Management and Application of Ozone in Aquatic Life Support Systems

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Abstract: Ozone is an effective treatment resource capable of significantly improving water quality and water clarity in aquatic systems. When applied and managed appropriately ozone can ameliorate contaminants that degrade water quality. However, poorly controlled ozone dosing may result in persistent, highly reactive and toxic by-products that can harm aquatic life. Reactive ozone by-products are collectively called residual oxidants. By understanding and using the concept of applied ozone dose (AOD), ozone can safely be applied and controlled to achieve desired benefits, while minimizing the risk of overdosing. Monitoring and recording oxidation-reduction potential (ORP), residual oxidants, water turbidity, animal behavior, and husbandry activities are an essential part of a comprehensive ozone-management strategy.

INTRODUCTION

Ozone is tri-molecular oxygen. It is a colorless gas at room temperature and has a pungent odor, detectable at concentrations less than 0.05 mg/L. Ozone is extremely corrosive and toxic, and is considered a health hazard to humans at concentrations of 0.1 mg/L when exposure lasts for a period of eight hours or more. Ozone is highly reactive and capable of oxidizing many organic and inorganic compounds in water. Ozone degrades quickly in water, producing hydroxyl free radicals, which are among the most reactive oxidizing agents. Ozone is very unstable and must be produced on-site.

Because of its high reactivity, ozone is a versatile and highly effective water quality management resource. When applied and managed appropriately, ozone can facilitate the removal of contaminants that degrade water quality, either by physical removal via foam fractionators or by destruction of molecules in a contact chamber. While the application of ozone provides many benefits to water quality, ozone and its by-products can be toxic (or even lethal) to aquatic life. Careful management of ozone is therefore required to attain associated benefits without harming animals housed within the water system.

To avoid overdosing ozone, a careful balance must be struck between the organic material within the water system, and therefore the oxidant demand, and the application of a corresponding oxidant, in this case ozone. This balance is dynamic; continually changing throughout the day as a result of food inputs, husbandry activities and the daily activity of aquatic specimens. Changes to bio-loads (e.g., adding or subtracting specimens), seasonal water parameter trends (e.g., temperature fluctuations) and equipment performance (e.g., foam fractionation performance) will all affect this balance too. Continuous monitoring of life support systems, key water quality parameters, and specimen behavior is an essential part of a responsible husbandry program for aquatic systems that use ozone.

It is not unusual for the application of ozone to be based solely on oxidation-reduction potential (ORP) measured by in-line electrodes or sensors. Electrodes that measure ORP generally lose accuracy over time, as they drift out of calibration or are affected by residues that collect on the sensor tip. In addition, signal wiring can be compromised, valves to electrode ports can be accidentally closed, or logic control systems can fail. Thus, even though ORP generally increases linearly with ozone concentration, it cannot be used as a sole predictor of residual oxidants and the possible risk to animals. Therefore ORP must be interpreted within the context of other parameters such as applied ozone dose (AOD), measured residual oxidants, water turbidity, husbandry activities, and animal behavior.

This chapter provides an outline of best practices for ozone implementation within aquarium life support systems. The procedures described also serve as a first step in troubleshooting ozone-related problems within aquatic living systems.

OXIDATION, REDUCTION AND ORP

Organic and inorganic solids, semi-solids, and other substances are continually being added to aquatic animal life support systems via feeding, animal excretion, etc., creating a dynamic chemical environment as various molecules and ions constantly interact with one another. The terms oxidation, reduction, and oxidation-reduction potential are useful when quantifying the dynamic chemical state of the water system. Aquarium staff must be well versed in these terms and be able to distinguish them from one another to successfully manage the aquatic environment.

Oxidation was originally defined as chemical processes where substances react with oxygen to form oxides. This original definition is still a useful way to think of oxidation, as these processes occur frequently in aquatic water systems. For example, nitrite (NO_2^-) is oxidized when it gains an oxygen atom and becomes nitrate (NO_3^-).

A second definition of oxidation describes a loss of electrons. When an atom, ion, or molecule has become more positively charged than it was before a reaction, it has lost electrons. To say a substance has lost electrons is also a way of saying it has been oxidized. When ozone is involved in a reaction it is usually the oxidant, adding oxygen or stealing electrons from its reaction partner. Ozone oxidizes most substances it comes in contact with and is reduced in the process.

Reduction is the chemical opposite and partner reaction of an oxidation reaction. Reduction does not occur without oxidation, and vice versa. When a substance is reduced it accepts electrons and ends up more negatively charged. Reactions involving oxidation therefore also involve reduction and are collectively known as oxidation-reduction or redox reactions. Both halves of the reaction pair —the reducing and oxidizing reactions—are known as half reactions.

Each half reaction has a measurable and predictable electrical potential, and the sum of the two potentials provides the electrical potential of the overall reaction. This sum of balanced half reactions is called the oxidation-reduction potential or ORP and is measured in millivolts (mV). Several examples of half reactions and their electrical potentials are shown below in Figure 1.

Since water in an aquatic system—a pond, an aquarium, a marine mammal pool, or a life support system reactor—contains dozens of reactions at any given time, ORP is typically measured using a dedicated sensor or electrode that sums the electrical potential for all half reactions within the system.

