

Zooplankton Mortality in Lake Water Treated by Pulsed Arc Electrohydraulic Discharge Plasma

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Abstract—Zooplankton play a significant role in the quality of drinking and inland sources and as such are of great importance in ballast water treatment. In the past, chemical inactivation combined with filtration has been used to kill zooplankton; however, chemicals injected may result in secondary contamination of organic compounds in inland waters. In this study, zooplankton were killed with pulsed arc electrohydraulic discharge (PAED) plasma to prevent secondary contamination problems. The zooplankton species used was *Daphnia magna* (1.5 to 2.5 mm; mean length of 1.81 mm) and the treatment applied was 0.5 kJ/pulse PAED in a 3-L reactor. Experiments were conducted with pulse charging voltage from 2.3 to 3.8 kV, PAED electrode gap distances from 0.5 to 1.5 mm, and plankton concentrations from 10 to 100 animals/L. Exposure of zooplankton to 10-minute PAED treatment resulted in 84.7% mortality (mean of 10 trials) immediately after treatment, and 96.9% to 100 % after waiting for an additional 24 to 48 hours. Treatments with a single pulse or 1 minute PAED yielded lower mortalities. Mechanisms of PAED mortality of zooplankton will be discussed based on pressure wave and discharge parameters.

Keywords— Mortality, Lake Water Treatment, Zooplankton, Pulsed Arc, Electrohydraulic Discharge Plasma

I. INTRODUCTION

Previous research in water treatment has been varied and extensive. In the past, water treatment research included remote plasma processes, such as ozone, UV and electron processes. In ozone processes, molecules of O₃ were generated by barrier discharge plasmas and injected into water. UV and electron beam processes are referred to as indirect plasma methods, where UV lights or electrons are generated under reduced gas pressure plasma and injected to water through windows in the apparatus. Electrohydraulic discharge (ED) is a relatively new direct plasma technology that has the ability to treat a wide range of aqueous contaminants within a single unit process [1,2] by combining both radical and UV processes. There are two main different ED techniques popularly used. The pulsed corona ED (PCED) deals with low-current/high voltage [2], while the pulsed power ED (PPED) deals with high current/high voltage sharp nanosecond wavefront processes [2]. A third ED technique, pulsed arc electrohydraulic discharge (PAED), injects energy directly into an aqueous solution through a plasma channel formed by a high-current/moderated high-voltage (few kV), slow microsecond wave front electrical discharge between two submersed electrodes [1,4-6,8,11]. The PAED process uses the creation of pulsed arc discharges within the water which in turn initiate a variety of physical and chemical processes, including UV

irradiation, radical reactions, electron processes, ionic reactions, thermal dissociation, and pressure waves [1, 2].

Optical emission from electrohydraulic discharges has been studied by several investigators. Sato et al. [13] observed existences of active species such as H, O, OH, etc., by an emission spectroscopy. Research by Sun et al. [17,18] confirmed that spark discharge has much higher optical emission than that of corona discharge (PCED). The optical emission ranges of UV-A, -B and -C have also been studied. More specifically, when studying optical emissions from PAED, Chang et al. [8] also observed high intensity optical emissions while the pulse width of emission was observed to be much wider compared to those found in both current and power pulse.

From the knowledge gleaned from past research, PAED seems to be a viable water treatment option. PAED may provide a multi-barrier approach to water treatment benefiting the drinking, ballast and waste water industries. PAED may have the ability to treat a wider range of contaminants (e.g., various classes of chemical contaminants and microbial contaminants) than those conventional and other emerging technologies; moreover, it is likely that PAED will be able to treat many of these contaminants concurrently due to the wider range of physical and chemical reaction mechanisms generated by the process. When treating acids and atrazine in water, Vel Leitner et al. [4] observed both oxidation and reduction reactions induced by PAED. When using PAED to treat ammonia compounds in water, Chang et al. [3] discovered that chemical kinetics illustrated the existence of oxidations, reductions, as well as photolysis. Angeloni et al. [5] treated MTBE (methyl tertiary butyl ether) by PAED and observed that oxidation may play a major role in the process based on ozone, hydrogen peroxide and photo catalytic reactions. Much of this past

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research has been driven by and supported by the immediate need for more ballast water treatment options.

