Sodium Carbonate Peroxyhydrate

Crops

Identification of Petitioned Substance

Chemical Names:
Sodium carbonate peroxyhydrate

Other Name:
Sodium carbonate peroxide
Sodium percarbonate
PCS
Disodium carbonate, compound with hydrogen peroxide (2:3)
Carbonic acid disodium salt, compound with Hydrogen peroxide (H_2O_2—2:3)
Peroxy sodium carbonate
Hydrogen peroxide sodium carbonate adduct

Trade Names:
Oxyper
Perdox
FB Sodium Percarbonate
Provox S
GreenClean Pro Granular Algaecide
TerraCyte
ECOX
PAK 27 Algaecide
Technical sodium carbonate peroxyhydrate
Phycomycin

CAS Numbers:
15630-89-4

Other Codes:
128860 (US EPA PC Code)
70299-3, 70299-4, 70299-6, 68660-8, 68660-9 US EPA Product Registration Numbers
InChlKey MSLRPWGRFCKNIZ-UHFFFAOYSA-J
PubChemIS 159762

Summary of Petitioned Use

Sodium carbonate peroxyhydrate is currently on the National List as:

§ 205.601 Synthetic substances allowed for use in organic crop production.
(a) As algaecide, disinfectants, and sanitizer, including irrigation system cleaning systems,
(8) Sodium carbonate peroxyhydrate (CAS #-15630-89-4)—Federal law restricts the use of this substance in food crop production to approved food uses identified on the product label.

As required by the Organic Foods Production Act, the National Organic Standards Board has the responsibility to review each substance on the National List within five years of its adoption to determine whether the substance should be renewed or removed from the National List. The NOSB has requested an updated technical evaluation report for sodium carbonate peroxyhydrate to support their decision-making.

The current listing for sodium carbonate peroxyhydrate is scheduled to sunset on 12/14/2015.

Characterization of Petitioned Substance

Composition of the Substance:

Sodium carbonate peroxyhydrate is the chemical name for an addition product produced by drying hydrogen peroxide in the presence of sodium carbonate (CAS No. 497-19-8). The pure substance contains 32.5 % hydrogen peroxide and 67.5 % sodium carbonate (based on weight). It combines dual properties of sodium carbonate and hydrogen peroxide, providing significant benefits when alkalinity and bleaching is required. Sodium carbonate peroxyhydrate is a white crystalline powder with a purity of > 85 % (Czerczak, 2005). Both shipment and storage are facilitated by this solid form when compared to requirements for liquid hydrogen peroxide solutions. Its molecular structure is depicted in Fig 1.

Source or Origin of the Substance:

Hydrogen peroxide is a natural photochemical product formed in waters under sunlight (Drabkova, 2007). Hydrogen peroxide is also available as a synthetic product manufactured internationally by a number of companies using the Riedl-Pfleiderer or anthraquinone process. This process was formalized in 1936 and patented in 1939, and involves the autoxidation of a 2-alkyl anthrahydroquinone (or 2-alkyl-9,10-dihydroxyanthracene) to the corresponding 2-alkyl anthraquinone (Campos-Martin et al., 2006; Riedl and

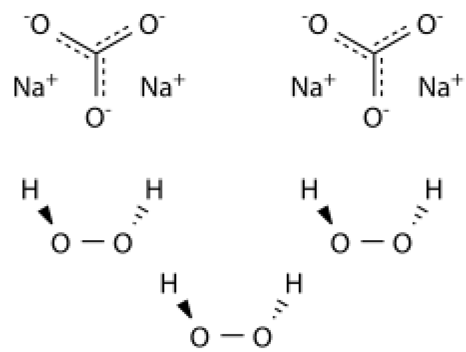

Fig. 1 Molecular Structure of Sodium Carbonate Peroxyhydrate

Pfleiderer, 1936). Sodium carbonate or soda ash is found naturally in plants; however, it has been produced synthetically with various alkaline salts and limestone by multiple chemical processes (Keifer, D., 2002). Sodium carbonate peroxyhydrate is also manufactured at a number of production sites throughout the world, but mostly by two large international chemical companies, Solvay Chemicals and OCI Chemicals. It is marketed under a number of different trade names, e.g. OxiClean, TerraCyte, PAK 27, GreenClean and Oxypers. OxiClean is a well-known product used in the laundry industry for stain removal.