A body of water with a high concentration of oxidizing compounds—such as the interior of an ozone contact chamber—will have a high ORP (e.g., 500 – 900 mV), while a body of water containing a high concentration of reducing compounds—such as filter backwash water—will have a low ORP (e.g., 100 – 225 mV). It is possible to have negative ORP values, for example, raw sewage or anoxic water in a denitrification system can have an ORP of -100 mV or lower. ORP measured on a natural coral reef ranges from 350 – 400 mV (Moe, 1989).

Ideal ORP for an aquarium varies from system to system. There is no set universal target ORP range. Rather, the ideal ORP for a given aquarium system should be arrived at in situ by correlating actual ORP readings with other water quality parameters (see the section "ORP and Total Residual Oxidant" later in this chapter). In general, however, seawater exhibits ranging from 250 mV to 400 mV typically correspond with healthy water quality conditions. Freshwater exhibits, because of their (usually) lower pH, can have a higher range of ORP (300 mV to 450 mV) with no associated presence of residual oxidant. It should be emphasized, however, that the operator must determine the safe ORP range for a given system by empirical comparison of ORP and residual oxidant data.

Sensors that measure ORP are frequently used in conjunction with a transmitter-controller to activate life support system actions and alarms based on pre-determined set points. A more detailed description of this process is given later in this chapter in the section entitled "Ozone Management and Automation".

Ideally, ORP sensors should be employed in two locations: (1) within the exhibit or the piping that exits the exhibit; and (2) within the ozone reactor or the piping that exits the reactor. Having information from both of these locations greatly increases the chance of successfully managing ozone dosing. Where lower concentrations of ozone are used—e.g., within foam fractionators (0.01 – 0.05 mg/L)—the need for two sensors is less important. In all cases, a sensor should be used to monitor conditions within the aquatic exhibit, as this will directly reflect the environment for exhibit animals provided that the system is uniformly mixed and not stratified.

Supervisory Control and Data Acquisition (SCADA) systems can log ORP readings and generate trend lines. Such ORP trends give valuable insight into ongoing changes within an aquatic system or reactor vessel—e.g., the interplay between daily feeding and the subsequent processing of generated waste products. Each aquatic system has its own idiosyncrasies and ORP trends can be employed to better understand how a system will react to changing conditions. It should be noted, however, that the usefulness of these trends as predictors depends greatly on the standard to which the ORP electrode(s) are maintained. Poorly maintained electrodes can begin to "drift" and provide inaccurate data; indeed some ORP trends can be used to identify when probes have been insufficiently maintained.

OZONE APPLICATION

When applied carefully, ozone can substantially improve water quality for animals and the aesthetics within an aquatic system. These improvements are typically achieved through two different processes: (1) enhanced flocculation of organic and inorganic material and its subsequent removal via a foam fractionator; and (2) direct oxidation of organic material in an ozone contact chamber.

Because ozone and its by-products can be toxic to aquatic life, great care must be taken during its application. For fishes and invertebrate systems, it is essential that the ozone-dosing rate not exceed oxidant demand. For marine mammal systems, ozone-dosing rate should only slightly exceed oxidant demand, such that an intended target residual oxidant concentration is reached. (See “Total Residual Oxidants” below).

Oxidant demand is defined as the sum of unwanted contaminants (or reductants) in the water column that will react with oxidants. Examples of target reductants include animal waste products, uneaten food, and microorganisms.

Although ORP sensors are convenient, they are not consistently reliable, as has been mentioned above. In addition, ORP is only an indicator of the relative oxidative state of the environment, not a measure of ozone or residual oxidant concentration in solution. To safely attain the benefits that ozone can offer, without risking aquatic organisms, the following parameters should all be carefully monitored and integrated into a comprehensive ozone management program, alongside ORP: (1) applied ozone dose; (2) residual oxidants; (3) system turbidity; (4) husbandry activities; and (5) animal appearance and behavior.

APPLIED OZONE DOSE

Applied ozone dose is defined as the mass of ozone applied to a known volume of water, typically in a specific reaction vessel, expressed as milligrams per liter (mg/L). Ensuring that an applied ozone dose is appropriate for a given application can significantly reduce the risks associated with ozone use, and at the same time ensure that it confers a beneficial effect. An excessively high applied ozone dose will produce residual ozone by-products that may harm animals. An excessively low applied ozone dose will have little beneficial effect on water quality. In this case, ozone, along with the capital expense in creating and delivering it, is wasted.

For the purpose of ozone management within an aquatic life support system a simple formula can be applied to calculate ozone dose (Figure 2). This formula intentionally omits parameters such as water temperature, mechanism of ozone delivery (i.e., air stone vs. Venturi injector) and other system characteristics that are included in more thorough calculations of applied dose. Such parameters affect ozone kinetics and will impact dosing, but they remain relatively constant in a given aquatic life support system. For the life support system operator, it is more useful to calculate *theoretical* applied ozone dose, within a given system, which focuses on parameters that vary rapidly over time; ozone generator output, gas mixture flow rate and water flow rate. The formula includes only those variables that are likely to have the greatest and most rapid impact on water quality and animal health over short periods of time (Figure 2).

