Use of GreenCleanPRO Granular Algaecide/Fungicide and GreenClean Liquid in the State of New York

Supplemental Environmental Impact Statement

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Table of Contents

1.0 Introduction

1.1 Purpose of the supplemental environmental impact statement

It is the purpose of this Supplemental Environmental Impact Statement (SEIS) to objectively evaluate the scientifically documented evidence regarding all aspects of the use of GreenCleanPRO or GreenClean Liquid for the control of algae in waters of the State of New York. This document is intended to present a general description of the potential positive and negative impacts from the use of this product within waters of the State of New York. The SEIS is being submitted to the New York State Department of Environmental Conservation (NYSDEC) by BioSafe Systems LLC, the manufacturer and distributor of GreenCleanPRO and GreenClean Liquid.

The SEIS has been prepared specifically for the evaluation of potential use of GreenCleanPRO or GreenClean Liquid in New York State and is applicable to algaecide formulations with Sodium Carbonate Peroxyhydrate (sodium percarbonate) as the active ingredient as well as our liquid formulation with hydrogen dioxide as the active ingredient. The information and technical data contained in this SEIS pertaining to the active ingredients, sodium percarbonate and hydrogen dioxide, is provided to allow full evaluation of GreenCleanPRO products and GreenClean Liquid, support selection of appropriate application setback distances and comparisons to other aquatic algaecides or alternative treatment options. The impact evaluation contained herein is not intended nor should it be used as a surrogate SEIS for other sodium percarbonate-containing products or hydrogen peroxide products. While sharing a common active ingredient, these products may differ widely in other formulaic components, resulting in physical and chemical properties that may significantly affect exposure and toxicity factors. Accordingly, NYSDEC should be contacted regarding establishing environmental safe conditions for application of alternative sodium percarbonate or hydrogen peroxide containing products in riparian and aquatic settings.

1.2 Objective of the SEIS

The development of the SEIS for GreenCleanPRO and GreenClean Liquid is intended to provide potential users of these products with a general understanding of the potential positive and negative impacts that might be associated with the use of GreenCleanPRO or GreenClean Liquid in the waters of the State of New York. GreenCleanPRO is an aquatic algaecide containing the active ingredient sodium percarbonate. GreenClean Liquid is also an aquatic algaecide containing the active ingredient hydrogen dioxide. By developing the SEIS, BioSafe Systems has provided the information necessary for individual potential applicators to easily develop the necessary permit applications. The preparation of this SEIS is intended to provide potential users and interested parties with information specific for GreenCleanPRO and GreenClean Liquid and its positive and negative impacts on surface water resources of New York State.

1.3 Regulatory framework

A Generic Environmental Impact Statement (GEIS) was prepared by the NYSDEC in 1981 to address environmental impacts from using pesticides that were registered for use at this time. The NYSDEC determined that the use of hydrogen peroxide in waters of the State, and the need for Aquatic Pesticide Permits, in accordance with Environmental Conservation Law (ECL) Section.0313, would have a significant adverse impact on the environment, and issued a positive declaration in accordance with SEQR. The product registrant, BioSafe Systems, LLC elected to submit a supplement to the GEIS to address the potential environmental impacts from the use of herbicides containing the active ingredient hydrogen peroxide.

The SEIS was prepared in accordance with 6 NYCRR Part 617, the New York State Environmental Quality Review Act (SEQR). The purpose of SEQR is to incorporate the consideration of environmental factors into the existing planning, review and decision-making processes of State, regional and local government agencies at the earliest possible time. An action is subject to review under SEQR if any state or local agency has the authority to issue a permit or other type of approval over that action.

Section 617.15 (a)(4) allows for the development of a SEIS to assess the potential environmental effects of an entire program or plan having wide application. The regulations concerning the use of pesticides in NYS are defined in 6 NYCRR Part 325 through 327. The regulations addressing the use of pesticides in wetlands are defined in 6 NYCRR Part 663 and within the Adirondack Park, 9 NYCRR Part 578.

1.4 Content and organization of the SEIS document

The SEIS document is organized in the following fashion:

- Section 1.0 Introduction – provides general overview of the product registration, SEQR process and associated regulations;
- Section 2.0 Description of the Proposed Action – Use of GreenCleanPRO and GreenClean Liquid- provides information on the aquatic algaecide, the general locale of its proposed application, its use in support of maintaining designated uses, and intended algae target species;
- Section 3.0 Environmental Setting – places the application of GreenCleanPRO and GreenClean Liquid in the context of the New York lake environment. The general characteristics of New York lakes are described. The overall objectives of aquatic algae management control by GreenCleanPRO and GreenClean Liquid are identified;
- Section 4.0 General Description of GreenCleanPRO and GreenClean Liquid and their Active Ingredients sodium percarbonate and hydrogen dioxide, respectively – provides a full description of GreenCleanPRO and GreenClean Liquid and their chemical formulations. This description includes proposed use, mode of action, and application factors.
- Section 5.0 Significant Environmental Impacts Associated with GreenCleanPRO and GreenClean Liquid - this section reviews direct and indirect impacts to non-target species, potential bioaccumulation and residence time in the water column;
- Section 6.0 Potential Public Health Impacts of GreenCleanPRO and GreenClean Liquid - evaluates the potential for concerns or issues associated with human exposure to the products;
- Section 7.0 Alternatives to GreenCleanPRO and GreenClean Liquid - describes and briefly reviews the advantages and disadvantages of alternative aquatic algae control methods and technologies.
- Section 8.0 References – contains the citations and sources of the information presented in the SEIS.

2.0 Description of the proposed actions/uses of GreenCleanPRO and GreenClean Liquid

The proposed actions are the use of the aquatic algaecides GreenCleanPRO or GreenClean Liquid for the control of nuisance algae in waterbodies located in the State of New York.

2.1 General description of the aquatic algaecide GreenCleanPRO

GreenCleanPRO is currently registered by the USEPA for the control of algae and cyanobacteria.

GreenCleanPRO is composed of 85% active ingredient, Sodium Carbonate Peroxyhydrate, or Sodium Percarbonate. Sodium Percarbonate is a solid form of hydrogen peroxide, the active ingredient, and sodium carbonate, a carrier for the hydrogen peroxide. Sodium Percarbonate contains 27.60% hydrogen peroxide by weight.

2.2 General description of the aquatic algaecide GreenClean Liquid

GreenClean Liquid algaecide is currently registered by the USEPA for the control of algae and cyanobacteria.

GreenClean Liquid is composed of 27.0% hydrogen dioxide. Hydrogen dioxide is a synonym for hydrogen peroxide.

2.3 Purpose of the products

GreenCleanPRO is a fast-acting algaecide proposed for the control of blue-green algae, green algae, and cyanobacteria in ponds, lakes, reservoirs, and other quiescent bodies of water. The active ingredient sodium percarbonate is a sodium carbonate and hydrogen peroxide compound that begins eliminating algae immediately on contact. GreenCleanPRO is a solid form of hydrogen peroxide (H_2O_2), which is the active ingredient. It contains sodium carbonate (Na_2CO_3) which acts as a carrier for the peroxide. The active ingredient has a nominal concentration of 27.6%. On dissolution, the product dissociates into its individual components – soda ash and H_2O_2.

$$2\ Na_2CO_3 \cdot H_2O_2 \rightarrow 2\ Na_2CO_3 + H_2O_2$$

On decomposition, H_2O_2 is converted to water and oxygen.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

GreenClean Liquid is an algaecide proposed for the control of a broad range of filamentous and planktonic algae in ponds, lakes, reservoirs, and other quiescent bodies of water. GreenClean Liquid eliminates algae on contact and results can be seen within 24 to 48 hours. The active ingredient is hydrogen dioxide. On decomposition, hydrogen dioxide is converted to water and oxygen.

On decomposition, H_2O_2 is converted to water and oxygen.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

Hydrogen peroxide is highly reactive with other substances, organic compounds, elements, radiation or cells. Generally speaking, degradation of hydrogen peroxide occurs rapidly due to the many degradation mechanisms that exist. The rate of decomposition depends on the types and amounts of catalyst or enzyme available, as well as temperature and light conditions.

2.3.1 Need for the products

The use of GreenCleanPRO and GreenClean Liquid can be important components of a comprehensive and integrated plant management approach to limit the spread of aquatic algae. Algal blooms in bodies of water may last for several months and can lead to the following circumstances:

- clogging of filters
- tainting of potable water
- pH change
- generation of toxins (by some species)
- decrease in the aesthetic quality of the body of water
- thermal and chemical stratification
- reduced dissolved oxygen (DO) as a result of the following:
  - poor light penetration prevents plant growth beneath the algae layer
  - impediment of gas diffusion to lower water levels

- o Increased biochemical oxygen demand (BOD) after death and decay of the algae.

  This low DO will in turn result in:
- o Development of anaerobic bacteria
- o Incidence of spontaneous fish kill

Therefore, the consequences of algal blooms include the following:
- make water unusable for consumption
- make water undesirable for recreation
- reduce availability of water for irrigation
- allow proliferation of nuisance species at the expense of plant and animal diversity
- create harmful toxins that are harmful to humans, animals and plants (through irrigation).

2.3.2 Benefits of the product

GreenCleanPRO and GreenClean Liquid are broad spectrum algaecides that provides an alternative means for management and/or control of blue-green algae (cyanobacteria) as well as other forms of algae. GreenCleanPRO and GreenClean Liquid do not bioaccumulate in the environment and provide immediate control of algal blooms. GreenCleanPRO and GreenClean Liquid releases oxygen while it works. Algae forms and dosage rates determine the selectivity of GreenCleanPRO or GreenClean Liquid allowing a Lake Manager to select product that provide the most efficient control. Because of the soft nature of its chemistry, waters treated with GreenCleanPRO or GreenClean Liquid can be used without interruption. GreenCleanPRO's as well as GreenClean Liquid's effectiveness is not limited to pH.

2.3.3 History of the product use

GreenCleanPRO and GreenClean Liquid are labeled by the EPA as broad spectrum algaecides for freshwater algae in surface waters. Both products are OMRI listed for Organic Crop Production and are also NSF/ANSI 60 Certified for drinking water applications. GreenCleanPRO is registered for use as an algaecide in all 50 U.S. states and Puerto Rico. The intention of this document is to address the aquatic uses and impacts for GreenCleanPRO and GreenClean Liquid. GreenCleanPRO or GreenClean Liquid can be used as full volume treatments or as spot treatments.

Granular applications of GreenCleanPRO can be made by broadcast application by hand or via mechanical spreader, spreading the product in burlap bags dragged behind a boat or aerially, via conventional aerial application. The versatility of application allows for the aquatic applicator to treat the present algae as it resides in the water column.
GreenClean Liquid can be applied as a spot treatment, water surface treatment to larger area, or injection treatment via piping system.

Application rates and techniques will be determined by the type of algae present. Most GreenCleanPRO and GreenClean Liquid applications are applied to the photic (limnetic) or benthic zones. The photic (limnetic) zone is the depth of a lake or pond that is exposed to sufficient sunlight for photosynthesis to occur. The photic (limnetic) zone is typically where algae thrive. As a surface application, GreenCleanPRO and GreenClean Liquid, is soluble up to 4 feet. The benthic zone is the final or bottom zone of a lake or pond. The characteristics of the benthic zone attract a variety of algal species. When making treatments with GreenCleanPRO or GreenClean Liquid to benthic algae treatments are made directly to the benthic algae using one of the above mentioned application techniques. GreenCleanPRO's and GreenClean Liquid's application rates are determined by the species present and density of the bloom. GreenCleanPRO and GreenClean Liquid are used in the marketplace as an alternative to heavy-metal based algaecides such as copper sulfate. GreenCleanPRO's active ingredient is a solid, stabilized form of hydrogen peroxide. Hydrogen Peroxide has been studied for use as an algaecide since the 1960's. GreenClean Liquid's active ingredient is Hydrogen Dioxide.

2.4 General location of the proposed action

For the purposes of this portion of the SEIS, the general location for the proposed action is in the surface waters of the State of New York. The proposed action is the use of the aquatic algaecide GreenCleanPRO or GreenClean Liquid for the control of aquatic algae. Under Article 24 of the Environmental Conservation Law, some ponded water may be described as wetlands. A specific description of the actual body of water in which GreenCleanPRO and GreenClean Liquid is intended for use would be included in the individual permit applications. This would also include any applications in New York State-designated wetland areas and non-designated wetlands. Further descriptions of New York lakes and wetlands and their characteristics are given in Section 3.0.