Properties of the Substance:

Sodium carbonate peroxyhydrate is a white granular, crystalline powder. It is an oxidizing agent containing an equivalent available peroxygen content of ca. 28% hydrogen peroxide, combined with sodium carbonate as a source of alkalinity. Sodium carbonate peroxyhydrate rapidly dissolves in water and dissociates into hydrogen peroxide and sodium carbonate. It decomposes to leave only water, oxygen, and soda ash (Czerczak, 2005; Solvay, 2013b; Solvay, S.A., 2002). The chemical identity and several physical/chemical properties are summarized in Table 1.

Table 1. Properties	
Chemical Formula	$2Na_2CO_3 \cdot 3H_2O_2$
Molecular Weight	314.06
Available Oxygen	min. 13 %
Bulk Density	900 -1200 kg/m^3
Mean Diameter (grade dependent)	300 - 900 µm
Solubility at 20^{o}C	ca. 150 g/l
Solubility at 30^{o}C	ca. 175 g/l
pH (1.5% solution)	10.4 - 10.6

Specific Uses of the Substance:

For applications where the use of liquid hydrogen peroxide is impractical, sodium carbonate peroxyhydrate provides the same oxidative/reductive action of hydrogen peroxide in a solid form making it an easy to use source of hydrogen peroxide for environmental control (Solvay, 2013b). Upon contact with water sodium carbonate peroxyhydrate breaks down into sodium carbonate and hydrogen peroxide. Hydrogen peroxide acts as both a chemical oxidant and reducing agent, as a supplier of molecular oxygen and acts to inhibit undesirable microbial growth including algae, bacteria, mosses, molds, slime molds and liverworts.

Sodium carbonate peroxyhydrate is also used as a bleaching chemical in laundry detergents, laundry additives and machine dishwashing products. The pure product is also available for consumers as a laundry additive. Sodium carbonate peroxyhydrate may also be used in products for drain cleaning, multipurpose cleaning or for denture cleansing (Solvay, S.A., 2002).

Approved Legal Uses of the Substance:

In its primary registration by the US Environmental Protection Agency (EPA) as a biopesticide, use sites for sodium carbonate peroxyhydrate include ornamental plants, turf grasses, terrestrial landscapes, commercial greenhouses, garden centers, nurseries and storage areas. Target pests included algae, moss, liverworts, slime molds and their spores. There was no food use authorized. The granular product is applied by a lawn spreader or other application method to ensure uniform coverage (EPA, 2002a, 2002b, 2002c).

The proposed rule by the USDA National Organic Program, published June 3, 2009 accepting NOSB's recommendation to add sodium carbonate peroxyhydrate to the National List stated the EPA had registered products containing the technical grade of the active ingredient sodium carbonate peroxyhydrate for applications in aquaculture, rice/wild rice fields and paddies, turf grasses, terrestrial landscapes, as well as commercial greenhouses, nurseries and garden centers (NOP, 2009). The rule also described consultations between NOP and EPA leading to EPA's explanation and NOP's restriction requiring applications in organic food crop production to be consistent with the approved food uses that are identified on the EPA approved product labels for algaecides containing sodium carbonate peroxyhydrate. Recently, the product label for sodium carbonate peroxyhydrate was updated and directed its use for control of blue-green algae in lakes, ponds, drinking water reservoirs, irrigation, drainage and conveyance ditches, canals, laterals, estuaries, bayous, lagoons, water gardens and water features, impounded water and waste water, and aquaculture (EPA, 2004, 2005, 2006, 2012). Both the consultation endeavored by NOP and recent label update provide additional evidence that use of this product in rice/wild rice fields and paddies is consistent with EPA approved label instructions.

Action of the Substance:

Sodium carbonate peroxyhydrate is a solid peroxygen compound with excellent storage stability and no shock sensitivity serving as a source of H_2O_2 in solution. Hydrogen peroxide produces a reactive oxygen species or free radical characterized by the production of unpaired valence electrons. Oxygen radicals are highly reactive and have the ability to damage cellular macromolecules including lipids, proteins and nucleic acids (MEDP, 2005). For example in lipid peroxidation, oxygen radicals react with unsaturated fatty acids in cell membrane phospholipids, sequentially damaging them and killing the cell in a chain reaction process. Oxygen radicals also react with other fatty acids, nucleic acids, and proteins in a similar manner.