Ozone generator output

The measurement of ozone concentration produced by a generator (variable "a" in Figure 2) is determined using a high concentration ozone monitor and is typically measured in milligrams of ozone per liter of gas (mg/L). Some monitors will display ozone concentration as a percentage of the entire gas mixture (% weight) and most will also display concentration as grams per cubic meter (g/m^3). Mathematically, mg/L and g/m^3 are equivalent—e.g., 1.5 mg/L = 1.5 g/m^3. If the ozone generator does not come equipped with a high concentration ozone monitor, a third-party unit can be purchased and installed separately.

Ensure that the high concentration ozone monitor is sampling downstream of any conditions that may change ozone concentration in the delivery piping, such as external shunts that allow ambient air to mix with the gas leaving the generator. In other words, measure the concentration of ozone gas entering the final reaction vessel.

Gas mixture flow rate

Gas mixture flow rate (variable "b" in Figure 2) is measured using a flow meter installed on the line delivering ozone gas to the reactor (i.e., contact chamber or foam fractionator). Ensure that the meter is only measuring the flow of gas to the final reaction vessel and does not measure gas flow that is then split and diverted to other systems, or that it does not measure ozone that is then mixed with an air source downstream of the meter.

The percentage of ozone from a generator is small, typically two percent or less when air is used as the feeder gas; and up to six percent or more when oxygen is used as the feeder gas. A meter designed to measure the flow of pure ozone will give a false reading, as it is engineered to respond to ozone density; which is heavier than both air and oxygen. An air flow meter, constructed of ozone-resistant materials, is a more appropriate device to measure gas flow rate.

Water flow rate

Water flow rate (variable "c" in Figure 2) is provided by a meter installed on the piping that conducts water to the reaction vessel. As with gas flow rate, ensure that the flow meter is only measuring the flow of water to the reaction vessel being studied and not water that is then diverted to some other life support system component.

By inserting the numbers obtained for the three variables described, it is possible to easily calculate the applied ozone dose (Figure 3). Convert all measured variables to metric units; conversion tools can be readily found on the Internet, various smartphone/tablet apps, built into calculators, etc.

Based on the parameters detailed above, it is possible to deduce key factors influencing applied ozone dose. These factors include: (1) changes to water flow rate; (2) changes to mixed gas flow rate; (3) ozone generator settings; and (4) ozone generator status—e.g., a corona-discharge generator in need of maintenance may be receiving humid feeder air; promoting arcing within the discharge cloud and a reduced ozone production rate. If any of these variables change, either by intention or unintentionally, the applied ozone dose will change and the aquatic system can be expected to respond in some manner.

Without flow meters and high concentration ozone monitors, it is difficult to calculate applied ozone dose. Under these circumstances any adjustment to ozone dosing is guesswork and therefore the management of ozone is left to ORP sensors alone. The questionable reliability of ORP sensors makes this a risky management strategy at best. Installation of appropriate flow meters and high concentration ozone monitors is encouraged for the management of any aquatic system that uses ozone as part of its treatment regimen.

TOTAL RESIDUAL OXIDANT

When ozone is added to seawater, a complex set of chemical reactions occur and many persistent oxidative by-products are formed. Principal among the persistent oxidants produced are the halide derivatives: bromide (Br^-), bromite (BrO_2^-), hypobromite (BrO^-), bromate (BrO_3^-) and hypobromous acid (HOBr). These root and derivative oxidants—with the exception of bromate and bromide ion—will react with dissolved organic material and in the process be reduced. Should dissolved oxidants exceed the demand required to process organic contaminants persistent residual oxidants will remain available to react with other molecules they encounter, including the delicate tissues of animals within the aquatic system. The respiratory tissues of aquatic organisms are easily attacked and damaged by elevated oxidants. As a result, aquatic organisms exposed to high concentrations of oxidants can be severely compromised and may even die. In addition, chronic exposure to low concentrations of oxidants may promote long-term maladies, such as hyperplasia of gill epithelia and possible susceptibility to other diseases.

The sum of persistent oxidants is collectively referred to as total residual oxidant (TRO). It is total residual oxidant that presents a risk to aquatic life, not ORP. As such, total residual oxidant should be the final control for ozone management. TRO should be measured in the aquatic exhibit prior to any ozone or other oxidant being added. This measurement becomes the *baseline TRO* for the system in question. As a general guideline, total residual oxidants within a system containing marine fishes and invertebrates should be prevented from exceeding the baseline TRO. A system containing marine mammals should be prevented from exceeding baseline TRO plus whatever minimum residual oxidant concentration is required to mitigate and control coliform bacteria in the pool—e.g., 0.10 – 0.50 mg/L as Cl_2.

These recommendations are based on two rationales. Firstly, although the effect of long-term exposure (i.e., weeks or more) to low concentrations of residual oxidants on sensitive tissues is not fully understood, it is assumed that some molecular interaction does take place and that it is probably detrimental. Residual oxidants should therefore be avoided in an aquatic exhibit maintaining fishes and invertebrates. Secondly, in the case of marine mammal exhibits, a low concentration of persistent residual oxidants is required to control the infectious flora of the mammalian gut, which will otherwise thrive within the pool. The additional TRO requirement for marine mammal exhibits should be based on empirical data; comparing TRO and coliform bacteria counts. The lowest concentration of oxidants above baseline, that sufficiently mitigates coliform bacteria counts, should be the target TRO for the exhibit.