2.5 Support of designated uses

All New York State surface waters are classified under 6 NYCRR Part 701.2 – 701.9, which delineates the protected or so-called designated uses inherent to such classifications. These designated uses for fresh waters include: source of water supply for drinking; culinary or food processing purposes; primary and secondary contact recreation; and fishing. In addition, the waters shall be suitable for fish, shellfish, and wildlife propagation and survival.

To protect these uses, New York has promulgated water quality standards (6 NYCRR Part 703) to support the best uses of the waters. These standards include several types including those pertaining to human health (water source and fish consumption), aquatic life (survival and propagation), wildlife (protection of piscivores) and aesthetic qualities. The latter is defined in a narrative water quality standard (6 NYCRR Part 703.2) that provides a general condition for all taste, color, and toxic and other deleterious substances shall not be in amounts "that will adversely affect the taste, color or odor thereof, or impair the waters for their best usages."

Presently there are no chemical-specific New York State water quality standards for sodium percarbonate (e.g., GreenCleanPRO) in effect. However, for purposes of the SEIS, information will be provided to show how proper use of the aquatic algaecide, GreenCleanPRO or GreenClean Liquid, for the control of nuisance aquatic algae will not adversely affect any of the protected or best uses of the treated waterbody. In addition, there can be secondary economic benefits by control of nuisance aquatic vegetation.

Protection of human health concerns (drinking water, fish consumption, primary and secondary recreation) are considered in Section 6.0; considerations for potential ecological impacts (aquatic life support function, wildlife) are considered in Section 5.0.

3.0 Environmental setting

This section describes the environmental setting in which the proposed action, the use of the aquatic algaecide GreenCleanPRO or GreenClean Liquid, is projected to occur. While this section presents the available data in as detailed an extent as is required, the information is fairly generic for the State of New York. Further site-specific information may be required for application in particular waterbodies, as well as for wetland areas, which are specifically permitted under Article 24.

3.1 General descriptions of New York State aquatic ecosystems

The aquatic ecosystems of New York State generally fall into four basic categories. These include standing freshwater systems (lakes, ponds, and reservoirs), flowing freshwater systems (rivers and streams), brackish systems (tidal estuaries), and saline coastal systems. Since the use of GreenCleanPRO or GreenClean Liquid is aimed principally at algae control in freshwater lentic (standing) systems, the focus will be on this category of aquatic ecosystem, but given the potential for application to algae in littoral or riparian zones, some information is also given regarding wetlands.

It is calculated that New York State has over 3.5 million acres covered by some type of surface water system. That includes over 7,500 lakes, of which over 1,500 are found in the Adirondack Mountains. The Adirondack Mountains also contain over 16,700 miles of significant fishing streams. The state's largest lakes are Lake George, Chautauqua Lake, Oneida Lake, and the major Finger Lakes; Canandaigua, Keuka, Seneca, Cayuga, and Skaneateles.

The specific characteristics of each aquatic system are partially determined by its physiographic setting within the state. Changes in the characteristics of each aquatic system will lead to changes in the endemic biota associated with that waterbody. Generally, waterbodies within New York State can be defined geographically by region and drainage basin location. Aquatic ecosystems in the eastern region, which includes the St. Lawrence/Lake Champlain/Black River basin, the Hudson-Mohawk basin, the Delaware basin, and Long Island are defined by either the Adirondack/Catskill mountain areas to the north or the New York Bight tidal estuarine area to the south. Aquatic ecosystems in the central region, which includes the Oswego-Ontario basin and the Susquehanna, are defined by areas of low relief with large areas of marshes to the north and broad, steeply sided valleys with limited natural storage capacity in the south. Aquatic ecosystems in the western region, which includes the Lake Ontario basin, the Erie-Niagara basin, the Genesee basin, and the Allegheny basin, are defined by the glaciated geology of that region.

In addition to the watershed drainage basin, it is also possible to classify lakes and ponds according to their respective ecoregions. Ecoregions are geographical map units that depict areas which share common geology, morphology, soils, climate, and other characteristics. Accordingly, due to these similarities in watershed characteristics, water chemistry within an ecoregion tends to be similar and often is distinctive from other ecoregions (unless impacted by human activities). For example, the USEPA has issued Ambient Water Quality Criteria Recommendations (or "reference conditions") for nutrients for lakes in the 14 national ecoregions. For New York, USEPA has established numeric nutrient criteria recommendations for lakes in the following Level III Non-Aggregate Nutrient Ecoregions:

- Ecoregion VII – Mostly Glaciated Dairy Region – this is the ecoregion for the majority of New York including western and central portions, as well as major river and lake plains;
- Ecoregion VIII – Nutrient Poor, Mostly Glaciated Upper Midwest and Northeast – found primary in the Adirondack and Catskill mountain regions;
- Ecoregion XI – Central and Eastern Forested Uplands – a small portion of the lower Hudson Valley is located in this ecoregion;
- Ecoregion XIV – Eastern Coastal Plain – metropolitan New York City region and Long Island are included.

US EPA has also issued waterbody-specific technical guidance, in the form of the Nutrient Criteria Technical Guidance Manual for Lakes and Reservoirs.

As noted above, water chemistry in each of these basins is influenced by the composition of the geological formations found within the region. For example, waters in the Adirondack Mountains and the Catskill Mountains can be influenced by geologic formations with little buffering capacity. In some lakes, this geological setting, coupled with anthropogenic inputs, has resulted in waters with pH values of less than 5 standard units (S.U.). Surface water systems in the Erie-Niagara basin in western New York State are characterized by high levels of dissolved solids (140 to 240 ppm) and hard water (108 to 200 ppm, expressed as $CaCO_3$ equivalents). Surface water in the Delaware River basin is characterized by low total dissolved solid levels (averaging 37 ppm) and an average hardness of approximately 37 ppm. The dominant ions are silica, calcium, bicarbonate and sulfate. The dissolved solid concentrations in surface waters in the Champlain-Upper Hudson basin rarely exceed 500 ppm. In surface waters of the Western Oswego River basin, dissolved solid concentrations range from 50 to 300 ppm.

Wetlands, both freshwater and coastal, are transitional areas where land and water interact. The State of New York is highly variable in its environment relative to terrain, climate, and other environmental factors, and the state's wetlands are similarly varied. Wetlands in New York are highly diverse and range from Long Island tidal marshes dominated by cordgrasses, emergent and shrub marshes along the clay flats of the Finger Lakes region and the Hudson River valley floodplain, forested wetlands common to the Adirondacks, as well as fringe wetlands along lake shores and riparian wetlands along streams and rivers throughout the state.

The typical wetland environments where application of an aquatic algaecide may be considered vary widely. This variation includes the nature of soil saturation among habitat types such as seasonally flooded freshwater marshes, wetlands located above the mean tide line of estuarine marshes, and marsh and shrub wetlands that exhibit perennially saturated surface soils but may never receive full inundation. Some of these wetlands occur in isolated pockets, characteristic of the "perched" wetlands found upon clay plains, but more often they are found on the periphery of a larger wetland/waterbody complex. Many lakes and ponds, particularly those formed in the glacially-affected landscape of New York, often have shallow aquatic marshes at their boundary with adjacent uplands. Such ecosystems that form in perennial shallow standing water are particularly susceptible to colonization by riparian invasives such as *Phragmites communis*, which exerts a strong competitive advantage due to its ability to colonize disturbed areas and tolerate variable water levels (Mitchell 2009).

3.1.1 Lake basin characteristics

The lakes in New York were created in two principal ways. Many lakes resulted from glacial activity approximately 12,000 years ago. Others were created by damming streams or by enhancing a small lake by damming its outflow. Most damming occurred during the early industrial age of the country when water power was a critical resource. Through natural processes, most lakes become shallower and more eutrophic (nutrient-rich) and eventually fill in with sediment until they become wet meadows. The aging process is not identical for all lakes, however, and not all start out in the same condition. Many lakes that were formed by the glaciers no longer exist while others have changed little in 12,000 years. Yet lake aging is reversible. The rate of aging is determined by many factors including the depth of the lake, the nutrient richness of the surrounding watershed, the size of the watershed relative to the size of the lake, erosion rates, and human induced inputs of nutrients and other contaminants.

Existing lakes can be subdivided into four categories. Nutrient-poor lakes are termed oligotrophic, nutrient-rich lakes are eutrophic, and those in between are mesotrophic. A fourth category includes lakes following a different path; these typically result in peat bogs and are termed dystrophic lakes. They are often strongly tea colored. Lakes in one part of the New York State may share many characteristics (depth, hydrology, fertility of surrounding soils) that cause them to be generally more nutrient-rich while another region may generally have nutrient-poor lakes.

Lakes that are created by man-made impoundments and damming streams often follow a different course of aging than natural lakes. At first, they may be eutrophic as nutrients in the previous stream's floodplain are released to the water column. Over a period of decades, that source of productivity tends to decline until the impoundment takes on conditions governed more by the entire watershed, just as for natural lakes. Impoundments in New York are commonly shallower than natural lakes, have larger watersheds (relative to lake area), and the pre-existing nutrient-rich bottom sediments may provide nutrients for abundant aquatic plant growth early in the life of the lake. However, most impoundments in New York are smaller, shallower systems with high watershed to lake area ratios.

Human activity can accelerate the process of lake aging or, in the case of introduced species or substances, force an unnatural response. Examples of unnatural response include the elimination of most aquatic species as a result of acid deposition, noxious algal blooms resulting from excessive anthropogenic nutrient enrichment, intentional or inadvertent stocking of non-indigenous fish species that leads to the elimination of native species, or the development of a dense monoculture of a non-indigenous aquatic plant and elimination of native aquatic plants. However, it would be unrealistic to assume that managing cultural impacts on lakes can convert them all into oligotrophic basins of clear water and/or clean bottoms, and this would not be an appropriate goal for many lakes. Understanding the causes of individual lake characteristics (i.e., understanding the lake ecosystem) is a fundamental part of determining appropriate management strategies (Mitchell 2009).

3.1.2 Hydraulic residence

Hydraulic residence time is a function of the volume of water entering or leaving the lake relative to the volume of the lake (i.e., the water budget). The larger the lake volume is, and the smaller the inputs or outputs, the longer will be the residence time.

Lake residence time may vary from a few hours or days to many years. Lake Superior, for example, has a residence time of 184 years. However, New York lakes typically have residence times of days to months. Very short residence times will mean that algae cannot grow fast enough to take advantage of nutrients before the algae and nutrients are washed out of the lake. Long residence times mean that algae can utilize the nutrients and that they will probably settle to the lake bottom rather than be washed out. Those nutrients may become available again to the rooted plants or may be moved by biotic and abiotic internal recycling mechanisms back into the water column for additional algal growth.

Water may flow into a lake directly as rainfall, from streams and from groundwater. Water may leave a lake as evaporation, via an outlet, or as groundwater. Human influences include direct discharges to lakes or withdrawals from them. Lakes that have no inlets or outlets are called seepage lakes while lakes with outlets are called drainage lakes. Seepage lakes are basically a hole in the ground exposed to the groundwater. Precipitation and evaporation may also be influential in such lakes, and will increase the concentration of minerals to some degree. Few particulates will be brought into the lake or leave it. Drainage lakes, on the other hand, may receive significant quantities of particulates and dissolved material from inlet streams. Because lakes slow the flow of water, many particulates will be deposited on the lake bottom. Precipitation, evaporation, and groundwater flow may have some influence, but drainage lakes are normally dominated by storm water flows (Mitchell 2009).

