MINLOX™

A SIMPLER CHEMICAL FOR WATER

TASTE & ODOR CONTROL

Introduction

Some taste and odors are caused by mineral constituents in the water, e.g. excess chlorine and hydrogen sulfide. However the majority of taste and odor issues are the result of biologic activity. Spring turnover of lakes and algal blooms are responsible for Blue-green algae (Cyanobacterium), Green algae and diatoms that introduce filter clogging organisms that also foul anion exchange resins, degrade effluent quality of demineralized water, which also interfere with flocculation and sedimentation and produce toxic organic compounds (negatively charged colloid oils) that contribute to taste and odor in the finished water.

People involved in water treatment speak generally of an "algae" problem. In fact, it is more accurate to use the term "plankton". This term includes all the micro-algae that under favorable conditions (the presence of ideal amounts of nutrients, heat, and sunlight in the environment) can undergo periods of explosive growth. It also includes animal plankton (zooplankton), which belong to a higher level in the food chain, as well as Actinomycetes. All these organisms are sized within a range of a few microns to a few millimeters. Examples of organism derived odors are:

Species	Moderate	Abundant
Cyanophyceae (Blue Green)		
Anabaena	Grassy	Septic
Aphanizomenon	Grassy	Septic
Microcytis	Grassy	Septic
Oscillatoria sp (filamentous)	Grassy	Musty
Chorophyceae (Green)		
Chlamydomonas	Fishy	Fishy
Chlorella	Fishy	Fishy
Pandorina	Fishy	Fishy
Pediastrum	Fishy	Fishy
Scenedesmus	Fishy	Fishy
Staurastrum	Fishy	Fishy
Volvox	Fishy	Fishy
Chrysophyceae (brown)		
Dinobryon	Violet	Fishy
Synura	Cucumber	Fishy
Bacillariophyceae (diatoms)		
Asterionella	Geranium	Fishy
Cyclolella	Geranium	Fishy
Melosira	Geranium	Musty
Stephanodiscus	Geranium	Fishy
Synedra	Geranium	Musty
Tabellaria	Geranium	Fishy
Euglenophyceae (Flagellates)		
Euglena	Musty	Musty
Actinobacteria		
Streptomyces	Earthy	Musty

Chlorophyll *a* is a photosynthetic pigment that serves as a measurable parameter for all algae production. Quantitative biomass estimates can be made noting that on average 1.5% of algal organic matter is chlorophyll *a.* Qualitative assessment of primary production on water quality can be based on chlorophyll a concentrations as noted below:

Chlr-*a* Concentration (g/l)	Water discoloration
<10	No discoloration
10-15	Some discoloration, some algal scum
20-30	Deep discoloration, algal scum
>30	Very deep discoloration, algal matting

Algae elimination by mechanical means of removing algae is a first choice. It effectively removes particulates that would significantly contribute to organic loading and removes particulates that would increase disinfection by-products for a water source.

When choosing a *chemical disinfectant*, it is helpful to know and plan accordingly to the chemistry oxidation potential and the oxidation energy it provides. When isolating specific compounds, e.g. peroxide, some portion of the peroxide becomes water and back to peroxide. Though the percent of peroxide to water appears stable, on a molecular level there is continuous movement back and forth and it is this constant movement of electrons that gives a measurable voltage. In this peroxide example, the reaction favors the peroxide side of the equation, hence gives a positive voltage. If the reaction favored production of water, the voltage reading would be negative. Therefore, a compounds relative ability to give up electrons is represented by a positive voltage:

Chemical	Reaction	Volts at 25 deg C
Ozone	$O_3 + 2H^+ + 2e$ <-> $O_2 + H_2O$	2.87
MINLOX™	Mixed oxygen radicals	Not determined
Peroxide (acid)	$H_2O_2 + 2H^+ + 2e$ <-> $2H_2O$	1.76
Permanganate	$MnO_4 + 8H^+ + 5e$ <-> $Mn^{2+} + 4H_2O$	1.46
Hypochlorite (acid)	$HOCl + H^+ + 2e$ <-> $Cl^- +$ H2O	1.49
Chlorine	$Cl_2 + 2e$ <-> $2Cl^-$	1.39
Chlorine Dioxide	ClO_2 (gas) + e <-> ClO_2^-	1.15
Bromine	$Br_2 + 2e$ <-> $2Br^-$	1.07
Hypochlorite (basic)	$OCl^- + H_2O + 2e$ <-> $Cl^- + 2OH^-$	0.90
Peroxide (basic)	$H_2O_2 + 2e$ <-> $2OH^-$	0.87
Oxygen	$O_2 + 2H_2O + 4e$ <-> $4OH^-$	0.40

A comparison of available data of strong oxidants applied to algae is:

