite use as an irrigation cleanser occur dermally or via inhalation. Contact with strong hypochlorite solutions may cause burning pain, inflammation, and blisters to the skin. Mild bleach solutions may cause mild and transitory irritation when they come in contact with the eye, while more concentrated solutions may cause severe injuries. Long-term exposure to low levels of hypochlorite can cause dermal irritation (ATSDR, 2002). Inhalation of chlorine gas released from concentrated hypochlorite solutions may cause nasal irritation, sore throat, and coughing.

Chlorine Dioxide

Inhalation and dermal exposure are the main routes of concern for human exposure when chlorine dioxide is used as a cleanser for irrigation systems. Chlorine dioxide is a severe respiratory and eye irritant.

According to the Occupational Safety and Health Administration (OSHA), inhalation can produce coughing, wheezing, respiratory distress, and congestion in the lungs. Irritating effects in humans were intense at concentration levels of 5 ppm. OSHA has set a limit of 0.1 parts of chlorine dioxide or chlorite per million parts of air (0.1 ppm) in the workplace during an 8-hour shift, 40-hour workweek (http://www.osha.gov/SLTC/healthguidelines/chlorinedioxide/recognition.html).

Evaluation Question #12: Is there a wholly natural product which could be substituted for the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)

Citric acid or other acids (e.g., acetic acids, ascorbic acid, citric acid, and vinegar) could be substituted for bleach materials. Natural acids eliminate the growth of pathogens because many pathogens cannot grow at pH levels below 4.5. Additionally, natural acids may possess bactericidal capabilities by: reducing the pH; disrupting the membrane transport, permeability, and/or anion accumulation; or reducing internal cellular pH by the dissociation of hydrogen ions from the acid (Parish et al., 2003). Many types of produce, especially fruit, naturally possess significant concentrations of organic acids such as acetic, benzoic, citric, malic, sorbic, and succinic acids. Citric acid is used as a drip irrigation cleaner, equipment cleaner, chelating agent, and pH adjuster. Citric acid is biodegradable and considered environmentally safe. According to the NOP Regulations (205.605(a)), nonorganic citric acid used as an ingredient in or on processed products labeled as "organic" or "made with organic" must be produced by microbial fermentation of carbohydrate substrates.

Evaluation Question #13: Are there other already allowed substances that could be substituted for the petitioned substance? (From 7 U.S.C. § 6518 (m) (6).)

The following substances could be substituted for chlorine materials:

- **Hydrogen peroxide:** Hydrogen peroxide is an oxidizing agent that is widely used as a disinfectant due to its reactive properties. The oxidizing potential of hydrogen peroxide is greater than chlorine or chlorine dioxide. In home-use formulations, hydrogen peroxide diluted to between three and ten percent is used medicinally as a cleanser for cuts and scrapes, whereas industrial uses involve more concentrated solutions (30 percent or greater). In 1977, EPA registered hydrogen peroxide as an antimicrobial pesticide approved only for indoor use on hard surfaces. Use sites include agricultural premises, food establishments, medical facilities, and home bathrooms. Hydrogen peroxide is registered for use in dairy/cheese processing plants, on food processing equipment and in pasteurizers in breweries, wineries, and beverage plants (EPA, 2003b). Unlike other chemical substance, hydrogen peroxide does not produce residues or gasses; however, high concentrations of hydrogen peroxide are required for disinfection. Additionally, hydrogen peroxide reacts with numerous substances and slowly decomposes into water and oxygen.

- **Ozone:** Ozone is produced by dissociating oxygen molecules into oxygen atoms through an energy source and subsequently colliding those atoms with oxygen molecules. Ozone is used in wastewater treatment and is generated by imposing a high voltage alternating current (6 to 20 kilovolts) across a dielectric discharge. Ozone is a powerful oxidant, and it reacts with most toxic organics. Ozone reacts with organic molecules in many ways, for example by: inserting oxygen into a benzene ring; breaking double bonds to form aldehydes and ketones; and reacting with alcohol to form organic acids. The following are advantages to using ozone: ozone is more effective than chlorine in destroying viruses and bacteria; the ozonation process utilizes a short contact time (approximately 10 to 30 minutes); there are no harmful residuals produced because ozone decomposes rapidly; there is no regrowth of microorganisms, except for those protected by the particulates; there are fewer safety problems associated with shipping and handling because ozone is generated on-site; ozonation elevates the dissolved oxygen concentration of the effluent, which in turn may eliminate the need for reaeration and also raise the level of dissolved oxygen in the receiving stream (EPA, 1999c).

> The following are disadvantages to using ozone: low dosage may not effectively inactivate some viruses, spores, and cysts; ozonation is a more complex technology than is chlorine or UV disinfection, requiring complicated equipment and efficient contacting systems; ozone is very reactive and corrosive; ozonation is not economical for wastewater with high levels of suspended solids, biochemical oxygen demand, chemical oxygen demand, or total organic carbon; ozone is extremely irritating and possibly toxic, so off-gases must be eliminated to prevent worker exposure; and the cost of treatment can be relatively high in capital and power intensiveness (EPA, 1999c).

Additional substances that could be substituted for bleach materials in organic crop production include the following: alcohols; ethanol; isopropanol; copper sulfate[13]; peracetic acid--for use in disinfecting equipment, seed, and asexually propagated planting material; and soap-based algicide/demossers (http://www.ams.usda.gov/nop/NOP/standards/ListReg.html).

Evaluation Question #14: Are there alternative practices that would make the use of the petitioned substance unnecessary? (From 7 U.S.C. § 6518 (m) (6).)

Steam sterilization is an alternative practice to bleach materials for cleansing equipment. Sterilization by steam under pressure is a simple process that exposes the product to dry saturated steam at the desired temperature and pressure. Generally, this process is carried out in a pressure vessel or retort designed to withstand the high temperature and pressure. To be effective at killing pathogens, uniform temperature distribution is needed (http://www.engineeringreference.com/Sterilization/select%20sterilization.htm). Although steam sterilization is an alternative practice, it is not very practical for cleaning irrigation systems.

UV radiation (generated from a special lamp) effectively destroys bacteria and viruses. A secondary disinfectant must be used to prevent regrowth of microorganisms. UV radiation can be attractive as a primary disinfectant for small systems because it is readily available, it produces no known toxic residuals, it requires short contact times, and the equipment is easy to operate and maintain. As with steam sterilization, UV radiation is not very practical for cleaning irrigation systems.

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[13] Copper sulfate (for use as an algicide in aquatic rice systems) is limited to one application per field during any 24-month period. Application rates are limited to those that do not increase baseline soil test values for copper over a timeframe agreed upon by the producer and accredited certifying agent.

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