A DPD (N, N-diethyl-p-phenylenediamine) total chlorine test will measure most forms of oxidants present in a body of water, whether the oxidant is derived from ozone, chlorine, bromine or other. A DPD test will not measure bromate or iodate (Phillips et al., in press), however bromate is a stable ion and not likely to react with organics, and iodate is present in such small amounts that it can be neglected. So, although DPD does not give a true measure of *total* residual oxidant it is a suitable means to measure all affective forms of oxidants present in an aquarium life support system. The total residual oxidant test should not be confused with the residual ozone test, which employs the ozone-specific indigo trisulfonate titration and only measures the portion of oxidant present in the form of ozone.

ORP and TOTAL RESIDUAL OXIDANT

Like ORP, total residual oxidant is dynamic; constantly changing as the amounts of oxidants and reducing agents increase and decrease within a system. Any measure of total residual oxidant is simply a snapshot of the conditions at a given point in time. In addition, there is no unconditional relationship between ORP and total residual oxidant, as it is modified by other water parameters (e.g., pH) that can vary greatly between different aquatic systems and may even change within the same system. By carefully studying and generating a history of ORP and total residual oxidant trends within an aquatic system, an increasingly reliable understanding of the dynamic relationship between the two parameters can be established. Because changing conditions within the system can further modify this dynamic relationship, empirical data should be regularly checked and verified. It is therefore important to test, electronically log and analyze ORP and total residual oxidant data on a regular basis.

A critical aspect of interpreting water quality parameters is their comparison to historic trends. Understanding water parameter changes over time is as important as the detection of acute problems. Only through an understanding of both rapid and slow changes in individual water parameters can a full picture of exhibit conditions be formed. It is therefore essential that high-quality, reliable and accessible water quality data records be maintained at all times (Smith and Baylina, in press).

TURBIDITY

Turbidity is the relative cloudiness or haziness of a fluid resulting from individual suspended solids that are typically invisible to the naked eye. Measured in nephelometric turbidity units (NTU), turbidity in aquatic systems corresponds to the relative burden of a mixture of suspended organic solids, organic dyes, inorganic solids and microorganisms. With the exception of inorganic solids, the majority of these suspended materials will add to the oxidation demand of a system—i.e., they are reductive compounds. An aquatic exhibit where ozone is applied and the life support system is working correctly will typically have turbidity in the range of 0.05 – 0.25 NTU.

Turbidity is a useful and quick adjunct to other testing mechanisms that characterize changes to an aquatic system. For example, if the system has a stable turbidity for several weeks and then a trend of increasing turbidity is observed over several days, this may indicate that the ozone generator needs maintenance and is producing less ozone, or that new specimens were recently added to the system and ozone dosing needs to be raised, or that more food was added to the exhibit than normal, or even that a vigorous cleaning session (e.g., algae scrub) was recently undertaken. On the other hand, if turbidity starts to drop suddenly, it may indicate that a feeding session was missed, or that the ozone-dosing rate has increased for some reason. When a precipitous drop in turbidity is observed workers are urged to immediately test for total residual oxidants and verify the accuracy of ORP sensors, as increased clarity may indicate that ozone application has outstripped system oxidant demand.

In some cases, when ozone dosing is initiated or slightly increased, exhibit turbidity may correspondingly increase. This phenomenon occurs when oxidants destabilize small, charged particles held in suspension and promote their agglomeration or micro-flocculation; the same effect anticipated and desired in ozone-fed foam fractionators. A sudden increase in turbidity should therefore also prompt an immediate review of the ozone system, the residual oxidants and ORP sensors.

Turbidity is readily measured with a dedicated meter (e.g., a Hach 2100P Portable Turbidity Meter) and it is recommended that all water quality laboratories possess such a device. It is also useful to employ non-instrument measurements to characterize turbidity—for example, the visibility of an object (e.g., Secchi disk) on the opposite side of an exhibit. Although this technique is more subjective, it can provide an immediate indicator of changes within the aquatic system and prompt more comprehensive testing.

ANIMAL HUSBANDRY and ANIMAL BEHAVIOR

Life support system management is not isolated from animal husbandry practices. An understanding of the interplay between husbandry activities and the life support system, and therefore corresponding changes to water quality, is an essential part of the effective and responsible management of an aquatic system with living flora and fauna.

Animal husbandry practices within an aquatic systems have a direct influence on total residual oxidant and ORP. Animal excretions and uneaten food represent reducing agents to a system; ORP can therefore be expected to drop following the daily feeding of a system. Conversely, a period of fasting will likely result in an increased ORP and possibly an increase in persistent residual oxidants. Cleaning an exhibit results in a sudden “influx” or suspension of reducing agents and turbidity can be expected to rise and ORP to fall when such activities are undertaken. In contrast, the use of oxidants (e.g., chlorine) to clean rocky surfaces in aquatic bird or marine mammal exhibits can result in an increased ORP, if these products are inadvertently rinsed into the exhibit. Such observed changes to ORP should encourage husbandry and engineering staff as they indicate that ORP sensors are appropriately responding to changing environmental conditions, which in turn provides part of the back-checking process required to better understand the relationship between ORP, total residual oxidants, turbidity and animal husbandry within the aquatic exhibit.