Oxidant	Dosage mg/l	Reaction time, min	% deactivation
Permanganate	1	30	9.5
Permanganate	2	30	68
Permanganate	3	30	89
Permanganate	1	60	68
Permanganate	2	60	98
Permanganate	3	60	100
Peroxide	100	30	50
Peroxide	100	60	75
Ozone	1	1	14
Ozone	2	1	64
Ozone	3	1	70
Ozone	1	5	26
Ozone	2	5	72
Ozone	3	5	76
MINLOX™	ORP > 400	30	99.999

Green algae and most diatoms, along with the excreted organics that cause odors are susceptible to conventional water treatment chemistry. But, Blue-green algae and protozoas require the more aggressive oxygen radicals to be deactivated as well as the organics released that cause odors. Especially when phytoplankton are senescent (the growth phase following maturity and prior to death, characterized by accumulated metabolic products, increased respiration, and loss of dry weight) and decaying. Blue-green algae (also known as cyanobacteria) are microscopic organisms found naturally in surface water. True algae and blue-green algae both utilize some form of chlorophyll to perform photosynthesis. True algae are essentially plants. Blue-green algae are actually bacteria that exhibit a blue or green color, similar to true algae, but contain cellular structures typical of bacterial cells. True algae and blue-green algae are very different organisms and therefore should not be treated the same. There are no known harmful toxins released by dying true algae. Blue-green algae, however, can contain harmful toxins within the cell wall which may be released during cell growth or death.

Toxins of critical concern:

Cyanophyceae (Blue Green)	
Anatoxin-a	neurotoxic
Cylindrospermopsin	Hepatotoxic
Microcystin	Hepatotoxic
Saxitoxin	Neurotoxic
Actinobacteria	
Geosmin (Geo)	Muddy smell
Methylisoborneol (MIB)	Musty smell

The choice of oxidizer must also consider the oxidizer impact on the toxins secreted by marine organisms. Data summarizing this impact is:

	Anatoxin-a	Cylindrospermopsin	Microcystin	Saxitoxin	Geo/MIB[5]
Chlorine[1]	Not effective	Effective (at low pH)	Effective	Not effective	Not effective
Chloramine[2]	Not effective	Not effective	Not effective	Not effective	Not effective
Chlorine Dioxide[2]	Not effective	Not effective	Not effective	Not effective	Not effective
Permanganate	Effective	Not effective	Effective	Not effective	Not effective
Ozone[3]	Effective	Effective	Effective	Not effective	Not effective
UV/peroxide	Effective	Effective	Not effective	Not effective	Effective
MINLOX[4]	Effective	Effective	Effective	Effective	Effective

1. Reactivity of chlorine with toxins is influenced by pH of the water and the loading of organic matter

2. Very high doses and long contact times can effect these toxins but will create compliance issues with residual concentrations of chlorite and chlorate

3. Ozone reacts quickly with all toxins but is not capable of providing a contact time needed to be effective against Saxitoxin and Geosmin/MIB, which require CT much in excess of 20 min.

4. Based on available data on the effectiveness of the joint action of multiple oxygen radicals catalyzed by Haber-Weiss and Fenton reagents.

5. Geo/MIB are susceptible to oxidation by hydroxyl radicals generated by the combination of peroxide and UV radiation of appropriate wavelength or by oxygen radicals catalyzed by "Fenton" reactions provided by MINLOX™.

Invertebrates comensal with algae

As sediment builds with any body of water, benthic organisms associated with algal growth are:

A. **Amphipods:** A small crustacean with laterally compressed bodies that range in size from 1-340 millimetres (mm) and are mostly detrivores and scavengers. There are 1900 known freshwater species.

B. **Codepods:** Meaning "oar feet", are small crustaceans 1-2 mm in size with a tear drop shape and large antennae, most are "planktonic" (drift with water current), some other are "benthic" (live in muds).

C. **Isopods:** Small crustaceans that are typically flattened dorsoventrally. Approximately 500 species live in freshwater and are mainly scavengers, some are predators and others are ectoparasites of fish.

D. **Ostracods:** A diverse small crustacean generally 1-30 mm in size. Their bodies are flattened and protected by a bivalve like calcareous shell. This group includes carnivores, herbivores, scavengers and filter feeders.

E. **Nematodes:** Round worms with a tubular digestive system and are parasitic.

F. **Water Mites/water fleas:** Though are normally benthic, they are good swimmers and are carnivorous and parasitic

G. **Insect larvae**

Though most invertebrates are captured in filter systems or die as a result of exposure to chemical treatments, some survive to reproduce in the system to have their larvae enter the distribution system. These invertebrates may harbor and protect bacteria from disinfection with chlorine and monochloramines at concentrations normally present in distribution systems. Associated bacteria, either enteric or colonizing the exoskeleton, may survive though the invertebrate is inactivated. Invertebrates may therefore:

1. Constitute a health hazard if they are carrying or become exposed to and associated with bacterial pathogens.

2. Contribute significantly to the organic load entering the distribution system.

3. Contribute to the continued colonization of distribution systems by invertebrate associated bacteria in spite of residual chlorine.