3.1.3 Mixing

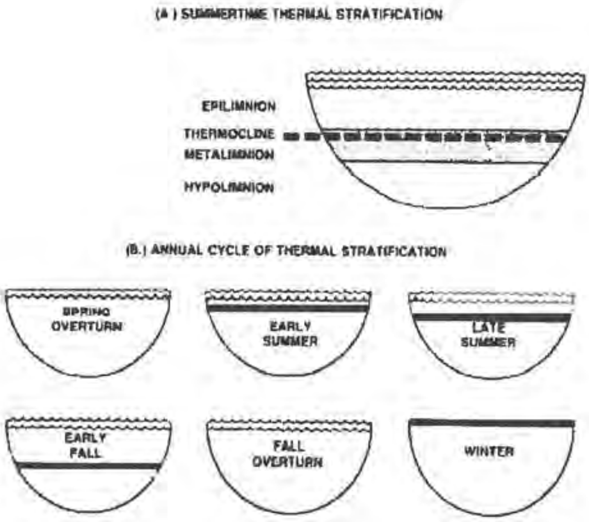
The thermal structure of lakes also determines productivity and nutrient cycling. For many shallow New York lakes, the mixed layer may extend to the lake bottom. Deeper lakes may form a three layered structure that throughout the summer consists of an upper warm layer (the epilimnion), a middle transition layer (the metalimnion, with the point of greatest thermal change called the thermocline), and a colder bottom layer (the hypolimnion).

A lake's thermal structure is not constant throughout the year (Figure 3-1). Beginning at ice out in early spring, all the lake's water, top to bottom, is close to the same temperature; the density difference is slight and water is easily mixed by spring winds. With warmer days, the difference between the surface and bottom waters increases until a layer (the metalimnion) is created where the incoming solar heat and wind-mixing effects are balanced. More heat and more wind moves the layer lower in the water column over the summer. Eventually, solar heating declines and the upper layer begins to cool. But the metalimnion does not retreat to the surface; it continues to move downward as wind mixes the remaining heat in the epilimnion ever deeper. Finally, in fall, the metalimnion arrives at the bottom and the lake is completely mixed again (turnover), but the upper layer is much cooler than during summer. In the early months of winter, the whole lake cools until it reaches 4°C. Further cooling which occurs only at the surface causes the surface water to be less dense. Ice forms at the surface and a new, inverse stratification (cold over cool water) is created and normally persists until spring.

This rather curious phenomenon affects many lake processes. During summer stratification, if incoming tributary water is relatively warm, it will float across the top of the cooler hypolimnion. Thus, during stratification, the effective residence time for incoming water and nutrients may be substantially less than when the lake is unstratified. If incoming water is especially cool, it may sink, often running along the thermocline as a sustained layer.

The cooler waters of the hypolimnion provide a refuge for so-called coldwater fish (e.g., salmonids) that are intolerant of warmer waters, as long as oxygen and related water quality is suitable. The metalimnion provides a one-way barrier for many materials. Photosynthetic organisms may grow in the epilimnion, but when they die they will settle by gravity into the hypolimnion. As they settle, they carry nutrients with them to the bottom where they may be incorporated into the sediments or may be recycled by bacteria that will convert the nutrients into an inorganic form. Thermal characteristics of a lake and its tributaries are therefore important to lake ecology and management.

Figure 3-1 Seasonal patterns in the thermal stratification of north temperature lakes

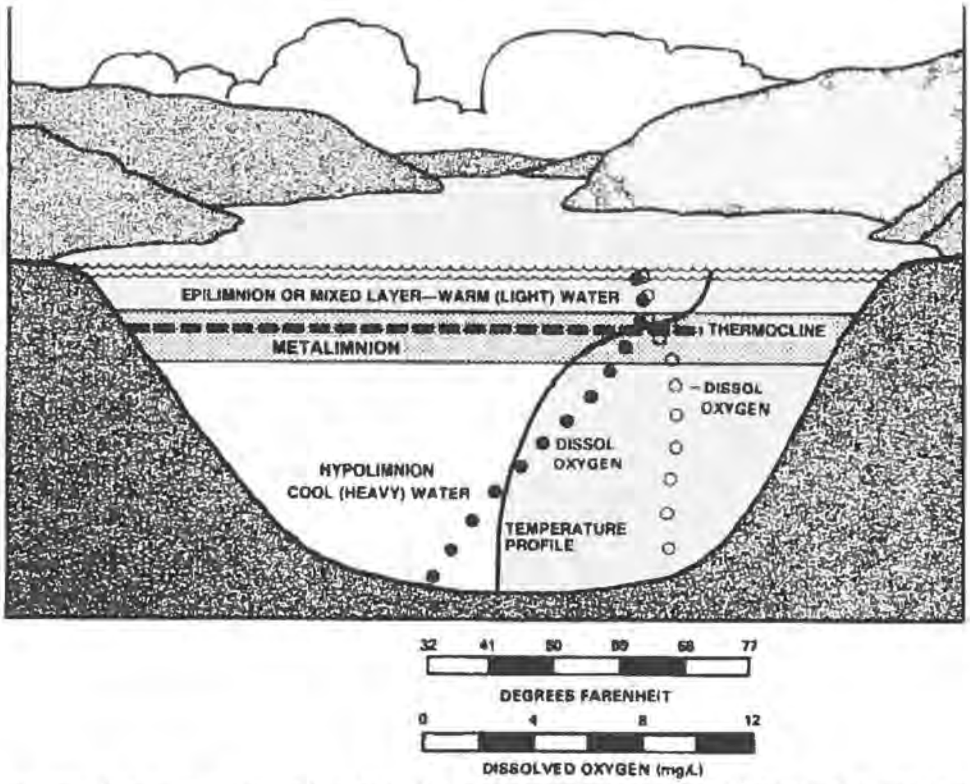


When the metalimnion is established, the hypolimnion no longer has a significant source of oxygen, either from exchange at the surface or as a result of photosynthesis. But animals and bacteria live in these lower waters and consume oxygen. If enough organic matter rains down to the hypolimnion, bacterial decay may consume all the oxygen and kill any fish and other aerobes which may require cooler waters (Figure 3-2).

Lakes can have oxygen problems for other reasons. During winter when the lake is ice-covered, there is little plant photosynthesis and reduced animal and bacterial respiration. When there is heavy snow on the ice cutting off most light, plant photosynthesis is especially low. If the lake has substantial organic material in the water column or surface sediments, bacterial decay can, by late winter, deplete the oxygen and kill oxygen dependent organisms such as fish. Ice-out may reveal a fishkill.

Figure 3-2 A cross-sectional view of a thermally stratified lake in mid-summer

Solid circles represent the dissolved oxygen profile in eutrophic lakes; open circles represent oligotrophic lakes.



Similarly, low oxygen levels may occur in areas of dense vegetation within highly enriched lakes as plants respire during darkness, particularly if the days have been very cloudy and photosynthesis has been lower than normal. A fish kill may occur in early morning after a night of heavy respiratory oxygen consumption. These are somewhat rare conditions, but all stratified lakes and some unstratified lakes reveal their trophic state by the degree of loss of oxygen. The greater the amount of primary productivity in the epilimnion, the greater the potential oxygen loss in the hypolimnion. If hypolimnetic oxygen progressively declines from year to year, these simple data provide an excellent record of increasing productivity. Conversely, increasing levels of dissolved hypolimnetic or winter oxygen under the ice is clear evidence of improvement (Mitchell 2009).

3.2 General characterization of aquatic plant and wetland communities in New York waterbodies

The characteristics of plant communities in aquatic settings are determined by the type of waterbody in which the community is located. Aquatic plants are often the dominant biotic factors in pond settings and are important ecological features of larger waterbodies such as lakes and reservoirs. New York State, with over 7,500 lakes, contains an extensive array of freshwater systems. This diversity is further increased by the inclusion of streams, rivers, and other bodies of flowing water. Waterbodies vary in terms of color, pH, temperature, silt loading, bottom substrate, depth, rate of flow if it is a moving body, and watershed area. Each of these characteristics will affect, to some extent, the type and distribution of the plant communities in that waterbody (Mitchell 2009).

3.2.1 Types of freshwater ecosystems

Freshwater ecosystems include lentic ecosystems, represented by standing waterbodies such as lakes and ponds; lotic ecosystems, which are represented by running water habitats (rivers and streams); and wetland habitats where water is present at or near the surface and flow may range greatly over the seasons. These habitats are discussed briefly below.

3.2.1.1 Ponds and lakes

Lentic systems (ponds and lakes) can be further subdivided in littoral, limnetic, profundal, and benthic zones. The littoral zone is that portion of the waterbody in which the sunlight reaches to the bottom. This area is occupied by vascular, rooted plant communities. Beyond the littoral zone is the open water area, or limnetic zone, which extends to the depth of light penetration or compensation depth. This is the depth where approximately 1% of the light incident on the water surface still remains. As a result of this decreased light, photosynthesis does not balance respiration in plants. Therefore, the light is not sufficient to support plant life. The water stratum below the compensation depth is called the profundal zone. The bottom of the waterbody, which is common to both the littoral zone and the profundal zone, is the benthic zone.

The bottom morphology (shape) of a lake is a key factor is determining the type and extent of plant communities that are present. The chemical quality of the water is another factor that influences the distribution of plant species. Soft water lakes (total alkalinity of up to 40 ppm and a pH of between 6.8 and 7.4) will often have sparse amounts of vegetation. Hard water lakes (total alkalinity from 40 ppm to 200 ppm and a pH between 8.0 and 8.8) will have dense growths of emergent species that can extend into deeper water. The distribution of species within a waterbody is determined by the bottom substrate, light intensity (function of depth and water clarity), and turbulence (currents or wave action) (Mitchell 2009).

3.2.1.2 Lotic systems

Lotic systems include rivers and streams. In lotic systems the distribution of plant communities is dictated by the velocity of the water flow and the nature of the bottom substrate. In fast moving waters, the system is usually divided into riffle and pool habitats. Riffles, which are areas of fast water, are centers of high biological productivity. However, the speed at which the water flows in these areas usually will not allow for rooted macrophytes to become established. Rooted vascular plants are more characteristic of pool habitats, which are interspersed with the riffle zones. In pool habitats, the softer bottom substrate and the slower current velocities allow for the establishment of rooted plants. This is also the case for slower moving streams and rivers. In larger rivers, as with lakes, ponds, and reservoirs, depth becomes a determining factor for the distribution of plant communities (Mitchell 2009).

3.2.1.3 Wetlands

Wetlands constitute a great range of habitat types which demonstrate different floristic, soil, and hydrologic characteristics, but most all share certain important characteristics. These include the ability to attenuate floodwaters, to cleanse surface water and recharge groundwater supplies, and to prevent soil erosion. Within wetlands ecosystems, sediment and associated pollutants from road runoff and other sources are deposited as water velocity slows and moves through the sinuous channels of natural swamps and marshes. Microbes intrinsic to wetland environments are capable of breaking down and using nutrients and contaminants that may otherwise be harmful to the environment. Similarly, chemical processes in saturated soils characteristic of most wetland types further preserve water quality through the uptake and immobilization of heavy metals, salts, and other contaminants.

In addition to these important biogeochemical attributes, such natural systems are also valued for their recreational and aesthetic characteristics and for provision of valuable habitat for fish and wildlife, particularly those emergent wetlands dominated by cattails, rushes or sedges. Large expanses of wetlands not only serve the purpose of protecting surface and ground water quality, but they are also often used for hiking and other outdoor recreational pursuits, waterfowl hunting, and fishing. Estuarine wetlands, and particularly tidal wetlands, are very important breeding and spawning grounds for a myriad of species of birds, fish, shellfish, and aquatic invertebrates. Not least importantly, wetlands are also valued and protected for their scenic beauty (Mitchell 2009).

3.3 Distribution and ecology of representative aquatic algaecide target species

Algae are a group of organisms characterized in that they contain chlorophyll, and so carry out photosynthesis during which oxygen is evolved. All lack the specialized structures found in the higher plants.

Algae may be divided into two categories:

- Prokaryotic or blue-green algae – these are akin to bacteria and can be as small as 1 μ and usually float in bodies of water. They are the culprit for the algae blooms in lakes, ponds and other surface waters. Examples include:
    - *Anabaena*
    - *Aphanizomenon*
    - *Oscillatoria*
    - *Microcystis*

- Eukaryotic or green algae – these are larger and can be as long as 50 m as in the case of seaweeds. They usually occur on the surface of water. Examples include:
    - *Chlamydomonas*
    - *Chlorella*
    - *Scendesmus*

Green algae are very important in surface water since they produce, through photosynthesis, the oxygen that other life forms need. The term "Green Algae" used in this document refers to most eukaryotic algal forms including members of phylum chlorophyta such as *Chlamydomonas*, *Chlorella*, *Scenedesmus* and phylum Chrysophyta such as diatoms. However, the term excludes other forms such as those from red algal lineage that belong to phylum Rhodophyta. However, pollution in the form of excessive nutrients (i.e. phosphorus and nitrogen) in the water can lead to rapid algal growth which results in algal blooms.