Combinations of the Substance:

Most preparations of sodium carbonate peroxyhydrate are prepared with additional sodium carbonate (13%) and can be coated with sodium silicate (CAS No. 1344-09-8) at a concentration of 1.5% (Solvay Chemicals, 2013). Other chemicals may be present as contaminants. Inert chemical may be added to stabilize this product for specific purposes such as its use in detergents and cleaning products including sodium chloride, sodium sulfate, magnesium sulfate, lithium sulfate, sodium hexametaphosphate and borate (Solvay, 2002). According to the EPA, disclosure of these inert substances in pesticides is not required. Combinations of product are generally not recommended by the manufacturers. Combinations should be evaluated for safety and effectiveness prior to use.

Status

Historic Use:

Sodium carbonate peroxyhydrate has been used in organic production as an algaecide, sanitizer and disinfectant since its addition to the National List in 2010. There are no food uses for this product.

Organic Foods Production Act, USDA Final Rule:

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International

Canada - Canadian General Standards Board Permitted Substances List –

Hydrogen peroxide is on the Canadian Organic Production Systems Permitted Substances Lists (CAN/CGSB-32.311-2006). It is listed for use as a fungicide. Sodium carbonate (soda ash) is considered a natural substance in the Canadian system. Sodium carbonate peroxyhydrate is not included in any of the Canadian permitted substance lists.

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labeling and Marketing of Organically Produced Foods (GL 32-1999) - ftp://ftp.fao.org/docrep/fao/005/Y2772e/Y2772e.pdf

Although Codex Alimentarius permits the use of sodium carbonate peroxyhydrate as an anti-bactericide in raw milk, it is not included in any list for organic use (Codex Alimentarius, 1991). The Joint FAO/WHO Expert Committee on Food Additives has also studied the use of hydrogen peroxide as an antimicrobial washing solution (JECFA, 2004).

European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008
http://www.organic-world.net/news-eu-regulation.html
http://eur-lex.europa.eu/LexUriServ/site/en/oj/2007/l_189/l_18920070720en00010023.pdf

Both sodium carbonate and hydrogen peroxide are listed in Commission regulation (EC) No 889/2008 and are permitted for use in cleaning and disinfection of buildings and installations for animal production. Sodium carbonate peroxyhydrate is not listed as a permitted substance for organic production. The EFSA has recently issued the opinion on the use of sodium carbonate peroxyhydrate as a combined oxygen generator and carbon dioxide absorbed in packaging containing whole fresh fruits that there is no safety concern (EFSA, 2013).

Japan Agricultural Standard (JAS) for Organic Production—
http://www.ams.usda.gov/nop/NOP/TradeIssues/JAS.html

Sodium carbonate peroxyhydrate, hydrogen peroxide and sodium carbonate are not specifically listed in the Japanese Agricultural Standard for Organic Plants (Notification No. 1605 of the Ministry of Agriculture, Forestry and Fisheries of October 27, 2005).

International Federation of Organic Agriculture Movements (IFOAM)

Sodium carbonate peroxyhydrate is not listed or discussed for use in the IFOAM norms (IFOAM, 2012). However, both hydrogen peroxide and sodium carbonate are listed as disinfectants.

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

<u>Evaluation Question #1: Indicate which category in OFPA that the substance falls 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?

Sodium carbonate peroxyhydrate is also listed by the US Environmental Protection Agency (EPA) as sodium percarbonate. It does not fall under an OFPA category. Nor is it classified as an EPA inert substance. Sodium carbonate peroxyhydrate is described in an EPA biopesticides registration action document under code PC 128860 (EPA, 2002b) for use as an algaecide, fungicide for the prevention and control of horticultural diseases in commercial greenhouses, garden centers, landscapes, nurseries, and interiorscapes. In 2004, it was approved as an algaecide with claims for control of blue-green algae in lakes, ponds and drinking water reservoirs (EPA, 2004a). Since that time the label has been updated (EPA, 2005, 2006, 2012)

<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)).

Sodium carbonate peroxyhydrate is manufactured by reacting sodium carbonate with hydrogen peroxide: $Na_2CO_3 + 1.5\ H_2O_2 \dashrightarrow Na_2CO_3 \cdot 1.5H_2O_2$ by the following processes (Czerczak, 2005):

1) The dry process involves spraying an aqueous stabilized hydrogen peroxide solution on solid sodium carbonate with continuous agitation. A solid-liquid reaction yields sodium carbonate peroxyhydrate. Completion of the reaction is followed by cooling and after which a dry, free flowing powder is obtained.