A. Lake Water and Ballast Treatment Techniques

Ballast water is one of the primary methods by which non-indigenous species (NIS, [21]) are rapidly introduced into novel aquatic environments around the world. Sea or lake water is taken up by boats to stabilize the ship when cargo is being unloaded, and is then de-ballasted at ports when new cargo is taken up [23]. In 2004, the International Maritime Organization (IMO) estimated that annually, 3 to 10 billion tonnes of ballast are taken up, transported and discharged around the world. The major problem with this practice is that ballast is not sterile, but contains on average 10^8 bacteria/L, 10^4 protists/L and 10^2 zooplankton/L. Canada alone receives 52 megatonnes of ballast water from foreign ports annually, and ships that enter the Great Lakes carry on average 10^6 autotrophic picoplankton/L and 10^3 zooplankton/L [26].

Once established, NIS can displace endemic species, and cause a major reduction in native biodiversity [19]. They do this by modifying existing habitat, creating new habitats, out-competing native fauna for prey, and acting as disease vectors [16]. Once an invasive species becomes integrated into an existing ecosystem (e.g., zebra mussels in the Great Lakes), it can facilitate the establishment of other NIS (i.e., round goby in the Great Lakes), and thus lead to "invasional meltdown". In an effort to curb the devastating ecological and economic impact of NIS on recipient ecosystems, the IMO adopted the 'International Convention for the Control and Management of Ships' Ballast Water and Sediments' in 2004. The convention stipulates that all ships with ballast water must perform an open-ocean exchange.

Unfortunately, open water exchange is not always possible due to safety concerns, nor is ballast exchange completely effective at preventing the introduction of NIS [18]. Although only a few plankton species can survive in the dark holding tanks, especially during long voyages, many produce resting eggs (e.g., diapause eggs of zooplankton) that can hatch once they are exposed to favourable conditions in the new port. Similar problems exist for No Ballast On Board (NOBOB) vessels (90% of all ships currently entering the Great Lakes), which are exempt from ballast exchange because their tanks are considered empty [15]. Nevertheless, the average NOBOB carries 10-15 tonnes (t) of residual sediment and 40-50t of water when entering the Great Lakes, which translates into an estimated 1.3×10^6 animals/t and 7.2×10^5 diapausing eggs/t in the residual sediments, with an additional 1.1×10^4 animals/t in the residual water [18].

Treatment of ballast water and residual sediment/water of NOBOB is probably the best way to prevent the introduction of NIS. The effectiveness of various treatment options may depend on the density of organisms in the ballast, the age of the ballast, as well as the trophic level of the organism in question [18]. Knowing the types of organisms found in ballast water

will help determine the feasibility of new ballast water treatment options.

1) Filtration

Filtration of water is not a new technology. Dobbs and Rogerson [17] showed that large volumes of coastal waters can be effectively filtered through 25 μ m-mesh to remove ichthyoplankton, invertebrate zooplankton, larger phytoplankton and heterotrophic protists, but not microorganisms. Tang et al. [17] concluded that physical filtration alone could not be used to treat ballast water.

2) UV Radiation

Ultraviolet radiation has been shown to be effective in both laboratory conditions and on a larger scale, as a treatment option for ballast water [17]. UV irradiation cause DNA in organisms to mutate, and this can either kill organisms outright or cause them to lose the ability to reproduce. UV radiation was used successfully to inactivate pathogenic organisms, but some acquired increased UV resistance, and this necessitated the use of higher dosage [20]. Some drawbacks of this treatment include technical problems associated with using a UV reactor on board a ship, as well as reported bacterial re-growth after treatment [17]. Re-growth occurs because ballast tanks act as incubators and breeding grounds for resistant fungi and micro-organisms [13].

3) Biocides/Chemical Treatment

Biocides and/or chemicals (e.g., oxidizing agents such as halides, bromine, chlorine and their derivatives) have also been used to disinfect water [17]. There are 3 main concerns with chemical treatments in ballast tanks: 1) chemicals can accelerate corrosion of tank walls and their protective coating, 2) concentrations of chemicals in the water may be too high to be released into natural environments and, 3) IMO would not likely approve the use of chemicals when there are associated risks to human and ecosystem health. Ideally, a biocide should be effective against a broad target group, and must also be stable so that it can be safely released [12]. Hence, even though chlorine is effective against a broad group of microbes, it forms toxic by-products that are carcinogenic, and treated water cannot be released into ports.

The search for a biocide with a low environmental impact is continuing, and the two that have received the most attention are ozone and hydrogen peroxide. Kuzirian et al. [22] suggested the use of hydrogen peroxide as a ballast water treatment, on the basis that it can be generated on-site in low concentrations, and can therefore be stored safely on board the ship.