Algal blooms in bodies of water may last for several months and can lead to the following circumstances:

- clogging of filters
- tainting of potable water
- pH change
- generation of toxins (by some species)
- decrease in the aesthetic quality of the body of water
- reduced dissolved oxygen (DO) as a result of the following:
    - poor light penetration prevents plant growth beneath the algae layer
    - Increased biochemical oxygen demand (BOD) after death and decay of the algae.
    - This low DO will result in:
        - Development of anaerobic bacteria
        - Incidence of spontaneous fish kill

Therefore, the consequences of algal blooms include the following:

- make water unusable for consumption
- make water undesirable for recreation
- reduce availability of water for irrigation
- allow proliferation of nuisance species at the expense of plant and animal diversity

4.0 General description of GreenCleanPRO and GreenClean Liquid

4.1 General description of GreenCleanPRO

GreenCleanPRO is a granular non-dusting white peroxygen compound. It is free flowing and easy to handle. All the inert ingredients in GreenCleanPRO have status as drinking water treatment chemicals under Standard 60 of the National Sanitation Foundation and/or have either Generally Recognized As Safe (GRAS) food additive clearances from the U.S. Food and Drug Administration (FDA) or exemptions from tolerances from the U.S. Environmental Protection Agency (EPA). The product has been used for years in wastewater treatment, to control hydrogen sulfide in pump stations and wastewater treatment plants. It is also used as a food-processing chemical and in some toothpaste formulations.

GreenCleanPRO is a solid form of hydrogen peroxide (H_2O_2), which is the active ingredient. It contains sodium carbonate (Na_2CO_3) which acts as a carrier for the peroxide. The active ingredient has a nominal concentration of 27.6%. On dissolution, the product dissociates into its individual components – soda ash and H_2O_2.

$$2\,Na_2CO_3 \cdot H_2O_2 \rightarrow 2\,Na_2CO_3 + H_2O_2$$

Upon decomposition, H_2O_2 is converted to water and oxygen.

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

The by-products of GreenCleanPRO are soda ash, water and oxygen, making it one of the least toxic chemicals available.

4.2 General description of GreenClean Liquid

GreenClean Liquid is a liquid formulation that contains 27% hydrogen dioxide as an active ingredient.

Upon decomposition, H_2O_2 is converted to water and oxygen.

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

4.3 Description of use

GreenCleanPRO and GreenClean Liquid are broad spectrum aquatic algaecides. Minimum application rates in order to control blue-green algae in bodies of water, requires a dose of 3-6.9lb/acre-ft. An application of GreenCleanPRO can be up to 90lb/acre-ft. An application of GreenClean Liquid can be up to 30gal/acre-ft. An acre foot of water is one surface acre, one foot deep. Application is made directly to the area of growth. For example, if the body of water to be treated is 10 feet deep and 1 surface acre then there is a total of 10 acre-ft of water. If the algae are present in the top 4 feet of the water column then the application rate would be applied to the area of growth which is 4 acre-ft. Efficacy is determined by the dosage rate versus type of algae present, amount of algae present and water composition. Below is a further explanation of the factors that can influence dosage rate:

- Stage of algae growth – young cells are more sensitive than adult cells, but a higher density of growth requires a greater dose.
- Species – the dose will depend on the type of algae to be treated. Different blue-green algae species vary in their susceptibility to GreenCleanPRO or GreenClean Liquid. Blue-green algae have varying degrees of susceptibility due to the thickness of their cell walls and whether or not they have mucilage layers.
- Water Composition – a high level of transition metal (Fe, Cu) or organic matter could affect dose.

A large body of water should be treated in sections in order to prevent the exhaustion of dissolved oxygen in the water and allow for recovery before another section is treated.

BioSafe Systems analyzes water samples to identify the types of algae present in each sample. This determines a safe and effective rate of GreenCleanPRO or GreenClean Liquid that can be used to control a mixture of algal cells or blooms. Different mixtures of algae (cyanobacteria and filamentous) may be present in specific waterbodies and will require different treatment dosing.

Table 1 and Table 2 show the application rates for surface water volume rates per surface acre.

Table 1. GreenCleanPRO Surface Water Volume Only Rates

Algae Type	Algae Density	Rate (lbs/acre-ft)	Theoretical H_2O_2 Conc. (PPM)
Preventative/Maintenance	Preventative/ Maintenance	2-10	0.20-1.01
Cyanobacteria (planktonic form)	Low	10-30	1.01-3.04
Cyanobacteria, Green Algae (planktonic form)	Moderate	30-60	3.04-6.09
Cyanobacteria, Green Algae (planktonic form)	High	60-90	6.09-9.13
Cyanobacteria, GreenAlgae (planktonic and filamentous forms)	Extreme	90	9.13

GreenCleanPRO can also be used by making a solution of at least one gallon of water to fully dissolve each 0.5 pounds of GreenCleanPRO. Dissolution of GreenCleanPRO in cold water takes approximately 5 minutes. Treatment rates are the same as the granular application rates given above.

Table 2. GreenClean Liquid Surface Water Volume Only Rates

Algae Type	Algae Density	Rate (gals/acre-ft)	Theoretical H_2O_2 Conc. (PPM)
Preventative/Maintenance	Preventative/ Maintenance	1-2	0.83-1.66
Cyanobacteria (planktonic form)	Low	2-4	1.66-3.33
Cyanobacteria, Green Algae (planktonic form)	Moderate	4-8	3.33-6.65
Cyanobacteria, Green Algae (planktonic form)	High	8-12	6.65-9.98
Cyanobacteria, Green Algae (planktonic and filamentous forms)	Extreme	12-30	9.98-24.95

4.3.1 Typical application methods

GreenCleanPRO can be applied to surface waters via an application from land delivered to the water column or an aquatic application (by water). GreenCleanPRO is effectively applied to surface waters in the following manner(s):

- Spreading/Broadcasting
- Spot Treatment
- Subsurface Injection – Granular or Liquid
- Subsurface
- As a Liquid Solution
- Aerial

GreenClean Liquid can be applied to surface waters via an application from land delivered to the water column or an aquatic application (by water). GreenClean Liquid is effectively applied to surface waters in the following manner(s):

- Spot treatment
- Liquid treatment
- Injection treatment

4.3.2 Treatment Options

When applying GreenCleanPRO or GreenClean Liquid to algal surface mats/blooms the treatment may not penetrate the water column below the infested area. A second treatment as a direct treatment may be necessary to treat algae growing in the benthic region. For benthic treatment, a direct injection treatment is recommended by injecting the product through piping system. For surface water treatment spreading/broadcasting, spot treatment, subsurface, or aerial are recommended.

4.4 Mode of action/efficacy

When activated with water, sodium carbonate peroxyhydrate releases sodium carbonate and yields hydrogen peroxide as the active component. Hydrogen peroxide oxidizes critical cellular components of the target organism and kills them. Hydrogen peroxide then degrades to oxygen and water, neither of which is of toxicological concern.

4.5 Factors affecting algaecidal properties

4.5.1 Nature of algae

GreenCleanPRO and GreenClean Liquid are more effective on blue-green algae than on green algae. GreenCleanPRO and GreenClean Liquid have an escalating efficacy in its dosage rates for blue-greens and green algae. Within each category, variations also exist between species.

4.5.2 Repeat application

If both blue-green and green algae are present, use a higher rate with repeat applications as necessary in order to be effective on both forms. Otherwise, an insufficient (low) rate might inhibit only blue-green forms and their decay will increase nutrients in water. A successive bloom may have a larger proportion of green versus blue-green algae reaching to a nuisance level.

4.5.3 Algae growth

Effects include:

- Inadequate protective systems in young cells make newer algae growths more susceptible to treatment.
- Higher-density algae growth may require higher rates or more frequent applications, in order to fully penetrate the algal bloom.

4.5.4 GreenCleanPRO and GreenClean Liquid concentration

Depending upon the concentration, activity can range from growth control to complete kill with no re-growth.

4.5.5 Light intensity

Sunlight enhances peroxide activity, possibly through the occurrence of photo-induced reactions (Solvay 2005). GreenCleanPro and GreenClean Liquid are most effective in sunny conditions.

4.5.6 Water temperature

A higher temperature enhances the biocidal activity of peroxide (Solvay 2005). The dosage rate may need to be adjusted dependent upon the temperatures of the water. A lower temperature water body may increase the dosage rate due to lower biocidal activity vs. water bodies of higher temperatures.

4.5.7 Water quality

Dosage rates may have to be evaluated and changed if pollutants are present in the waterbody. Hydrogen peroxide has the tendency to rapidly degrade in the presence of certain pollutants already found in waterbodies.

Potential problem pollutants include:

- Metals present in high concentration could lead to peroxide decomposition.
- Clay particles, e.g. humus, may enhance peroxide degradation by maintaining the reactivity of transition metal ions.
- Organic matter itself, especially in the form of particulates, could also catalyze peroxide decomposition.

If sewage is a main contaminant, then a large amount of organic matter is expected. If a high level of agricultural runoff is taking place, then large concentrations of transition metals may be present. In both cases, greater levels of GreenCleanPRO or GreenClean Liquid may be needed to compensate for partial decomposition. However, testing done in the field has shown the low effect of these contaminants on peroxide activity, possibly due to quick absorption of peroxide and the short effective contact time.

4.5.8 Synergistic effects

Because of its mode of action (oxidation) and its affect on algae, GreenCleanPRO or GreenClean Liquid can be used in combination or coordination with other algaecidal products, i.e. copper sulfate ($CuSO_4$), to achieve an integrated approach of algae control. Although this technique is not necessary the consumer may apply GreenCleanPRO or GreenClean Liquid and follow up with a treatment of copper sulfate when algae are still present. If algae are still present after treatment with GreenCleanPRO or GreenClean Liquid and retreatment using copper sulfate is desired, copper sulfate may be used. An integrated approach will reduce dosage requirements. GreenCleanPRO and GreenClean Liquid will weaken the cell walls of the algae and less copper sulfate would need to be used resulting in less residual copper lingering in the water. Copper is not biodegradable, and once it is released into the environment, it accumulates in organisms' and sediments (Qian 2010). The oxygen release by GreenCleanPRO or GreenClean Liquid can help offset the oxygen demand from copper based algaecides (Solvay 2005).

4.6 Fate of Sodium Percarbonate in the aquatic environment

Sodium percarbonate rapidly dissolves in water and dissociates into sodium ions, carbonate ions and hydrogen peroxide:

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

<u>Hydrogen peroxide</u>

Hydrogen peroxide is a reactive substance. Both biotic and abiotic degradation processes are important routes in removal of hydrogen peroxide in the environment:

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

Abiotic degradation of hydrogen peroxide is due to either reaction with itself (disproportionation), or reaction with transition metals, organic compounds capable of reacting with hydrogen peroxide, reaction with free radicals, heat or light (European Commission, 2003b). Hydrogen peroxide is normally a short-lived substance in the environment but half-lives vary greatly depending on the circumstances.

Sodium carbonate

Both sodium and inorganic carbonate have a wide natural occurrence (UNEP, 1995; OECD, 2003). The sodium concentration was reported for a total number of 75 rivers in North and South America, Africa, Asia, Europe and Oceania, with a 10th percentile of 1.5 mg/l, mean of 28 mg/l and 90th percentile of 68 mg/l (UNEP, 1995). Also the bicarbonate (HCO3 -) concentration was reported for a total number of 77 rivers in North-America, South-America, Asia, Africa, Europe and Oceania. The 10th percentile, mean and 90th-percentile were 20, 106 and 195 mg/l, respectively.

A discharge of sodium carbonate to water will result in an increase in alkalinity and tendency to raise the pH value:

$CO_3\,2^- + H_2O \rightarrow HCO_3 - + OH^-$

$HCO_3^- + H+ \rightarrow CO_2 + H_2O$

In water the carbonate ion will re-equilibrate until equilibrium is established. The increase in pH depends on the buffer capacity of the water, which in most cases is determined by the natural background concentration of bicarbonate. To underline the importance of the buffer capacity, a table is included with the concentration of sodium carbonate needed to increase the pH to a value of 9.0, 10.0 and 11.0 at different bicarbonate concentrations. The data of Table 2 were based on calculations (Solvay 2005).