As a side note, it is theoretically possible to engineer a life support system where ORP-modulated micro-adjustments of ozone dosing result in a flat-line ORP. However, it is not recommended that such a system be implemented as it short-circuits the back-checking process and relies on the continued accuracy of ORP sensors, which as stated before can be capricious.

Another key indicator of water quality is, of course, the animals themselves. It is critical for the husbandry and life support team to recognize the normal appearance and behavior of the animal collection. This knowledge acts as a benchmark against which any observed behavioral or physical changes can be judged. For example, the authors have observed that some shark species (i.e., sandbar sharks, *Carcharhinus plumbeus*, and blacknose sharks, *Carcharhinus acronotus*) will increase their swimming speed in the presence of residual oxidants. Other possible indicators of changing water quality include, but are not limited to, animals exhibiting increased ventilation, congregation of animals at the surface or the bottom of an exhibit, and/or animals exhibiting a blotchy or pale coloration of the skin.

In natural ecosystems, fluctuations to ORP can occur as biological processes change throughout the day—e.g, the photosynthesis and respiration of zooxanthellae in response to the day:night light cycle. These trends are typically echoed in artificial habitats (e.g., a living tropical coral reef exhibit) and should be anticipated when interpreting observed ORP data. This phenomenon emphasizes the value of determining baseline ORP trends within an exhibit before ozone is applied; similar to establishing baseline total residual oxidant concentrations.

OZONE MANAGEMENT and AUTOMATION

While total residual oxidant would be the best parameter to use as a controller of ozone dosing, it is impractical to use as the basis for an automation system. In-line DPD testing equipment *is* available, but it is expensive, delicate and as yet unreliable. Conversely, ORP is not the best parameter to use to quantify the oxidative environment within an exhibit, but it is better suited to continually monitor water conditions and trigger life support system actions and alarms. By compiling data for both parameters it is possible to generate an empirical relationship between ORP and total residual oxidant for each system within which ozone is applied. Under these controlled conditions, where a given ORP is known to correspond to a given total residual oxidant, ORP can be employed as a means to monitor water quality conditions and, in the right hands, control and trigger life support system actions. Of course regular maintenance and calibration of ORP sensors is an essential part of any such monitoring program.

ORP transmitter-controllers typically trigger automated responses by referencing predetermined high or low set points. Automated responses can be actions such as starting or stopping the supply of ozone, triggering high or low ORP alarms, etc. In some cases a low-low set point and high-high set point may also be employed. In this case the low and high set points trigger ozone dosing and the low-low and high-high set points trigger audible alarms, may page or email a life support system operator, and may even cut the power supply to the ozone generator.

Figure 4a shows a typical ORP trend reaching a high set point and triggering an automated cut-off to the supply of ozone. Note that ORP continued to rise beyond the cut-off point before starting to fall again. This hysteresis results from excess residual ozone by-products continuing to react within the system until the available reductive compounds have consumed them. Thus, water with a relatively high ORP will continue to enter the exhibit from the ozone reactor for a short period of time after the ozone supply has been stopped. As a result of this lag, high ORP set points should be established at levels approximately 15 – 35 mV lower than the actual high ORP level desired. Once the supply of ozone has stopped, and the latency effect has tapered off, ORP will start to fall. Over time ORP will reach the low set point, the ozone supply will be triggered to start again and ORP will start to rise (Figure 4b).

In general, an applied ozone dose that matches oxidant demand (Figure 5a) is far superior to an applied ozone dose that exceeds oxidant demand and promotes wild fluctuations in ORP (Figure 5b). The first scenario is better because the beneficial effects of ozone (i.e., disinfection and/or micro-flocculation) are applied continuously to water passing through the reactor. Frequent on-off cycling of the ozone supply (Figure 5b) is a clear indication that the applied ozone dose is set too high. Under these conditions water can pass through the reactor untreated and, when the ozone supply is on, there is a greater risk of overdosing and producing persistent residual oxidants. It should be noted that in smaller systems (<50 m^3) it is likely that no matter what adjustments are made, ORP will hit the high and low set points at some point during the day. However, the goal should be to approximate an ORP curve akin to that depicted in Figure 5a, as much as possible.

Thus, ORP-modulated control of ozone dosing should only ever be considered a backup and not the primary mechanism of control. Not only is there the questionable reliability of ORP sensors to consider, but also the risks of ozone being applied intermittently and/or ozone being over-dosed. A human operator referencing ORP, total residual oxidants, turbidity, animal appearance and animal behavior is a much better modulator of ozone dosing. ORP is thus relegated to the role of a backup mechanism; alerting the operator to anomalous life support system operation and shutting the ozone supply off should ozone production exceed oxidant demand.

In short, the life support system operator should manage ozone application manually, via manipulation of applied ozone dose, observation of changes within the aquatic system, observation of animal responses to water conditions, and the re-manipulation of applied ozone dose, as required. It should be the goal of the operator to establish a steady flow of ozone that matches system oxidant demand, maintains ORP within a relatively narrow and desirable range, minimizes the risk of producing excess residual oxidants, and, of course, achieves high water quality for the animal collection. Figure 6 outlines an implementation strategy directed at achieving these goals when first starting up a new ozone system. The implementation strategy is also useful for operators wishing to troubleshoot an existing ozone system.