The other common biocide is ozone. Ozonation involves infusing water with molecules of O_3 , which in turn is a powerful oxidizing agent and disinfectant. The main drawback of this method is the length of time required for a complete disinfection since different organisms need different exposure durations [14].

4) Water Deoxygenation

Deoxygenation of water can be accomplished by addition of nitrogen to purge the oxygen in ballast tanks [25]. Several advantages of this method are cost-effectiveness, reduced corrosion of ballast tanks that are known to accompany the use of biocides, and the reversible condition of hypoxia once water is released into the native ecosystem. There was a clear reduction in survivorship of three invertebrate larval species after exposure to hypoxic conditions, when compared to normoxi controls.

In this work, zooplankton mortality in lake water treated by PAED plasma was experimentally investigated.

II. METHODOLOGY

The PAED system utilized in our experiments consists of a spark-gap-type power supply (0.5 kJ/pulse) and a reactor with eccentrically-configured rod-to-rod electrodes [5,6]. The 3 L reactor was operated in flow-through mode, and was equipped with four ports for the measurement of voltage, current and pressure waveforms, as well as a quartz window for the measurement of UV emissions. UV dosage and chemicals generated from this PAED system have been well characterized and depend significantly on charging voltage, arc electrode gap distances and water properties [4,8].

Figure 1 shows a schematic of the reactor and the experimental set-up. Applied voltage was measured by a high voltage probe (Tektronix, P6015A) and discharge current was measured by a current probe (Ion Physics Corporation, Model CM-01-L; 0.001V/A). The waveforms of current and voltage were measured by a digital oscilloscope (Tektronix, TDS420A). Pressures in the reactor were simultaneously measured at four locations (one for the top and bottom of the reactor and two on the inner side walls) by piezo-electric transducers (Columbia Research Laboratories Inc., Model 4103). The waveforms of pressure were measured by another digital oscilloscope (Tektronix, TDS3014B). UV radiation was measured through the quartz window by UV radiometers (Cole-Parmer Instrument Co.) for UV-A (=365nm, Serial No. M01 0938) and UV-B (=254nm, Serial No. M01

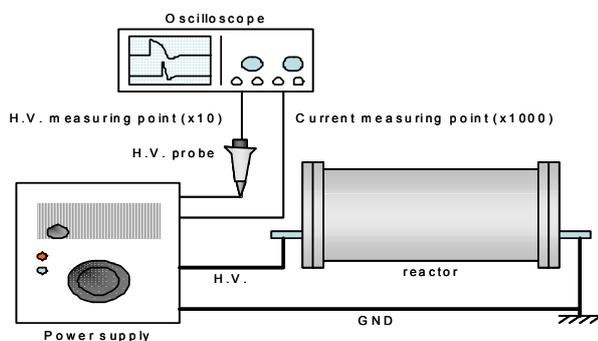


Fig. 1. Experimental apparatus .

TABLE I
INITIAL PROPERTIES OF WATER BEFORE PAED TREATMENT.

pH	Conductivity (mS/m)	Dissolved Oxygen (mg/L)
7.6	2.9	9.2
Temperature (°C)	Salinity (%)	Total Dissolved Solids (g/L)
22.4	0	0.02

0943). In addition, Ocean Optics optical spectrometer was used for 200 to 950nm range. The optical emission from the discharge was measured at 11 cm distance from arc centre through a quartz window [28].

For each of our experiments, zooplankton were added to distilled water immediately before treatment. The initial properties of the distilled water are summarized in Table 1. After adding zooplankton, the properties of water before PAED treatment may change slightly depending on the number of zooplanktons added. For the single pulse and 10-minute treatments, the properties of water after PAED treatment also slightly changed depending on the treatment parameters such as charging voltages and arc electrode gaps.