Table 3: Concentration of sodium carbonate (mg l) needed to increase the pH to values of 9.0, 10.0 and 11.0 (De Groot et al., 2002).

Buffer capacity^A	**Final pH^B**		
	9.0	**10.0**	**11.0**
0 mg/l HCO_3^- (distilled water)	1.1 (0.6)	16 (6.1)	603 (61)
15 mg/l HCO_3^- (10th percentile of 21 European rivers)	2.3 (16)	28 (21)	725 (76)
128 mg/l HCO_3^- (mean value of 21 European rivers)	12 (129)	120 (134)	1646 (189)
233 mg/l HCO_3^- (90th percentile of 21 European rivers)	20 (234)	206 (239)	2502 (294)

^{A} The initial pH of a bicarbonate solution with a concentration of 15 – 233 mg/l is 8.3 (calculated).
^{B} Between brackets the final concentration of bicarbonate is given.

Internal study conducted by BioSafe Systems with GreenClean PRO has shown that pH rise is determined by initial pH, dosage rate and water alkalinity. In water with moderate alkalinity (100-200 PPM $CaCO_3$), the average pH increase can be moderate and is also determined by the initial pH (Figs. 4 and 5). Study also found that any pH rise with application of GreenClean PRO at highest label rate is temporary and will slide down over a short period of time (Fig. 5). In surface waters with pH values close to the state pH standard, a dose response test will be conducted and an appropriate rate is recommended to ensure back ground pH levels do not cross state pH standard (8.5). If required, an acid buffer is recommended prior to application of GreenClean PRO.

Figure 4. GreenClean PRO and Water pH of Water Samples

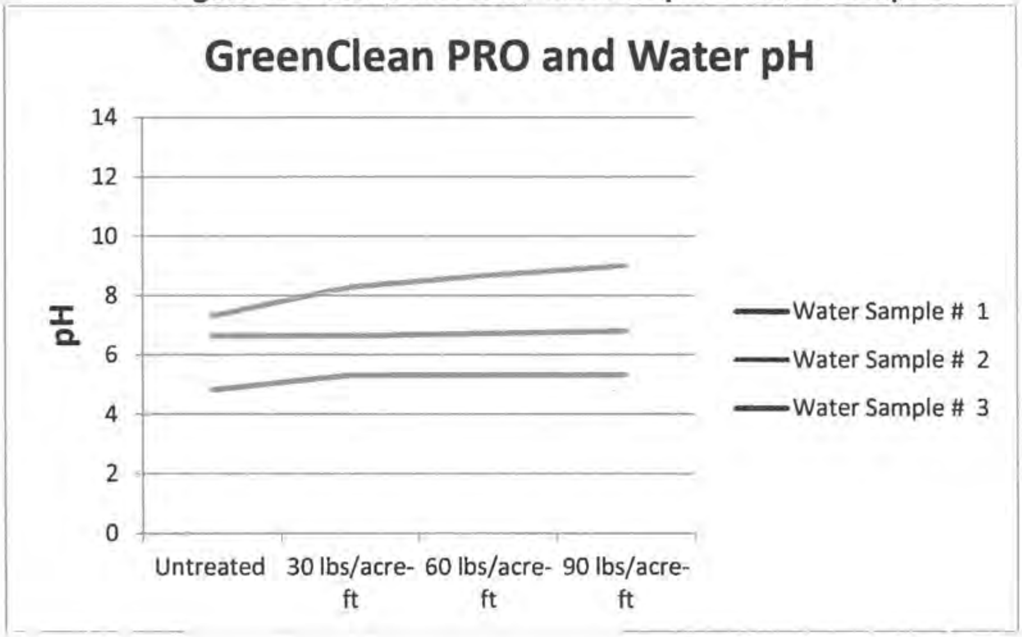
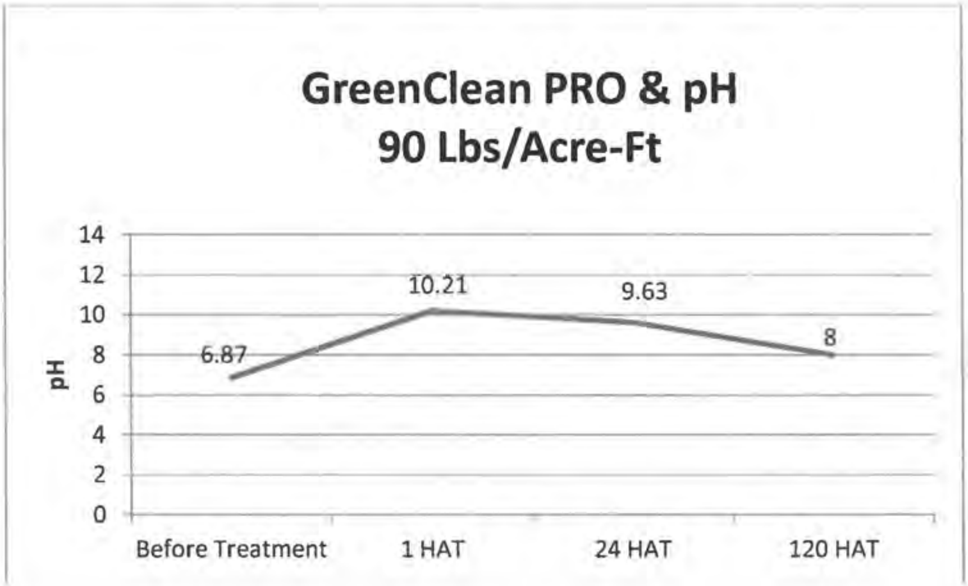


Figure 5. GreenClean PRO and pH Changes Over Time



4.6.1 Transport between Environmental Compartments

For solid sodium percarbonate no transport to the air is expected because of the negligible vapor pressure. When sodium percarbonate is dissolved in water, it dissociates to sodium carbonate and hydrogen peroxide rather easily. The high water solubility and low vapor pressure indicate that sodium carbonate will be found predominantly in the aquatic environment. Volatilisation of hydrogen peroxide from surface waters and moist soil is expected to be very low, while it is expected to be highly mobile in soil. It can be concluded that the aquatic compartment is the main compartment for sodium carbonate and hydrogen peroxide (Solvay 2005).

4.6.2 Biodegradation

Standard ready biodegradation tests are not applicable to the inorganic substances like hydrogen peroxide. However, the data set available was regarded as sufficient to draw conclusions upon the degradation of hydrogen peroxide. Enzymes produced by aerobic bacteria convert hydrogen peroxide to water and oxygen. Furthermore hydrogen peroxide is rapidly degraded in a biological waste water treatment plant. Not only a biological waste water treatment plant but also other domestic clarifiers are able to degrade hydrogen peroxide (Solvay 2005).

The following environmental conditions will change the persistence of sodium percarbonate/hydrogen peroxide:

- Alkaline (high degradation)
- Temperature
- Light conditions
- High concentrations of algae/bacteria (high degradation)

The rate of degradation of hydrogen peroxide (H_2O_2) in the environment was shown to be rapid based on data from multiple studies discussed below (Boulos et al. undated; Kay, et al. 1984; Ma DEP, 2010; Quimby and Kay, 1984).

A. Study by Boulos et al (unpublished) with a product similar in composition to GreenCleanPRO has shown a 93-100% degradation of H_2O_2 by 24 hrs after treatment (Table 4).

Table 4. Hydrogen Peroxide Concentration Versus Time (Boulos et al; Undated)

Sodium Carbonate Peroxyhydrate Conc. (lbs/acre-ft)	Theoretical H_2O_2 Conc. (ppm)	Residual H_2O_2 8 hr (%)	Residual H_2O_2 24 hr (%)
2.5	0.26	0	0
6.5	0.68	19	0
14.5	1.50	23	7
20.0	2.05	37	0

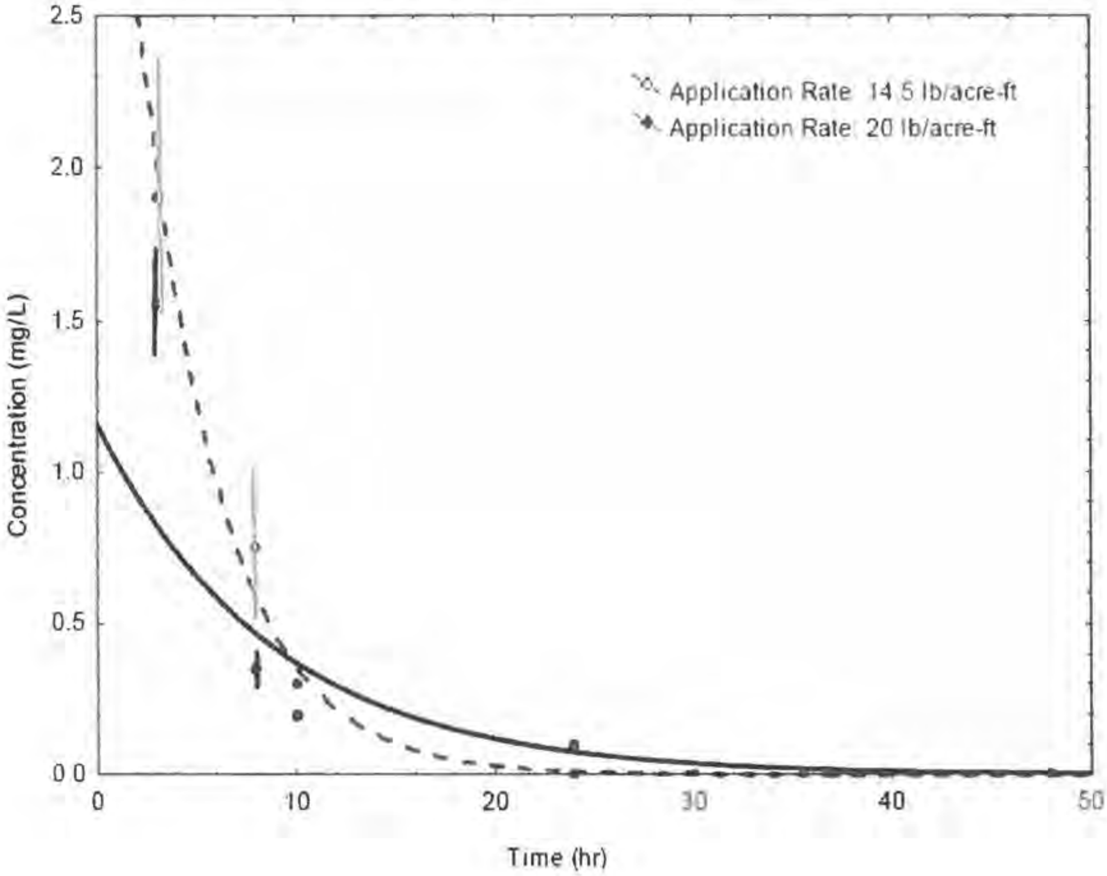
B. Similarly, results from the study by Kay et al (1984) has shown that 94% of initial 0.137 mM H_2O_2 had disappeared by 4 hours after treatment of a *Raphidiopsis* culture (Table 5).

Treatment	Measured Concentration of H2O2 (mM)		
	Initial	4h	24h
Control	0.001 ± 0.000	0.002 ±0.000	0.003 ±0.001
0.137 mM H2O2	0.115 ±0.002	0.008 ±0.001	0.003 ±0.001

Table 5. Degradation of H2O2 in a Treated Algal Suspension of *Raphidiopsis* (Kay et al. 1984)

C. A water column degradation study (OPP, 2004; As cited in Ma. DEP, 2010) conducted using a granular product similar in composition to GreenCleanPRO at different rates (2.5-20 lbs/acre-ft) and.time increments (0-50 hrs) has demonstrated rapid dissipation of residual H_2O_2 levels over time and mostly undetectable by 24 hrs after treatment (Fig.6).