Throughout the process of establishing an optimal applied ozone dose, the operator should monitor and record the effects of food input, exhibit cleaning and changes to the specimen collection, on ORP, total residual oxidants and turbidity. Over time, general patterns will start to emerge and expected system responses will be anticipated. The operator should feed this knowledge back into their management strategy to optimize conditions for the aquatic collection within their care. The life support system operator is encouraged to carefully experiment with their aquatic system, to better understand the inherent oxidant demand and ORP dynamics, and thus establish safe operating limits whereby ozone is neither over- or under-applied.

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Hydrogen	$2H^+ + 2e^- \rightarrow H_2$	**Eo = 0 mV**
Oxygen	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	**Eo = 401 mV**
Sulphate	$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	**Eo = -936 mV**
Ozone	$O_3 + 2H_2O + 2e^- \rightarrow O_2 + 2OH^-$	**Eo = 1,240 mV**

Figure 1.

Example half reactions, showing the hydrogen cell, the standard against which all others are measured, and the highly reactive oxidant, ozone. In general, larger positive potentials indicate an increasing tendency to oxidize, while larger negative potentials indicate an increasing tendency to reduce. Source: Atkins and Beran, 1989.

Formula to calculate Applied Ozone Dose

$$\text{Applied Ozone Dose} = \frac{\text{Milligrams of Ozone / Minute}}{\text{Liters of Water / Minute}}$$

$$\text{Applied Ozone Dose} = \frac{\underbrace{\left(\frac{\text{Milligrams of Ozone}}{\text{Liters of Gas}}\right)}_{❶} \times \underbrace{\left(\frac{\text{Liters of Gas}}{\text{Minute}}\right)}_{❷}}{\underbrace{\left(\frac{\text{Liters of Water}}{\text{Minute}}\right)}_{❸}}$$

Figure 2.

Formula to calculate applied ozone dose, defined as the mass of ozone applied to a volume of water and expressed as mg.L^{-1}. The numbers denote three critical parameters: ❶ = mass of ozone in gas mixture expressed as mg.L^{-1}; ❷ = volume of gas entering the reactor vessel (i.e., the total air-ozone or oxygen-ozone mixture) expressed as L.min^{-1}; and ❸ = volume of water entering the reactor vessel expressed as L.min^{-1}.

Example of an Applied Ozone Dose calculation

Ozone is used to disinfect water in a 750 m^3 aquatic animal system via an ozone contact chamber. The contact chamber receives water at a rate of 60.0 m^3 per hour (variable Ž) and is dosed with ozone via a venturi injector at 15 L of gas per minute (variable ❷). The concentration of ozone (variable ❶) is determined to be 24.0 milligrams per liter of gas, using a high concentration ozone monitor.

Insert numbers into the applied ozone dose equation and cancel out like units …

$$\text{Applied Ozone Dose} = \frac{\overset{❶}{\left(\dfrac{24\ \text{mg}\ O_3}{\cancel{\text{L of Gas}}}\right)} \times \overset{❷}{\left(\dfrac{15\ \cancel{\text{L of Gas}}}{\cancel{\text{Minute}}}\right)}}{\underset{❸}{\left(\dfrac{1{,}000\ \text{L of Water}}{\cancel{\text{Minute}}}\right)}}$$

… resolve equation …

$$\text{Applied Ozone Dose} = \frac{24 \times 15\ \text{mg}\ O_3}{1{,}000\ \text{L of Water}}$$

… to obtain final applied ozone dose …

$$\text{Applied Ozone Dose} = 0.36\ \text{mg.L}^{-1}\ O_3$$

Figure 3.

Example of an applied ozone dose calculation. Imperial units have been converted to metric units prior to making the calculation.