2) In the spray granulation process, solutions of sodium carbonate and aqueous stabilized hydrogen peroxide are sprayed onto a bed of sodium carbonate peroxyhydrate nuclei in a fluid-bed granulator. The product bed is kept in movement by a stream of heated air. Product is continuously withdrawn from the dryer and the desired grain-size fraction is obtained by classification. The fines and ground oversize are recycled to the fluid-bed granulator as nuclei.

3) The crystallization process takes advantage of the high solubility of sodium carbonate peroxyhydrate. In this method, sodium carbonate peroxyhydrate is salted out of aqueous solutions with sodium chloride. A sodium carbonate/NaCl suspension is reacted with stabilized hydrogen peroxide under stirring and cooling. The crystallized sodium carbonate peroxyhydrate is separated from the mother liquor by centrifugation, and drying in a fluid-bed dryer.

Because they are subject to free radical formation when exposed to moisture, sodium carbonate peroxyhydrate products are often coated with single or multiple layers of hydrophobic substances in order to improve stability and increase storage time. Examples of these coatings are fats, waxes, or phosphatides; surfactants dissolved in a hydrophobic liquid; disilicate combined with a chelating agent, such as glutaric acid, pimelic acid, citric acid, or dicarboxylic acid, and inorganic compounds selected from alkalai, and alkaline earth metal carbonates, sulphates, chlorides and nitrates (HERA, 2002; Yun and Baoguo, 2004).

<u>Evaluation Question #3:</u> 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)).

Sodium carbonate peroxyhydrate is manufacture by a chemical process from two components sodium carbonate and hydrogen peroxide. Sodium carbonate is a naturally occurring mined mineral salt. It is also called soda ash. It can be manufactured from limestone and sodium chloride by a method referred to as the Solvay process. Although present naturally in small quantities, hydrogen peroxide is synthetically manufactured from anthracene. Sodium carbonate peroxyhydrate a combination product consisting of sodium carbonate and hydrogen peroxide is manufactured synthetically by one three commercial processes, 1) dry process, 2) spray granulation process or 3) crystallization process.

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

Sodium carbonate peroxyhydrate may be released into the environment during its production and formulation, as a result of the use of household cleaning products, and through its use in agriculture as an algaecide or fungicide. In water, sodium carbonate peroxyhydrate rapidly dissociates into hydrogen peroxide and sodium carbonate. Hydrogen peroxide will be further degraded and sodium carbonate will be neutralized to sodium bicarbonate ($NaHCO_3$).

$$2Na_2CO_3 \cdot 3H_2O_2 \rightarrow 4\ Na^+ + 2\ CO_3{}^{2-} + 3\ H_2O_2$$

The half-life for this process is approximately eight hours. Hydrogen peroxide, a reactive substance in the presence of other substances, elements, radiation, materials or cells is normally short-lived in the environment. Both sodium and inorganic carbonate have a wide natural occurrence. Although basic in pH, release of sodium carbonate into water or soil will not usually result in an increase in alkalinity, because most natural waters and soils contain buffering systems (Ponnamperuma, 1972).

Anthracene, a polycyclic aromatic hydrocarbon (PAH), is used in the production of hydrogen peroxide (Pope and Slotnick, 1982). Anthracene is produced from coal tar. PAHs are known to be potentially persistent pollutants (USGS, 1982).

Sodium carbonate or soda ash is produced by one of two industrial methods. Both methods are very similar, differing only in the recovery stage in primary treatment of the raw material used. The principal emissions are particulates, and emissions from combustion such as carbon monoxide, nitrogen oxides, sulfur dioxide and carbon dioxide occur from direct-fired process heating units such as ore calcining kilns and soda ash dryers. Remediation measures include venturi scrubbers, electrostatic precipitators, and/or cyclones.

<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)).

Sodium carbonate peroxyhydrate rapidly dissociates into hydrogen peroxide and sodium carbonate. Hydrogen peroxide is the active component. Hydrogen-peroxide-based products work by exogenously oxidizing organic matter. However, because hydrogen peroxide is a natural byproduct of cell metabolism, present at a low level in all living cells, and secreted by some bacteria, living organisms are naturally subject to oxidative damage from both exogenous and endogenous hydrogen peroxide (Apel and Hirt, 2004). In their defense, living cells are naturally protected from endogenous hydrogen peroxide by an antioxidant protection system composed of three enzymes: superoxide dismutase, catalase and glutathione peroxidase. Moreover two vitamins, vitamin C and vitamin E also serve as intracellular antioxidant scavengers (MDEP, 2010). Expression and utilization of these enzymes and vitamins varies between species. As a result, some species are better protected from oxidative damage than others. Thus, sodium carbonate peroxyhydrate may differentially kill some algal, protist or bacterial species while permitting the survival or even the enhancement of others (White et al., 1998; .Schrader et al., 1998; Matthijs et al., 2012).