Figure 6. Time Decay of Hydrogen Peroxide Concentrations Applied to Water. Vertical Lines represent Range of Reported Values. Fitted lines are Exponential decay Curves (OPP, 2004; As cited in Ma. DEP)



D. Studies conducted by Quimby and Kay (Quimby and Kay, 1984) has shown that an application of 3 ppm H_2O_2 declined to background levels (0.2 ppm) by 24 hours after treatment in the presence of a blue green algae suspension. In another study conducted at the Bill Evers Reservoir in Florida, the water was treated with a dose of 2 ppm H_2O_2 (equivalent to 40.29 lbs GreenCleanPRO Granular/acre-foot). Hydrogen peroxide levels were reduced to 0.75 ppm after eight hours and were completely decomposed after 24 hours (Quimby and Kay 1984).

Based on above studies, It's been consistently shown that hydrogen peroxide from products like GreenCleanPRO and GreenClean Liquid is not likely to persist in the water column long enough to pose any adverse effect on non-target species. The dissipation of H_2O_2 is so rapid in the presence of algae and organic matter that the exposure of non-target species to toxic levels of H_2O_2 is very minimal to none.

4.6.2.1. Biodegradation in Water

When sodium percarbonate is dissolved in water, it dissociates to sodium carbonate and hydrogen peroxide. Sodium and carbonate can not be biodegraded, although carbonate can be neutralized to bicarbonate.

4.6.2.2. Biodegradation in Sediment

There are no from standardized biodegradation systems available. No remarkable adsorption of hydrogen peroxide to sediment is expected and it may be assumed that the adsorbed portion of hydrogen peroxide may still be effectively degraded because normally sediments contain a lot of abotic and biotic material capable of degrading hydrogen peroxide. Rapid degradation is expected (EU, 2003).

4.6.2.3. Biodegradation in Soil

In soil hydrogen peroxide is normally a short-lived substance. Rapid degradation will occur due to high concentration of catalytic material such as transition metals, enzymes, easily oxidized or reduced substances and living microbes.

Hydrogen peroxide is used as a source of oxygen (for aerobic microbes) in polluted ground water sites (enhanced bioremediation). Therefore, specific information on degradability in soil is available. Degradation occurs too rapidly upon hydrogen peroxide being introduced to the soil. Observed half-lives of hydrogen peroxide in soil was noted to be between several minutes (soil with higher cells/gram counts of total solids with the presence of iron and manganese) and 15 hours (soil without microbial activity and limited minerals) (EU, 2003).

4.6.3 Bioaccumulation

When sodium percarbonate is dissolved in water, it dissociates to sodium carbonate and hydrogen peroxide. The sodium ion and carbonate ion will not accumulate in living tissues. Hydrogen peroxide is reactive and a short-lived polar substance and no bioaccumulation is expected (Solvay 2005).

5.0 Significant environmental impacts associated with GreenCleanPRO and GreenClean Liquid

5.1 Direct and indirect impacts to non-target species

5.1.1 Zooplankton

A 1996 study with a sodium carbonate peroxyhydrate product similar in composition to GreenCleanPRO was conducted in the Bill Evers Reservoir. Applications of sodium percarbonate at 0.5-20 lbs/acre-ft. were applied periodically throughout the year. Zooplankton and algae counts were compiled and statistically analyzed. The results indicate there was no correlation between the zooplankton population in the reservoir and applications of sodium percarbonate at 0.5-20 lbs/acre-ft. The population and distribution did vary throughout the year, with peaks in the spring and fall. The water chemistry that favors algae growth seems to reduce zooplankton. In seasons of low algae, zooplankton bloom. As the algae start to grow, zooplankton levels drop prior to any chemical treatment applications. The zooplankton appeared to rebound after the algae treatment season and drop as the algae blooms started, before treatment.

Treatment with sodium carbonate peroxyhydrate appears to not have any long term effects upon zooplankton in surface waters. Statistical analysis of the monitoring data for the year 1996 also clearly demonstrates that peroxygens have no persistent effects on zooplankton or algae over the long term. (Boulos and Moore, undated).

5.1.2 Aquatic plants and algae

Levels up to 3.25 ppm H_2O_2 had no effect on the green algae *Pandorina morum*, whereas the toxicity threshold for the blue-green algae *Oscillatoria rubescens* was found to be 1.75 ppm.

The threshold toxicity for the green algae *Ankistrodesmus* under laboratory conditions was between 7 – 10 ppm H_2O_2. On the other hand, the blue-green algae *Raphidiopsis* and *Microcystis* have threshold toxicity below 0.3 and 0.2 ppm H_2O_2 respectively. H2O2 levels up to 2 ppm had minimal impact on chlorophyll α concentration in a column of water infested primarily with green algae
The difference in susceptibility to H_2O_2 between blue-green and green algae was speculated to be due to eukaryotic algae having a photosynthetic apparatus "partitioned from the cytoplasm by a pair of limiting membranes giving rise to discrete cell organelle, the chloroplast, which protects the pigments against external incursions." In blue-green algae, the photosynthetic apparatus "does not segregate into discrete organelles and has a direct connection with the plasma membranes of the cell."

5.1.3 Vascular Plants

Several studies have evaluated the effect of H_2O_2 on submerged vascular plants. Negative effects were observed at levels of H_2O_2 at least one order of magnitude higher than those required to control blue-green algae.

Myriophyllum spicatum, Carex riparia, and the *Chara sp.* all survived a treatment by up to 20 ppm H_2O_2. *Elodea canadensis*, however, was killed at 10 ppm H_2O_2.

Several submerged vascular plants were injured after one hour exposure to 34-48 ppm H_2O_2. The injury was in direct proportion to the quantum flux density to which these plants were exposed. Examples included Fanwort (*Cabomba caroliniani* Gray), *Egeria* (*Egeria densa* Planch), Hydrilla (*Hydrilla verticillata*) and others.

Hydrilla and Coontail can be affected by continuous exposure for 5 days at 34 ppm H_2O_2. Under similar conditions, alligatorweed and waterhyacinths were not significantly affected.

This biocidal dose is significantly higher than the H_2O_2 dose suitable for killing blue-green algae.

5.1.4 Fish

A semi-static acute toxicity study with fathead minnow (*Pimephales promelas*), a freshwater species, and sodium percarbonate has been conducted according to GLP (Good Laboratory Practice) and EPA (Environmental Protection Agency) test guidelines. Test solutions were renewed daily and the hydrogen peroxide concentration was determined before and after renewal using a titration with potassium permanganate. The measured hydrogen peroxide concentration was used to calculate mean measured sodium percarbonate concentrations. Fish were exposed for 96 hours to mean measured sodium percarbonate concentrations of 0; 1.1; 7.4; 34; 81; 465 and 937 mg/L and observations were made after 24, 48, 72 and 96 hours. The LC50 and NOEC (No Observed Effect Concentration) of sodium percarbonate were 71 and 7.4 mg/l, respectively. No control mortality was observed (Boulos and Moore, undated).

In a preliminary study of sodium percarbonate conducted by Springborn Laboratories, rainbow trout were exposed under static conditions to GreenCleanPRO at nominal concentrations of 1.0, 5.0, 10.0, 50.0 and

100.0 mg/L and a dilution water control. The results showed no mortality or adverse effects were observed in any of the treatment levels or the control. A second preliminary test was conducted exposing rainbow trout under static conditions to GreenCleanPRO at nominal concentrations of 500 and 1000 mg/L and a control. Following 24 hours of exposure, 100% mortality was observed in the 500 and 1000 mg/L treatment levels. No mortality or adverse effects were observed in the control. Based on these preliminary tests, nominal sodium percarbonate concentrations of 65, 110, 180, 300 and 500 mg/L were chosen for the definitive study.

In the definitive study results were as follows, the 96-hour LC50 was estimated by probit analysis to be 150 mg/L with 95% confidence limits of 130 and 160 mg/L as shown in Table 6. Although 5% mortality was recorded in the 110 mg/L treatment level, no sublethal effects were observed and the mortality was considered to be within the range of naturally occurring variability. Thus the No-Observed-Effect Concentration (NOEC) was determined to be 110 mg/L (Machado 2001).

Based on these results and criteria established by U.S. EPA (1985), GreenClean would be classified as "practically non-toxic" to *Oncorhynchus mykiss.*

Table 6. LC50 Values and NOEC for Rainbow Trout

		95% Confidence Limit	
	LC50 (mg/L)	**Lower (mg/L)**	**Upper (mg/L)**
24hr	150	130	170
48hr	150	130	170
72hr	150	130	160
96hr	150	160	130

Many studies have been conducted to evaluate the effects of hydrogen peroxide on fish, but most of these involve very short-term exposures and so only a few are relevant for risk assessment purposes (EU, 2003). The lowest hydrogen peroxide LC50 for a 96-hour semi-static test in fish is on the fathead minnow (Pimephales promelas), reported to be 16.4 mg/L (Shrutleff, 1989a, as reported by EU, 2003). Hydrogen peroxide is a reactive substance, and undergoes degradation by both biotic and abiotic reactions (EU, 2003). This ready degradability of hydrogen peroxide is expected to minimize the potential exposure of fish to hydrogen peroxide from the use of GreenClean products.

Table 7 shows a study on short-term toxicity test results for aquatic species exposed to hydrogen peroxide. Due to its high reactivity, hydrogen peroxide applied to water will dissipate fairly quickly (Mass DEP 2010).

Table 7. Short Term Toxicity of Hydrogen Peroxide on Aquatic Animals

Species	Test Type	Duration (Hours)	Value (mg/L)
		Fish	
Pimephales promelas	Semi-static LC50	96	16.4
Leuciscus idus	Static LC50	72	35
Ictaluras punctatus	Semi-Satic LC50	96	37.4
		Invertebrates	
Daphnia pulex	Semi-static EC50	48	2.4
Daphnia magna	Static EC50	24	2.3 (2.0-2.6)
Gammarus sp.	Semi-static EC50	48	4.4

Physa sp.	Semi-static EC50	48	17.7

5.1.5 Invertebrates

A number of studies have been conducted to evaluate the effects of hydrogen peroxide on aquatic invertebrates, and daphnids appear to be among the most sensitive to the effects (EU, 2003). *Daphnia pulex* were exposed in a semi-static test of hydrogen peroxide in freshwater composed of 50% distilled water and 50% lake water. The 48-hour EC50 was 2.4 mg/l, based on the measured concentration of hydrogen peroxide (Shurtleff, 1989b, as reported by EU, 2003). In a second study on *Daphnia magna*, the EC50 for a 24-hour static study was 2.3 mg/l (Bringmann and Kuhn, 1982, as reported by EU, 2003). Hydrogen peroxide is a reactive substance, and undergoes degradation by both biotic and abiotic reactions (EU, 2003). This ready degradability of hydrogen peroxide is expected to minimize the potential exposure of aquatic invertebrates to hydrogen peroxide from the use of GreenClean products.

The effects of sodium percarbonate on the water flea *Daphnia pulex* have been studied by Shurtleff (1989b) according to GLP and EPA guidelines. Daphnids were exposed for 48 hours and they were transferred to fresh test solutions daily. The hydrogen peroxide concentrations were measured before and after each renewal using a titration with potassium permanganate. The measured hydrogen peroxide concentration was used to derive mean measured sodium percarbonate concentrations. Mean measured test concentrations were 0; 2.0; 12; 46; 89; 416 and 835 mg/L. The EC50 and NOEC of sodium percarbonate were 4.9 and 2.0 mg/L, respectively. No control mortality was observed (Boulos and Moore, undated).

Table 8. 1-hr pulse study shows the concentration is higher than the 48-hr concentration in the *Daphnia magna* (Mass DEP 2010).

Table 8. Hydrogen Peroxide Studies in *Daphnia magna*

Test Type	Exposure Duration (hours)	Value (mg/L)
Static EC 24-hr	1	High control response
Static LC 48-hr	1	10.7
Static EC 24-hr	4	Between 3.0-9.6
Static LC 48-hr	4	5.37
Static EC 24-hr	48	5.37
Static LC 48-hr	48	5.37

Table 9 illustrates the range of recommended label application rates and their resulting water concentration for each active ingredient. The table shows the application rate with the lowest effect concentrations for invertebrates and fish. Also, this table summarizes the effect levels. When data is limited the "no adverse effect level" is determined by taking the number for "low adverse effect level" and dividing by a factor of 10. The MATC (maximum acceptable Toxicant Concentration" falls between the "no adverse effect level" and the "low adverse effect level."