4. Decrease the effectiveness of chlorination by increasing the chlorine demand of the water.

5. Contribute to the cause of taste and odors, water discoloration, water meter clogging and high turbidity.

Chemical control of invertebrates

a. **Insect larvae:** Chlorination as high as 50mg/l with CT of 24 hours has been shown to be ineffective against insect larvae. Copper sulfate is also ineffective.

b. **Codepods:** Chloramine is preferred over free chlorine.

c. **Amphipods:** Amphipods will survive in distribution systems by living off rust and are cannibalistic to dead amphipods. Laboratory observations revealed a 58% survival rate with a chlorine residual of 1 mg/l. They are resistant to normal chlorine residuals and will live for up to a year. Survivability was slightly decreased with a chloramines residual.

d. **Water fleas and Water mites** are more sensitive to chlorine residual than chloramine levels greater than 0.22mg/l with a CT of less than 10 hrs

e. **Nematodes:** Nematodes are 3 to 4 times orders of magnitude more resistant to free chlorine than bacteria and exhibit CT coefficients of between 450 to 2550 mg*min/l

f. **MINLOX™:** The aquarium industry has written extensively on the importance of ORP control and reports that an ORP above 400 will kill all invertebrates. Necropsies of chickens has revealed that MINLOX™, as a water treatment (ORP of 550), desiccates intestinal nematodes. Bacteria associated with Invertebrates

Bacteria are associated with invertebrates

Bacteria are associated with invertebrates and are either enteric or may colonize their exoskeleton. Most common pathogens associated with invertebrates are:

Bacteria	Associated diseases
Acinetobacter sp	Perodontitis, blood infections, urinary tract infections, pneumonia, bacteremia, meningitis
Achromobacter xylooxidans	Bacteremia
Aeromonas hydrophila	Dysenteric gastroenteritis, cholera, myonecrosis, eczema, cellulitis
Bacillus sp	Gastroenteritis
Chromobacter violaceum	Skin lesions, sepsis, liver abscesses
Enterobactor sp	Urinary infections, respiratory infections
Flavobacterium meningosepticum	Meningitis, endocarditis, bacteremia, necrotizing fasciitis, sepsis
Klebsiella sp.	Pneumonia, urinary infections, septicemia, meningitis, diarrhea
Moraxella sp.	Respiratory infections, pneumonia, conjunctivitis
Pasteurella sp	Sepsis, respiratory infections, cellulitis, arthritis
Pseudomonas sp	Nosocomial infections
Salmonella sp.	Gastroenteritis, typhoid fever, blood stream infections
Serratia sp	Infections of blood, respiratory system and urinary tract, meningitis, arthritis, endocarditis, osteomyelitis
Staphylococcus sp	Gastroenteritis

Control of invertebrate associated bacteria

Bacteria associated with invertebrates always survive better than similarly unassociated bacteria. Free available chlorine (FAC) at equivalent contact times and concentrations is mostly more effective in inactivating associated bacteria than monochloramine, regardless of temperature. Enterobacter and Salmonella behaved similarly in the presence of FAC at all concentrations and temperatures, while Klebsiella was mostly susceptible to inactivation with FAC at both 4 deg C and 20 deg C. Enterobacter was more resistant to inactivation with monochloramines than the other bacteria at all concentrations and temperatures. Enterobacter, after disinfection with monochloramines for 2 hours, that which survived either decreased slightly or increased activity.

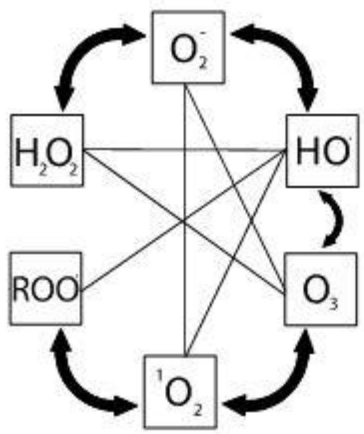
Tests revealed that bacteria are able to escape inactivation by either FAC or monochloramines, and survive better than the same bacteria unassociated in the water column. Bacteria associated with particulate granular activated carbon were afforded enhanced protection from inactivation with FAC and monochloramines when compared to unassociated bacteria under similar conditions. Therefore, the association of bacteria with invertebrates affords protection to recently attached bacteria as well as to their natural flora.