Sodium carbonate peroxyhydrate is predominantly used for disinfection and water treatment. It has become an important tool in the selective removal of toxic or nuisance cyanobacteria, mold and scum in bodies of water and recently rice paddies. Cyanobacteria are prokaryotic, and lacking organelles for photosynthesis appear to be more sensitive to hydrogen peroxide than other species of phytoplankton, such as green algae or diatoms (Drabkova et al., 2007). Sodium carbonate peroxyhydrate completely inhibits the growth of *Oscillatoria cf. chalybea*, while it does not affect the green algae, *Selenastrum* *capricornutum* (Schrader et al., 1998). *Oscillatoria cf. chalybea* produces the musty, off-flavor compound 2-methylisoborneol, which can taint the flesh of channel catfish and render them unmarketable. Sodium carbonate peroxyhydrate is one of the most desirable compounds to use as a cyanobacterial algaecide in food-fish ponds due to its environmentally-safe nature i.e., no toxic residuals are formed from the breakdown of sodium carbonate peroxyhydrate. In its use for the purpose of disinfecting catfish eggs, sodium carbonate peroxyhydrate was found to be efficacious, and contributed to the beneficial increase of dissolved oxygen in the hatching trough (Small, 2009). The breakdown products of sodium carbonate peroxyhydrate are water, oxygen and sodium carbonate, none of which concentrate or persist in the environment or represent environmental hazards. Slight increases in pH can occur from the introduction of sodium carbonate to an aquatic environment in the absence of a buffered system.

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

An emission of sodium carbonate peroxyhydrate to the environment could potentially occur during production, formulation and use of the substance. The main use of sodium carbonate peroxyhydrate is as a bleaching chemical in laundry detergents, laundry additives and machine dishwashing products. In most cases, the household cleaning products, which contain sodium carbonate peroxyhydrate, are added to tap water during use. For example laundry detergents are dissolved in water during the laundry washing process, while machine dishwashing products are also added to water. After use, the spent washing liquor will be disposed via the drain and finally it will be discharged to aquatic ecosystems (e.g. rivers, lakes, estuaries, sea) after a treatment. Sodium carbonate peroxyhydrate rapidly dissolves in water and dissociates into sodium, carbonate and hydrogen peroxide.

$$2\ Na_2CO_3 \cdot 3H_2O_2 \rightarrow 4\ Na+ + 2\ CO_3^{2-} + 3\ H_2O_2$$

Sodium, carbonate and hydrogen peroxide do not adsorb to sediment. Furthermore, there is no distribution or transport to the atmosphere, thus the environmental risk assessment is focused on the aquatic compartment. Hydrogen peroxide is rapidly degraded in a biological waste water treatment plant, while sodium carbonate will be neutralized by such a treatment (Czerczak, 2005). Hydrogen peroxide is considered a green oxidant that decomposes into water and oxygen. Its production has an enormous geographical footprint. Hydrogen peroxide is used industrially as a bleaching agent for pulp, paper recycling, and textiles; in the intermediate chemical synthesis of propylene oxide and caprolactone; as a disinfectant; for cleaning and etching and in the mining industry. Worldwide, hydrogen peroxide production is over 3.8 million tons/year. The soda ash manufacturing sector is closely regulated by the EPA for emissions of greenhouse gases. Production plants are required to monitor and report CO_2, CO_2 combustion, methane, and N_2O from each manufacturing line. An emission of sodium carbonate to water will result in an increase in alkalinity and a tendency to raise the pH value:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

Because most natural waters have a buffering capacity that exceeds 130 mg/l of HCO_3^-, the likelihood of a large environmental shift in pH as a result of the introduction of sodium carbonate peroxyhydrate is remote (HERA, 2002).

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)).