Table 9. Application Rates and Associated Toxicity

Active Ingredient	Label Application Rate (per acre-ft)	Estimated Water Concentration (mg/L)	Toxicity Range (mg/L)		Application Rate Associated with Lowest Effect Concentration (per acre-ft)	
			Invertebrates	Fish	Invertebrates	Fish
GreenCleanPRO						
Hydrogen Peroxide	9-90 lb	0.9-9.1	2.3-17.7	16.4-37.4	23 lb	162 lb
GreenClean Liquid Hydrogen Peroxide	1.2-30 gal	1.08-30	2.3-17.7	16.4-37.4	1.89 gal	13.47 gal

Using the "no adverse effect levels" of GreenCleanPRO or GreenClean Liquid as a basis for the maximum application rate would prove to be ineffective. The rates would be too low to see any effect take place and the condition prior to treatment would still be present (MA DEP 2010).

Conclusion:

Since half life of hydrogen peroxide from application of products like GreenCleanPRO and GreenClean Liquid is very low in the water with almost 100% degradation within 24 hrs in most cases, the products show low toxicity to the aquatic habitat with toxicity effects on non-target species being very minimal to none. While estimated water concentrations of hydrogen peroxide from the label rates may be within the toxicity ranges of some non-target species, the fact that hydrogen peroxide dissipates so rapidly may not provide a chance for the non-target species to get exposed to constant levels of toxic H_2O_2 concentrations for a determined time period and end concentrations of H_2O_2 in the water will quickly drop to at or below NOEC values.

5.1.6 Wetlands

Hydrogen peroxide does not bind to soil particles assuming that hydrogen peroxide's physical properties are similar to water's physical properties (U.S.EPA 2007). Microbes intrinsic to wetland environments have the ability to break down and use nutrients and contaminants that can be harmful to the environment. Hydrogen peroxide is also used in oxidizing or recovering various contaminants in soils or waters. Wetlands have the ability to cleanse surface water, recharge groundwater supplies, as well as the ability to attenuate floodwaters. Hydrogen peroxide has little effect on wetlands when using the appropriate application rate for the given area.

5.1.7 Discussion/Conclusion

The toxicity data of hydrogen peroxide indicates that there is a pattern of rapid degradation and is less likely to persist in water long enough to impose a toxic effect. Rapid degradation has been observed in numerous studies and has been a consistent result in the environment. The residual hydrogen peroxide percentage at 24 hours is similar to the background concentrations and controls. The variation of hydrogen peroxide percentage remaining in the waterbody is dependent upon the concentration of application as well as the pollutants present in the water body.

Hydrogen peroxide degradation data suggests that target and non-target species are not exposed to toxic levels of hydrogen peroxide for a long duration. Many factors including time of day for treatment, plant morphology, population densities, growth habit, stage of growth, water temperature and light quality, may influence the efficacy of hydrogen peroxide. These factors may increase toxicity or decrease toxicity in water bodies depending on the current conditions of the water body as well as the characteristics of the inhabiting species. Low temperatures and poor light quality may hinder degradation causing a longer contact time to non-target species indicating application rates may need to be adjusted.

GreenCleanPro or GreenClean Liquid should be applied on a calm sunny day and when the water temperature is at least 60° F. It is recommended to avoid treatment of waterbodies during prime fish feeding times, including very early in the morning. A large body of water should be treated in sections in order to prevent the exhaustion of dissolved oxygen in the water and allow for recovery before another section is treated. The depletion of biota and subsequent anoxia from decaying organic matter may occur if treating all at once. Benthic biota populations must be able to recolonize to avoid damaging the ecology of the waterbody.

On the basis of the toxicity and environmental exposure data examined, there is no significant threat to the environment, the populations of organisms residing therein, or public health and safety when hydrogen peroxide concentrations are applied at or below the recommended application rates and guidelines. Hydrogen peroxide is a reactive substance, and undergoes degradation by both biotic and abiotic reactions (EU, 2003). This ready degradability of hydrogen peroxide is expected to minimize the potential exposure of aquatic organisms to hydrogen peroxide from the use of GreenClean products. GreenClean products are unlikely to pose an adverse effect upon the environment, due to the facts that hydrogen peroxide is not likely to persist in the water column, rapidly breaking down to water and oxygen, and the limitation of treatment areas in large scale applications allows for repopulation of potentially impacted species in treated areas.

6.0 Potential public health impacts

6.1 Brief overview of GreenCleanPRO and GreenClean Liquid toxicity

6.1.1 Acute toxicity of GreenCleanPRO

Oral

A number of oral acute toxicity studies have been carried out in rats using solutions with different concentrations of sodium percarbonate.

An acute oral study has been conducted with rats according to EPA test guidelines and EPA GLP guidelines. An LD50 of 1034 mg/kg bw (body weight) was calculated when groups of 5 rats/sex were given aqueous suspensions containing 700, 1000 or 1500 mg/kg bw orally. Toxic effects included depressed activity, poor co-ordination, diarrhea, facial staining (red), labored breathing, absence of pain reflex, excessive salivation and, in the glandular portion of the stomach, coloration changes with occasional thickening of the wall.

Rats were dosed with sodium percarbonate, as a 10 % suspension in maize oil, at dose levels of 1000, 1700, 2900 and 5000 mg/kg bw. This study was not performed according to GLP or standard test guidelines. A total number of 24 rats was used in this study (3/sex/dose) and the observation period was 14 days. The LD50 was 2000 mg/kg bw and the clinical signs of the surviving animals were raised hair, incontinence, dehydration and atrophy of the testes (further details of clinical signs not available). Necropsy findings indicated that an effect was present in the stomach. Inflammation and necrosis were observed. Death was always found to be associated with the stomach and intestine being enlarged and filled with gas.

Another acute oral study has been conducted with mice and sodium percarbonate. This study was not performed according to GLP or standard test guidelines. A total number of 130 female and male mice were dosed with a solution of 4 % sodium percarbonate in water at dose levels of 1500 – 3040 mg/kg bw. The LD50 value was 2050 mg/kg for the males and 2200 mg/kg for the females. Observed effects were decreased activity, swollen abdomen, diarrhea, unspecified "behavioral symptoms". At necropsy, dead animals presented a slight degree of congestion or blood spots in the stomach mucosa, and blood was mixed with the stomach contents. Furthermore distension of the gastro-intestinal tract was observed and, in high-dose animals that died, slight congestion of the brain and lungs was found.

The results of these studies are in accordance with results obtained from acute oral studies with hydrogen peroxide at comparable concentration levels.

Dermal

A single dose of 2000 mg/kg bw sodium percarbonate was administered to the intact skin of 10 New Zealand White rabbits according to EPA test guidelines and EPA GLP guidelines. The rabbits were exposed to the test substance for 24 hours under occluded conditions. No mortality and no treatment-related overt systemic toxicity were observed during the study and therefore the LD50 in rabbits was > 2000 mg/kg bw. The level of dermal irritation was severe. No other macroscopic findings were observed at necropsy.

The results of this study are in accordance with results obtained from acute dermal studies with hydrogen peroxide at a comparable concentration level.

Inhalation

A reliable acute inhalation toxicity study was not available. The following data was reported without any quality assessment: LC0 rat > 4.58 mg/l at an exposure time of 1 hour. An acute respiratory irritation study has been conducted with male mice. No clinical signs and no indication of treatment related effect as observed at necropsy and no indication of a treatment effect on lung weight was obtained. This study has been described in detail in section 3.1.3.

Conclusion

Standard acute oral and dermal toxicity studies with a high reliability are available. Acute oral LD50 values ranged between 1034 and 2000 mg/kg bw, while the acute dermal LD50 was > 2000 mg/kg bw. The existing animal data on acute toxicity show that sodium percarbonate has a local effect and that systemic effects are not to be expected (Solvay 2005).

6.1.2 Chronic toxicity of GreenCleanPRO

In view of the breakdown of the pesticide product in the presence of water to hydrogen peroxide and sodium carbonate, and the subsequent breakdown of hydrogen peroxide on contact to water and oxygen, cumulative effects are not expected.

6.1.3 Acute toxicity of GreenClean Liquid

Exposure to high concentrations of hydrogen peroxide via inhalation, ingestion, and dermal exposure lead to higher rates of absorption, which leads to oxygen bubble formation in the blood vessels. Inhalation and ingestion exposure may be harmful. Pulmonary, cerebral or other systematic embolization may also occur (Mass DEP 2010).

6.1.4 Chronic toxicity of GreenClean Liquid

Long term exposure of hydrogen peroxide may be very corrosive and irritating to skin and especially to eyes. Respiratory system irritation as well as skin bleaching had been observed in occupational studies (Mass DEP 2010).

6.2 Brief overview of cyanotoxins in water bodies

Most types of algae are harmless to humans and are an essential part of the food chain. Blue-green algae are microorganisms that can cause harm to humans, domestic animals and livestock. Blue-green algae possess characteristics of algae (chlorophyll-a and oxygenic photosynthesis) and are not actually algae, but instead cyanobacteria, a phylum of bacteria. Algal blooms, specifically cyanobacteria, generate cyanotoxins that are released into water bodies as cells naturally die off and begin to break down. These toxins are also thought to increase in concentration after treating water bodies with an algaecide due to the amount of lysed cyanobacterial cells. The cyanotoxin concentration may exceed acceptable levels and the water body may be restricted from use until cyanotoxin degradation occurs.

Cyanobacteria occur especially in eutrophic inland and coastal surface waters, when conditions are favorable and have the potential to rapidly multiply in surface water to form blooms and scums. There are several groups of cyanotoxins based on their biological effects which include hepatotoxins, neurotoxins, cyanotoxins and toxins with irritating potential, also acting on the gastrointestinal systems (Funari and Testai, 2008). Microcystis is the most common bloom-forming genus, and is almost always toxic. Microcystins are produced from microcystis and has recently undergone evaluation of carcinogenesis from microcystin exposure by the International Agency for Research in Cancer. This agency has determined that Microcystin-LR is possibly carcinogenic to humans (Group 2B), and has been linked to incidences of human liver and colon cancer (U.S. EPA, 2013). Microcystin-LR one of the most potent microcystins in acute cases (Falconer *et al.*, 1999).

The WHO has proposed an upper limit for microcystin-LR in drinking water and recreational water bodies as indicated in table 10 (Falconer, Ian *et al.*, 1999). Also, WHO guideline values and probable health effect from exposure to cyanobacteria are presented in table 11 (WHO, 2003). Currently, there are no U.S. federal regulatory guidelines for cyanobacteria or their toxins in drinking water or recreational waters.

Table 10.

WHO Guideline for microcystin-LR in water bodies		
Type of Water Body	**Risk of Exposure**	**Upper Limit**
Drinking Water	Relatively low	1.0 µ/L
Recreational Uses	Relatively low	4.0 µ/L
	Moderate probability	20.0 µ/L
	High probability	Scum present

Table 11. Health Effects from Exposure to Cyanobacteria: WHO Guideline Levels

Probability of Adverse Health Effect	Guideline Level	
	(Cyanobacterial Cells/mL)	Chlorophyll-a µg/Liter
Low	20,000	10
Moderate	100,000	50
High	Scum	-

6.2.1 Health risks associated with cyanotoxins

There are three routes of exposure to cyanotoxins in recreational waters which include direct contact of exposed body parts as well as areas covered by a swimsuit; accidental swallowing; and inhalation of water. Sensitive areas of the body include ears, eyes, mouth and throat (Kupier-Goodman *et al.*, 1999).

Health effects due to accidental swallowing of water containing cyanotoxins includes headaches, nausea, vomiting, central abdominal pain, sore throats, muscular pains, painful diarrhea, fever, flu like symptoms, mouth ulcers and blistering of the lips. Cases of inhalation can cause pneumonia or other respiratory problems. Direct contact with the water can cause skin rashes, eye and or ear irritations (Kupier-Goodmand *et al.*, 1999).

6.2.2 Recommended treatment protocol

Before treating any water body with an algaecide, a water sample should be analyzed to determine the algae type and density especially if blue-green algae is suspected. If the water sample contains cyanobacteria another test should be completed to determine the concentration of toxins in the water body prior to treatment. A sample should also be analyzed post treatment to determine if cyanotoxin concentrations have changed.