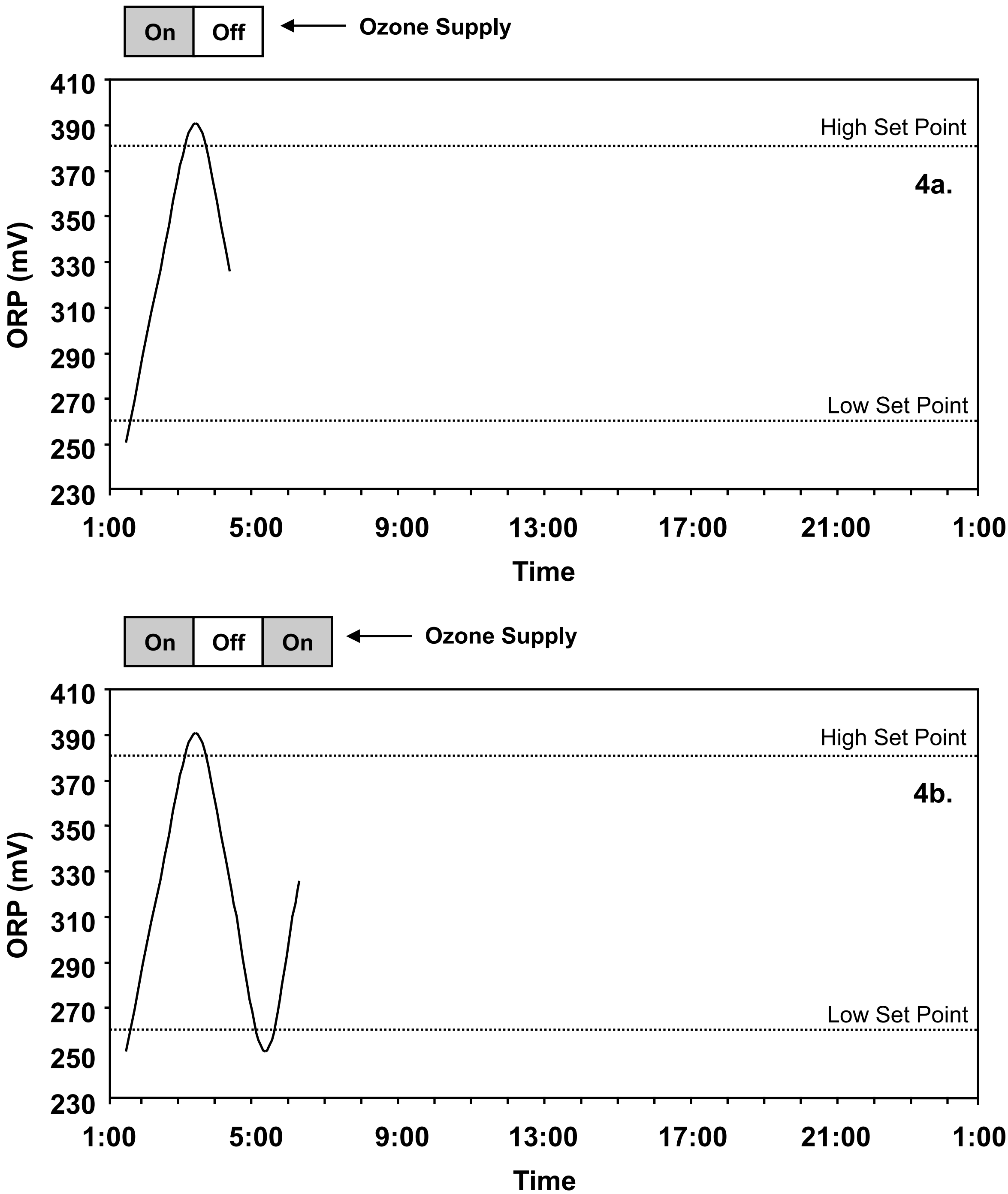

Figure 4.

Graphical representation of ORP within an aquatic system over a 24-hour period, showing: (**a**) rising ORP exceeding a high set point and triggering ozone cut-off; and (**b**) falling ORP exceeding a low set point; triggering the supply of ozone and resulting in rising ORP.