The rate of decomposition sodium carbonate peroxyhydrate can be increased by the presence of soluble impurities and/or contact with active surfaces. High and low pH will also destabilize sodium carbonate peroxyhydrate. pH affects the activity of the catalytic impurities and the stabilizers which are present. Self-heating can rapidly accelerate the decomposition rate of destabilized hydrogen peroxide. Large amounts of oxygen and steam can be formed quickly. The amount of oxygen formed may reach ten-fold the volume of sodium carbonate peroxyhydrate. Hydrogen peroxide is a very reactive chemical, and an extremely powerful oxidizer under certain circumstances. Hydrogen peroxide of strength higher than 40% by weight can also form explosive mixtures with organic compounds. Such mixtures can equate to conventional high explosives in power, but may be much more sensitive in terms of detonation. Spontaneous reactions can occur between sodium carbonate peroxyhydrate, acids, bases and organic mixtures. Combustible materials are particularly susceptible. Because there are a number of substances used in organic production having a potential to react with sodium carbonate peroxyhydrate, any attempt to use combinations of sodium carbonate peroxyhydrate with other substances for algal control, such as water, transition metals, organic solvents, acids, bases reducing agents, or soil, should be carefully evaluated for safety and efficacy (Jones, 1999). The active ingredient of sodium carbonate peroxyhydrate, hydrogen peroxide is potent inhibitor of blue green algal growth. H_2O_2 also effect the production of a potent blue green algae toxin, mycrocystin. Its effect is to decrease the expression of the microcystin transport gene, and prevent transport of the toxin into the water (Qian et al., 2010).

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)).

There are a number of potential applications for sodium carbonate peroxyhydrate in organic crop production. These applications can include both terrestrial and aquatic settings. In a terrestrial setting, for example, sodium carbonate peroxyhydrate can be used to kill moss growing in a pasture (Fery, 2007). In an aquatic setting, sodium carbonate peroxyhydrate may be used to kill algae in a tank, a pond or a lake without killing the fish or higher plants (Quimby et al., 1988). In the terrestrial application, sodium carbonate peroxyhydrate application provides a short term increase in oxygen. Furthermore, it has been shown that the additional oxygen resulting addition of sodium carbonate peroxyhydrate to petroleum contaminated soils from the tundra can stimulate bacteria necessary for bioremediation at least two orders of magnitude (White et al., 1997). pH increases resulting from the dissociation of sodium carbonate peroxyhydrate into sodium carbonate and hydrogen peroxide in soil were found to be short lived as a result of natural buffering. In experiments investigating the effectiveness of sodium carbonate peroxyhydrate on *Phytophora capsici* in cucumbers, pH levels of water containing zoospores climbed to 9.57 after administration. Zoospores treated with sodium carbonate peroxyhydrate were found unviable (Granke and Hausbeck, 2010).

Evaluation Question #9: Discuss and summarize findings on whether the use of 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)).

Aquatically, toxic effects of sodium carbonate peroxyhydrate on fish have been reported, but the sensitivity of different fish species depends on final hydrogen peroxide concentration, water temperature, and life stage. Concentrations lower than 19.7 mg/L (H_2O_2) are safe for most fish, and have been tested with bluegill, channel fish, yellow perch, fathead minnow fry or fingerlings. Hydrogen peroxide in concentrations between 2.5 and 5 mg/L is toxic to water fleas. Sodium carbonate peroxyhydrate represents an optimal decomposition property since it degrades itself into sodium carbonate, water and oxygen (Jancula, 2011). Sodium carbonate peroxyhydrate is a strong oxidizing agent, and can be used to degrade or mask the use of chemical residues, e. g., pesticides in soil or water (Katagi, 2002).

Undissolved sodium carbonate peroxyhydrate is toxic to birds when ingested. However, once applied and dissolve in water sodium carbonate peroxyhydrate is not expected to be toxic to birds. Sodium carbonate peroxyhydrate is also highly toxic to bees and it should not be allowed to drift to flowering plants or used when contact with bees might occur. Other insects also may be affected (WDNR, 2012)

Sodium carbonate peroxyhydrate acts quickly to dissociate into sodium carbonate and hydrogen peroxide, the latter oxidizing its intended target. Shortly thereafter, hydrogen peroxide is degraded to oxygen and water. These are naturally occurring substances. Furthermore, none of the environmental evaluations considering the safety and efficacy of sodium carbonate peroxyhydrate implicate it with any risk for contamination or damage to the environment (EPA, 2002b; Czerczak, 2005; Solvay, S.A., 2002). Based on the data available, this substance itself does not appear to present a potential threat to the environment.

Evaluation Question #10: 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)).