Abraxis *Microcystin Strip Test Kits* are available to monitor recreational waters. This type of test is a rapid immunochromatographic test, designed solely for the use in qualitative screening of Microcystins and Nodularins in recreational water and is also available for source drinking water and finished drinking water. A rapid cell lysis step performed prior to testing is required to measure total microcystins (dissolved or free, plus cell bound). This test only provides preliminary qualitative test results and if necessary, positive samples can be confirmed by ELISA, HPLC or other conventional testing methods. The test strips results range from 0 ppb to 10 ppb. Results are read in 5 minutes after completing the assay procedure (Abraxis).

BioSafe Systems' recommended protocol is to treat water bodies with GreenCleanPRO or GreenClean Liquid before algal cells reach a high or even moderate density (≥ 100,000 cyanobacterial cells per mL or 50 µg of chlorophyll-a per Liter) Frequent monitoring of the water body's algae content is necessary to efficiently maintain algae-free waters as well as limit the toxins released into the water body. Prevention is the most effective method to eliminate toxins in water bodies since no toxins will be generated in algal cells.

Applicators should set a threshold to prevent heavy algae growth form occurring and treat while algal density is low. The health risk is eliminated or reduced once the water body is consistently algae-free or algae remain at a low density, respectively. Cyanotoxin release is inevitable when heavy growth has occurred and water bodies may become restricted from use until toxin levels have dissipated. Microcystin degradation occurs within a few days. Around 5 days post treatment another sample should be taken to ensure the toxin levels are within safe ranges for un-restricted water body use (Bishop *et al.*, unknown).

6.2.3 Forthcoming studies

Numerous reports of poisoning incidents in humans and livestock have been caused by cyanobacteria or their toxins and the most frequently cited organism is Microcystis (Kupier-Goodman *et al.*, 1999). The most common and dangerous hepatotoxin found in freshwater environments is Microcystin-LR. Research suggests that all of the currently known toxins are oxidizable suggesting free oxygen being used to cleave and biologically "neutralize" the cyanotoxins. To date, there are no efficacy studies completed to validate the theory, but studies are underway as Microcystin-LR is now commercially available for testing.

6.2.4 Discussion/conclusion

Indeed, there are health risks associated with waterbodies containing harmful algal blooms and lake managers must be aware of the toxins produced by cyanobacteria. However, there are steps to avoid these health risks. Treating waterbodies with GreenCleanPRO or GreenClean Liquid when algae densities are low is the most effective step. The only risk to humans using recreational waterbodies is when a bloom or scum is present. Recreational water managers must be aware of the potential health risks and create a treatment protocol and maintenance plan for cyanobacteria control. Waterbodies may need to be restricted for recreational use, but this can be prevented if a proper threshold is set and the waterbody is treated once cyanobacteria are detected. GreenCleanPRO and GreenClean Liquid products keep cyanobacteria under control without destroying beneficial green-algae and will limit the health risks associated with cyanotoxins with regular use.

6.3 Summary of human health risk concerns

Based on normal habits and uses, the consumer exposure to sodium percarbonate by inhalation, oral uptake and skin contact to solid sodium percarbonate is negligible and therefore the associated risk is also negligible. However, two relevant exposure scenarios were identified and the potential risks will be characterized for both scenarios.

6.3.1 Skin contact with GreenCleanPRO/GreenClean Liquid via solutions

The estimated exposure to sodium percarbonate due to laundry hand washing was 5.4×10^{-4} mg per event. This is equal to an exposure of 0.54 µg sodium percarbonate, which is equivalent with 0.18 µg hydrogen peroxide, 0.21 µg carbonate and 0.16 µg sodium. Due to the rapid degradation the amount of 0.18 µg will not increase the concentration of hydrogen peroxide in the blood. The amount of 0.21 µg carbonate will not affect the pH of the blood, while the amount of 0.16 µg sodium is negligible compared to the normal daily dietary uptake of sodium of 3.1- 6.0 g (Fodor et al., 1999). For this reason it can be concluded that the exposure to sodium percarbonate via solutions has no systemic effect on the consumers.

Data about the relationship between sodium percarbonate concentration and skin irritation potential are not available. However, to predict the skin irritation potential of sodium percarbonate solutions the hydrogen peroxide concentration could be used. Based on the evaluation of the EU Commission Working Group on the Classification and Labeling of Dangerous Substances a hydrogen peroxide concentration of 50 % and higher is corrosive, while concentrations of 35-50 % are irritating to the skin.

Because sodium percarbonate contains 32.5 % hydrogen peroxide, irritant levels of hydrogen peroxide can not be achieved in solutions. Based on the laundry hand washing scenario (with sodium percarbonate as extra laundry additive) the sodium percarbonate concentration in the solution would be 0.4 %, which is equivalent with a hydrogen peroxide concentration of 0.13 %. When humans are exposed to such a solution the hydrogen peroxide content in the solution is still about 250 times lower than the lower irritation limit of hydrogen peroxide (32.5 %). Therefore it can be concluded that local effects on the skin are not expected when consumers are exposed to sodium percarbonate via solutions (e.g. laundry hand washing) (Solvay 2002).

6.3.2 Accidental or intentional overexposure

Accidental or intentional overexposure to sodium percarbonate may occur via the oral route, via exposure of the eyes (e.g. due to splashing) or via inhalation.

Acute oral LD50 values were 1034 and 2000 mg/kg body weight, while the acute dermal LD50 was > 2000 mg/kg body weight. Based on these LD50 values the uptake of sodium percarbonate by humans must be very high (> 50 g) to reach acute lethal effects. The amount of the household cleaning product which must be ingested is even higher and or this reason it is very unlikely that accidental overexposure results in lethal or severe effects. Typically one would estimate that not more than 5 g of detergent or 1.25 g of sodium percarbonate could be swallowed. For a 10 kg child this would result in a dose of 125 mg/kg bw. Lethal effects in animals occur from 1034 to 2000 mg/kg bw in rodents. However, it is likely that due to the liberation of hydrogen peroxide in the stomach humans will vomit and not be able to take up lethal amounts of detergents. The poison centre records that have not registered any fatal poisonings due to the swallowing of detergents, and normally only immediately reversible irritation reactions of relatively benign nature corroborate this. Furthermore acute cases of oral poisoning, due to sodium percarbonate ingestion, were not found in the literature.

In vivo eye irritation tests show that the powder sodium percarbonate is highly irritating to corrosive to the eye (not rinsed). Therefore solid sodium percarbonate or household cleaning products which contain sodium percarbonate (e.g. detergents) could potentially result in eye irritation. However, the eye irritation potential of products which contain sodium percarbonate depends on many factors e.g. the sodium percarbonate content, the other components and also the particle size distribution.

An evaluation of hydrogen peroxide by the EU Commission Working Group on the Classification and Labeling of Dangerous Substances revealed that concentrations of 5-8 % will be labeled as "irritating to eyes" (R36), concentrations of 8-50 % will be labeled with "risk of serious damage to eyes" and concentrations higher than 50 % will be "corrosive". Based on these data "risk of serious damage to eyes" would only occur if the sodium percarbonate concentration is higher than 25 % in a solution.

A solution used for laundry hand washing contains only 0.39 % sodium percarbonate (= 0.13 % of hydrogen peroxide) and for this reason there is no risk for eye irritation if eyes were accidently exposed to such a solution (e.g. due to splashing). Effects on human eyes, due to exposure to sodium percarbonate as such, were not found in the literature. However, a few cases of relatively mild eye irritation have been reported after exposure to detergents.

Although accidental oral, eye or inhalation exposure to the product sodium percarbonate has not been found in the literature, ingestion and inhalation of laundry detergent powder by children has been reported in the Unites States. The predominant symptoms were stridor, drooling and respiratory distress. It is unknown if similar cases of accidental inhalation exposure have occurred in Europe (Solvay 2002).

6.3.3 Discussion/conclusion

Sodium percarbonate has a low acute toxicity via the oral and dermal route (LD50 > 1000 mg/kg bodyweight). The existing animal data on acute toxicity show that sodium percarbonate has a local effect. In animal tests a slight irritating effect on the skin was reported for solid sodium percarbonate and it was highly irritating to the rabbit eye (not rinsed). Sodium percarbonate did not have sensitising properties in a test with guinea pigs.

When consumers are exposed to sodium percarbonate, neither hydrogen peroxide nor sodium carbonate will be systemically available due to their effective detoxification (degradation or neutralisation) in the body. Consequently it is to be expected that the concentration of hydrogen peroxide and sodium in the blood and the pH of the blood will not be increased. Therefore, neither sodium percarbonate itself nor hydrogen peroxide or carbonate will reach the organs or the foetus and there is no risk for systemic, developmental or reproductive toxicity. With regard to genotoxicity and carcinogenicity the properties of sodium percarbonate also resemble those of hydrogen peroxide and it can be concluded that there is no concern for humans with regard to a possible genotoxicity or carcinogenicity of sodium percarbonate. The only critical endpoint for sodium percarbonate seems to be local irritation.

Consumers can be exposed to sodium percarbonate due to skin contact with solutions which contain sodium percarbonate, which can be laundry hand washing. However, the estimated concentrations of sodium percarbonate in these solutions are too low to cause skin irritation.

Accidental exposure of the eyes to dry products which contain sodium percarbonate or to solutions of household cleaning products which contain sodium percarbonate could result in eye irritation. In cases where the sodium percarbonate concentration is higher than 25%, as is the case with GreenCleanPRO, irreversible damage to the eye could occur if the eye is not immediately washed out.

Acute cases of oral poisoning or effects on human eyes, due to accidental or intentional overexposure to sodium percarbonate, have not been found in the literature (Solvay 2002).

Given that application of this product would likely not be made while people were present and the products are expected to degrade relatively quickly, it is unlikely that use of these products as specified on the product labels would result in significant exposures to humans using the waterbodies recreationally. As the product label specifies, undiluted granules should not be allowed to remain in an area where humans or animals may be exposed (Mass DEP 2010; 1).

Based on the available data, the use of sodium percarbonate in New York State waters has no adverse effect on consumers.

7.0 Alternatives to GreenCleanPRO or GreenClean Liquid

The following measures are currently available/approved for algae control in surface water.

7.1 Retardation of Algae Formulation

7.1.1 Nonpoint source pollution reduction

The key nutrients for algae growth are phosphorous and nitrogen. In a study reviewing different pollutants in surface water, nutrients were found to be the second highest after siltation. It is rather difficult to maintain nutrients at low enough levels to control algae growth. Phosphate levels would have to be dropped to ~ 25 ppb in order for this to become a limiting factor in algae growth.

Efforts towards reducing the introduction of nutrients into ponds and lakes are ongoing. Reduction of agriculture fertilizer runoffs would probably lead to the greatest nutrient reduction.

7.1.2 Chemical addition

Addition of buffered alum or calcium compounds is another option to reduce dissolved nutrients. These tie up phosphorous and reduce its availability for algae growth. However, effectiveness depends heavily on the water retention time for the lake, and phosphorous in the sediment reenters water in periods of anoxia.

7.1.3 Mechanical aeration

Air injection in water leads to the following:

- forces cold bottom water to the surface which retards algae development
- reduces light exposure, which prevents photosynthetic activity and algal growth

This technique has the following limitations:

- it is energy dependent
- high capital cost for installation of aerators
- high electrical cost for running aerators
- continuous maintenance costs
- does not completely eliminate algae problem.

7.2 Physical removal

Various methods were tried for the physical removal of algae from lakes such as algae coagulation. These have been tested only in small trials as they are expensive to use on a large scale. Physical removal can lead to further inoculation since some algae can reproduce through fragmentation.

7.3 Algaecidal treatment

7.3.1 Copper based algaecides

Copper based algaecides, e.g. copper sulfate ($CuSO_4$) were, until recently, the only chemicals approved by the EPA for algae control. These have the following limitations:

- Cu precipitates under alkaline conditions, formulations include ingredients such as organic acids or chelating agents to maintain Cu activity. These lead to a higher chemical cost and have their own safety concerns.
- Cu has a tendency to accumulate in mud and sediments.
- Cu is recognized for its toxicity to fish and invertebrates.
- High levels of copper in aquatic plants can accumulate from a very low level in water, when exposed for long periods of time.

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