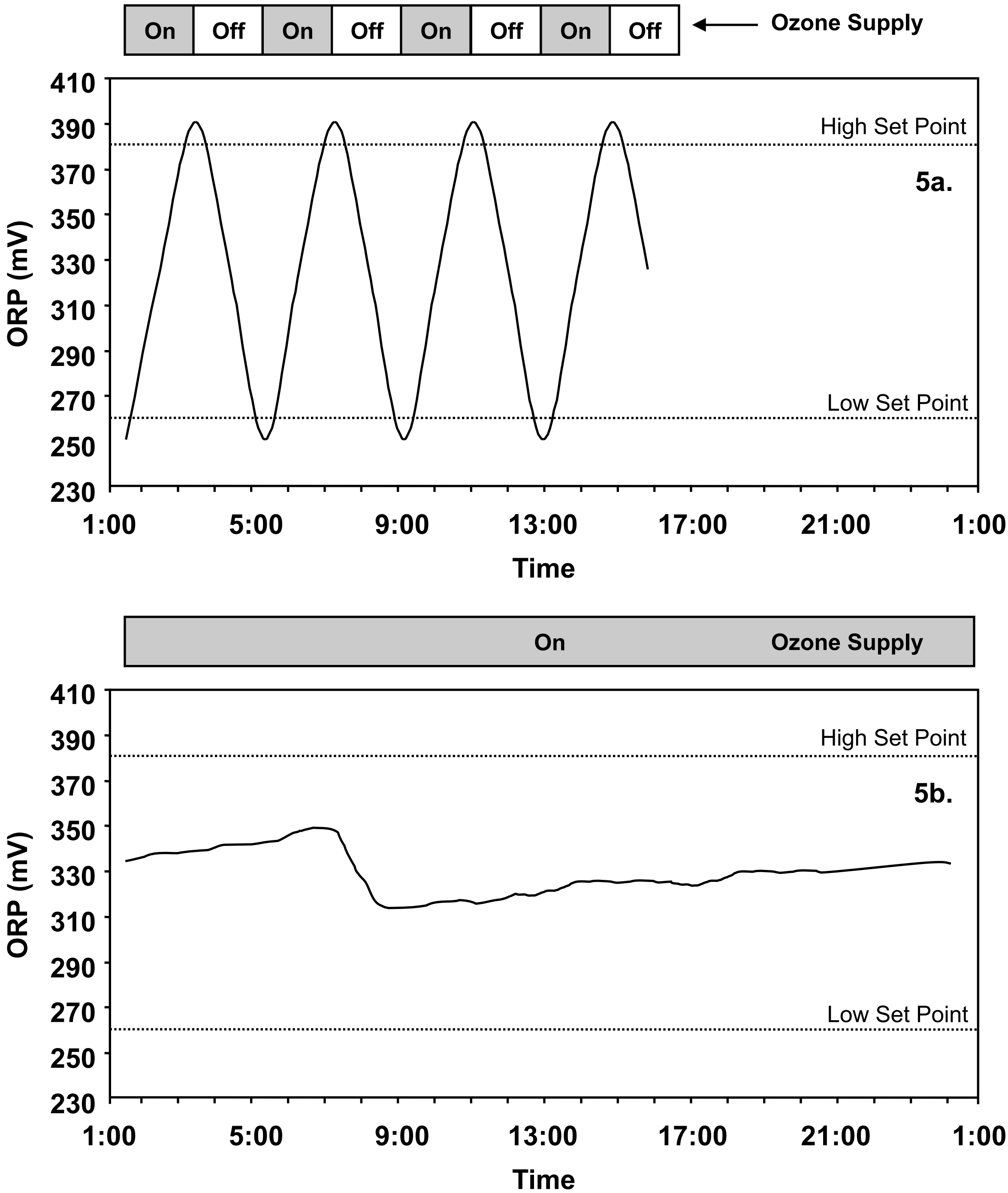

Figure 5.

Graphical representation of ORP within an aquatic system over a 24-hour period, showing: (**a**) a swinging sinusoidal curve characteristic of an excessive applied ozone dose; and (**b**) an appropriate applied ozone dose that matches oxidant demand so that ORP remains stable and ozone is dosed continuously.

Ozone Implementation Strategy - I

1. Select what you believe to be an appropriate applied ozone dose. Typical dosage ranges include 0.10 - 1.00 mg.L^{-1} for ozone contact chambers and 0.01 - 0.05 mg.L^{-1} for foam fractionators.

2. Change the subject of the applied ozone dose formula to determine a mixed gas flow rate (variable ❷) or ozone concentration (variable ❶) that will achieve the chosen dose. For example, solving the equation for mixed gas flow rate (variable ❷) we obtain …

$$\underbrace{\text{Liters of Gas per minute}}_{❷} = \frac{\left(\text{Applied Ozone Dose}\right) \times \underbrace{\left(\frac{\text{L of Water}}{\text{Minute}}\right)}_{❸}}{\underbrace{\left(\frac{\text{mg } O_3}{\text{L of Gas}}\right)}_{❶}}$$

3. Measure the flow rate of water entering the reactor (variable ❸), choose a starting ozone concentration (variable ❶)—e.g., near the recommended operating minimum for the generator—and solve for the mixed gas flow rate (variable ❷).

Note: the equation could easily be solved for ozone concentration (variable ❶), if the operator prefers to use that variable as their principal mechanism to adjust ozone dosing.

4. Program high and low ORP set points into the SCADA. One set of limits should be used for ORP within the exhibit (e.g., a low set point of 250 mV and a high set point of 350 mV) and, if applicable, another set of limits should be used for ORP at the exit of the reaction vessel.

5. Ensure ORP sensors have been calibrated. Measure and record background ORP within the exhibit—i.e., without dosing ozone.

Figure 6.

Strategy for implementing ozone in an aquatic system, applicable for system start-up or general trouble-shooting.

Ozone Implementation Strategy - II

6. Measure background total residual oxidant and turbidity. Note the relationships between ORP, total residual oxidants and turbidity.

7. Begin ozone dosing and carefully monitor the response of the aquatic system—in particular, ORP, total residual oxidant, turbidity and animal behavior …

7a. Applied ozone dose too high: If system ORP rises rapidly toward the high set point, it is likely that the applied ozone dose is too high. Check total residual oxidant. A high total residual oxidant will confirm that the applied ozone dose is indeed excessive. Return to step 1 above and choose a lower applied ozone dose—e.g., by reducing the mixed gas flow rate.

Note: If there is a sudden change in turbidity or unusual animal behavior is observed, immediately check for total residual oxidant and be prepared to shut off ozone dosing immediately.

7b. Applied ozone dose too low: If substantial time elapses (e.g., 24 hours) and there is little change to ORP and/or water clarity, or indeed either start to decrease, a similar iterative adjustment process should be applied. Check total residual oxidant. If no total residual oxidant is measured, then the applied ozone dose is likely to be too low—i.e., it is not high enough to match system oxidant demand. Return to step 1 above and choose a higher applied ozone dose—e.g., by increasing the mixed gas flow rate.

7c. Applied ozone dose correct: If an appropriate applied ozone dose is chosen ORP should rise steadily and then start to fluctuate slightly within a desired range, without ever reaching the set low or set high points—akin to the trend line shown in **Figure 5b**. A 24-hour cycle may be observed with a depression of ORP immediately following food input and a subsequent slowly increasing ORP throughout the remainder of the day. If ozone dosing is continuous, ORP is relatively stable and within the range 250 mV - 350 mV, total residual oxidant is acceptably low, turbidity is low and animals are behaving normally, then you have established an appropriate applied ozone dose.

Figure 6. (continued)

Strategy for implementing ozone in an aquatic system, applicable for system start-up or general trouble-shooting.