Sodium carbonate peroxyhydrate is not absorbed into the skin, because it is hydrophilic. Contact with body fluids will cause it to dissociate into hydrogen peroxide, carbonate and sodium ions which are all naturally present in the human body. Hydrogen peroxide will not be systemically available, since it is rapidly degraded in the body. Carbonate is a part of the natural human buffering system, thus there will be no disturbance of the body's normal acid/base balance. Similarly for sodium carbonate peroxyhydrate exposure is not expected to contribute significantly to the sodium load of the body. The mode of action is characterized by the local irritation potential to mucous membranes. Acute oral, lethal dose (LD_{50}) values ranged between 1034 and 2200 mg/kg of body weight (bw), while the acute dermal LD_{50} was > 2000 mg/kg bw. The existing animal data on acute toxicity show that sodium carbonate peroxyhydrate has a local effect and that systemic effects are not to be expected. In animal tests, a slight irritating effect on the skin was reported for solid sodium carbonate peroxyhydrate and it was highly irritating to the rabbit eye (not rinsed). Sodium carbonate peroxyhydrate did not have sensitizing properties in a test with guinea pigs. Sodium carbonate peroxyhydrate is not genotoxic, mutagenic, teratogenic, or carcinogenic (Czerczak, 2005). Sodium carbonate peroxyhydrate is safe to use as an oxygen generator in packaging designed to preserve whole fresh fruits (EFSA, 2013).

Evaluation Question #11: 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)).

The National List (7 CFR 205.601) provides sodium carbonate peroxyhydrate as an algaecide, disinfectant and sanitizer, including irrigation system cleaning systems. Also in this category are ethanol, isopropanol, calcium hypochlorite, chlorine dioxide, sodium hypochlorite, copper sulfate, hydrogen peroxide, ozone, peracetic acid, and soap-based algaecides and demossers. The actions of all these substances including sodium carbonate peroxyhydrate is a single or multiple application for cleaning or removal of fungi, bacteria, algae or liverworts as required by the application (Matthjis et al., 2012). Sodium bicarbonate is not listed for use in crop production on the National List. However, sodium bicarbonate has been shown to be effective for moss control in creeping bent grass (Kennelly et al., 2010).

The State of California has 4 fungicides (algaecides) registered for use on rice (CA, 2010). Two of these, copper sulfate and sodium carbonate peroxyhydrate are on the National list. In 2010, in California, one million three hundred and eighteen thousand pounds of copper sulfate were applied in 1442 applications to 97,757 acres and sixteen thousand, six hundred and fifty pounds of sodium carbonate peroxyhydrate were applied in 31 applications to 1,177 acres. Respectively, 17.4 and 0.3% of California rice acreage. The state of California does not perform water quality sampling for products that contain sodium carbonate peroxyhydrate, although it does perform water quality sampling for copper sulfate. Copper sulfate is effective as an algaecide, but retains differential toxicity to terrestrial and aquatic organisms (Osunde, 2003). Copper accumulates in the environment having potential for mobility and availability to susceptible populations well after application (Salam and El-Fadel, 2008).

The recommended application of copper sulfate for algae control in rice fields with alkaline water is 1.0 mg/L, copper sulfate is a known toxin to the freshwater prawn *Machrobrachium rosengergii* and other shrimp species at a concentration of 0.46 mg/L (Osunde et al., 2003). This conflict makes the coexistence of rice and prawn production impossible, in spite of a natural ecology that includes both species, but enables a dual use for copper sulfate as a pesticide to control tadpole shrimp (*Notostraca* spp.). Copper sulfate is also toxic to amphibians particularly frogs and toads with a 50% lethal dose of approximately 0.10 mg/L (Garcia-Munoz et al., 2009). Copper sulfate application may potentially exacerbate algal growth (Ramakrishnan et al., 2013). Broad application of copper sulfate to inhibit harmful algae can also result in secondary pollution including additional release of the potent blue green algal toxin microcystin (Ross et al., 2006). Because the use of phosphate fertilizer is prohibited for organic farming, algae and cyanobacteria may be less of a problem for organic producers inasmuch as phosphate is a limiting nutrient for these organisms (Spencer, 2010). Copper sulfate cannot be used with natural algal inhibitors such as rice straw because the copper ions are bound by the rice straw and prevent natural inhibitory substances from working (Spencer, 2007).