The failure of conventional approaches to inactivate invertebrates and associated bacteria points to the need to apply advanced oxidation technology. As an alternative to the impact of mg/l of a chemical agent, the ability of a chemical agent to impart significant ORP energy is a viable alternative. Research has revealed that an ORP of greater than 400 is very effective in inactivating both invertebrates and associated bacteria. MINLOX™ effectively enables application of ORP energy with far less concentrations than conventional oxidizer applications.

MINLOX™: ORP Control by generating Oxygen Species in Water.

Aquaculture and aquarium science has determined that an ORP above 400 is sufficient oxidation energy to deactivate invertebrates, algae, comensal bacteria and detoxify algae related toxins. To reach ORP 400 with ozone, small batches of water must be treated with CT of 20 minutes or more. Conventional chlorine derivatives, to reach ORP 400 will result in compliance issues with excess chlorites and chlorates. With peroxide/UV protocols, there is the expense of UV equipment, then the calculations of peroxide to kilowatt-hrs relative to the organic load to be deactivated. MINLOX™ is a high energy (derived from oxygen radicals) liquid that is easily injected and gives ORP control without risk of compliance issues.

Active oxygen species are very good oxidizers and are generated in water environments. The decomposition of water, and oxo-compounds, generate several oxygen products. These oxygen products are various oxidation states of oxygen called: superoxide [O_2^-], hydroxyl [OH^-], nascent oxygen [$^1O_2$], hydroperoxyl [HO_2 -], and peroxide [O_2^{2-}].

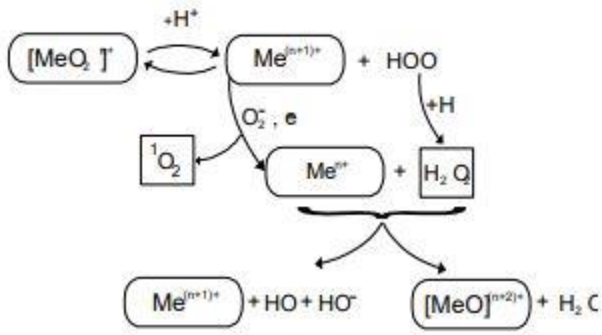


These oxygen radicals play a double role of both oxidant and antioxidant. As oxidant, oxygen species exert harmful effects on living water organisms. Oxygen species also are very important antioxidants transferring pollutants present in lakes and rivers into non-toxic products by their oxidative degradation, usually in the free radical and singlet oxygen way. The hydroxyl radical has a very high oxidation potential (2.8V), compared to singlet oxygen (2.7V). Additionally, hydroxyl and singlet radicals show very high values of second order rate constants for organic compounds. This means after an oxygen radical initially reacts with organic material, substantial energy is available to continue breaking down the organic compound, i.e. the oxygen radical is not limited to reacting with organic material just once. Also, with MINLOX™, oxygen radicals are generated during the combination with the metal/mineral constituents of MINLOX™. These reactions are referred to as “Haber-Weiss” and “Fenton” reactions.

1. $Me^{[n+1]+} + O_2$ - -------$2H^+$---> $Me^{n+} + H_2O_2$

2. $H_2O_2 + Me^{n+}$ ----> HO. + $HO^- + Me^{[n+1]+}$

It is this property of MINLOX™ that enables reliable and effective ORP measurement, catalyzed oxygen reactions with organics,



improved second order rate reactions, and low concentrations of chemistry vs mg/l concerns with conventional treatment protocols and makes MINLOX™ effective as a:

- Disnfectant; kills bacteria and viruses
- Oxidation of organics
- Oxidation of inorganics
- Color removal
- Odor removal; sulfur and organic odors
- Algae control
- Micro-coagulation aiding filtration
- BOD/COD reduction
- VOC elimination

Bibliography

1. Levine I.N: Physical Chemistry, 4th edition, McGraw-Hill Inc.1995

2. Ebbing D.D.: General Chemistry 4th edition, Houghton Mifflin Co., 1993.

3. Manhan S.E.: Environmental Chemistry 6th edition, Lewis Publishers 1994.

4. Loudon G.M.: Organic Chemistry 2nd Edition, Benjamin-Cummings Pubishing Co., 1988.

5. Stryer L.: Biochemistry, W.H. Freeman & Co., 1975.

6. Cotton F.A.: Advanced Inorganic Chemistry 6th edition,John Wiley & Sons Inc., 1999.

7. Martell A.E., Chemistry of the Metal Chelate Compounds, Prentice-Hall Inc., 1953.

8. Kruk I.: Environmental Toxicology and Chemistry of Oxygen Species, Springer-Verlag Berlin Heidelberg, 1998.

9. Brock T.D.: Biology of Microorganisms, Prentice Hall Inc., 1991.

10. Lodish H.: Molecular Cell Biology 3rd Edition, W.H. Freeman & Co. 1995.

11. McFeters G.A.: Drinking water Microbiology, Brock-Springer, 1990.