Rice straw extract has been shown to inhibit the growth of the bloom-forming cyanobacterium *Microcystis aeruginosa*. Growth of *M. aeruginosa* was inhibited by rice straw extract concentrations ranging from 0.01 to 10 mg/liter. This activity was attributed to the synergistic effects of various phenolic compounds in the rice straw and to secretions of macrophytic organisms growing in the rice straw microenvironment (Park et al., 2006; Abou Ella et al., 2007). A number of additional algal inhibitory substances such as esters, alkalis, and ketones including tannins, quinones and lignins, some non-specific and other species dependent were also found to be present in barley straw, straw of *Arundo donax* L. and Ragi straw. However, *Arundo donax* is considered an exotic and invasive weed in parts of California, where appropriate insect predation is not present (Hong et al., 2011; Mohan, 2012, Spencer, D.F., 2012). In California, a study was performed to determine the effectiveness of barley straw on algae bloom that would otherwise disturb plant rice seed. The study, although inconclusive, did not find the use of barley straw effective, but recounts the addition of copper sulfate during the study and low temperature inhibition of rice straw decomposition affecting the subsequent release of inhibitory substances (Spencer and Lembi, 2007). Small differences in the study designs using straw to inhibit algal growth may result in widely differing results, however; straw products can potentially have a role in inhibiting algal blooms.

Red tide is caused by marine microalga that are similar to cyanobacteria. Experiments in aquaculture with extracts from five Chinese herbs from Chinese traditional medicine proved these were effective in inhibiting growth of the algal species that produce red tide. The extracts used at $< 0.1\%$ were golden thread (*Rhizoma coptidis* Huang Lian) and areca seed (*Semen arecae* Bing Lang) having the best inhibitory effect, followed by indigowood (*Isatis tinctoria L.),* and with the least effect light yellow sophora *(Sophora flavescens* Ait.) and chameleon plant (*Houttuynia cordata* Thunb.—(Zhou et al., 2007)).

In addition to Chinese herbs, garlic extracts were also found to be effective in reduction or prevention of algal growth (Zhou et al., 2008; Lee and Gao, 2012). A survey of conventional and organic rice production in India recommends using the organic sprays panchagavya and amruthajalam, 2-3 times during the active period of growth at a concentration of 25 parts per thousand. Algae and the azolla are used as sources of nitrogen (Surekha et al., 2008). These methods have not been applied to rice farming in the US.

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

Rivers and streams containing high levels of residual nitrogen in the form of urea, attributed to the use of nitrogen fertilizers in conventional farming can become the unintended sources of irrigation water for organic farms (Charles, 2013). Eutrophication producing unwanted blue green or brown algae otherwise requiring the use of algaecides such as sodium carbonate peroxyhydrate, can be approached alternatively with solutions such as recycling phytoplankton as a source of nutrients and minerals (Roger and Watnabe, 1984). The blue green algae are also useful as denitrifiers (Gajibhiye, 2011). The removal of algal scum in fields can be approached by turning over the affected soil, keeping the water level low if scum begins to form, preventing the drained field from drying out, and sowing rice early (Olsen, 1957).

Phosphate rapidly leaches from improperly maintained soil. On conventional rice farms, algal blooms occur because phosphate is applied early in the growing cycle, i.e., pre-planting (Lundy et al., 2012). In organic farms, crop rotations reduce loss of phosphate and promote its preservation in humus. Furthermore, the introduction of compost composed of manure and rice straw over a four or eight year cycle with an arable break adds more bound phosphate than is taken out (Sykes, 1949). Inositol phosphate has been identified in humus and humic acid (Stevenson, 1995).

In developing countries, there is interest in the adoption of organic farming methods to save cost and prevent environmental issues. Allelopathic plants are increasingly providing solutions to algal bloom contamination and weed control (Khanh et al., 2007). Allelopathy is the chemical interaction that occurs between and among plants and microorganisms via releases of biologically active compound into the environment (Inderjit and Keating, 1999). Considerable effort has also been placed on the development of macrophyte allelopathy (Hu and Hong, 2008). For example, this work has found that macrophytes such as barley straw contain epiphytic organisms that produce inhibitory compounds capable of preventing the growth of blue green algae in rice paddies.

Finally, it has been shown that herbivorous (macrophytophagous) and algivorous (microphytophagous) fish can be successfully used in the control of weeds and algae in the rice fields. The fish found useful in this purpose are *Puntius javanicus* in Asia, *Tilapia rendalli* and *T. zilli* in Africa, which are herbivorous and *T. mossambica* in Asia, which are algivorous (Kutty, 1987).

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