III. RESULTS

Typical discharge current and charging voltage waveforms for 0.5kJ/pulse and water arc gap distances ($d=0.5\text{mm}$) are shown in Figure 2. Figure 2 shows that the maximum pulse discharge current is approximately 28 kA and the discharge period is approximately 320 μsec . This indicates that significant generation of electrons have occurred and active radical species are expected in a specific proportion, where the electron density, N_e , in the

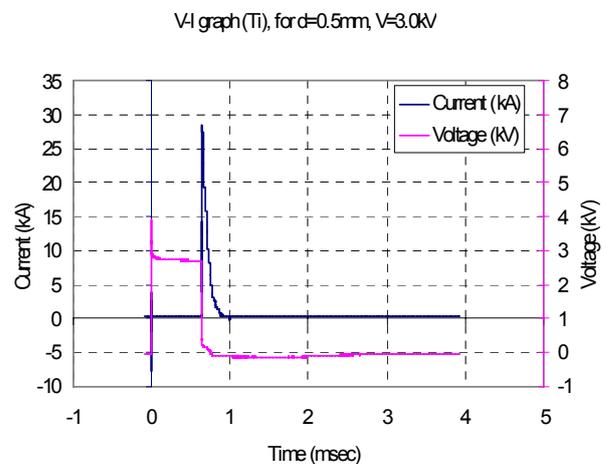


Fig. 2. Typical discharge current and voltage waveforms for charging voltage $V=3$ kV and arc electrode gap distance $d=0.5\text{mm}$.

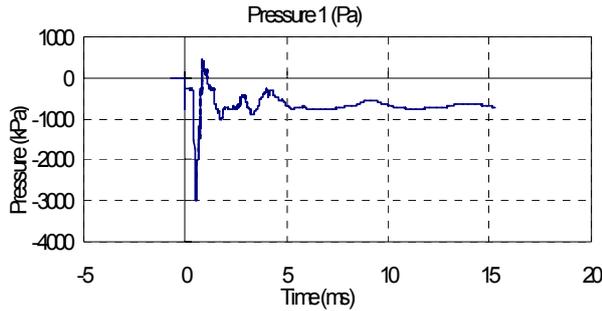


Fig. 3. Typical pressure wave waveform measured at the inner wall of the reactor bottom near the discharge electrode gap for charging voltage $V=2.8\text{kV}$ and arc electrode gap distance $d= 0.5\text{mm}$.

arc channel is proportional to the discharge current $I = eN u_e EA$.

Here e is the elementary charge, u_e is the mobility of electron, E is the electric field and A is the arc electrode surface area. Since the charging voltage of 2.8 kV decreased at approximately 600 μsec , the input pulsed plasma power had a maximum of approximately 68 MW and the pulsed power continued injection up to the 680

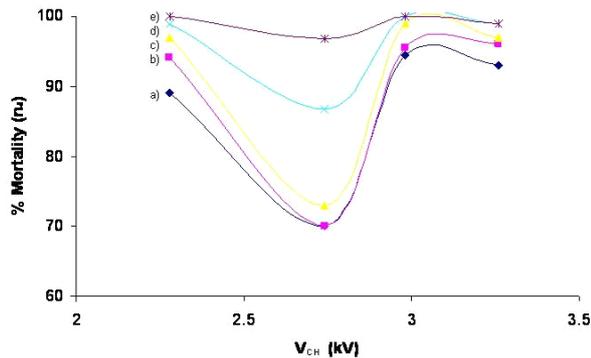


Fig. 4. Effect of charging voltage on Daphnia mortality at varying time intervals. Gap distance = 0.5mm, $N = 30/L$, $t_R = 10\text{min}$, $f_P = f(V_{CH})$. a) $t = 0\text{hours}$, b) $t = 1.5\text{hours}$, c) $t = 3\text{hours}$, d) $t = 24\text{hours}$, e) $t = 48\text{hours}$.

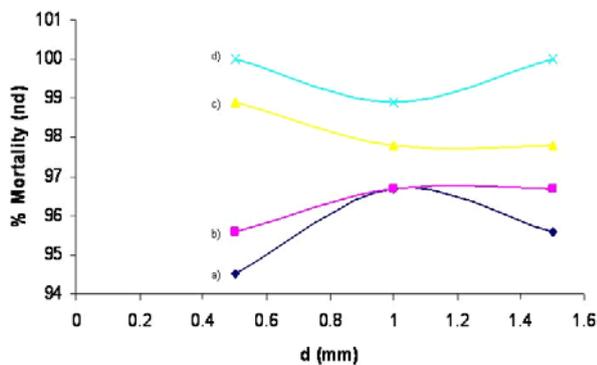


Fig. 5. Effect of discharge electrode gap distance on Daphnia mortality at varying time intervals. $V_{CH} = 2.98\text{-}3.04\text{kV}$, $N = 30/L$, $t_R = 10\text{min}$, $f_P = f(V_{CH})$. a) $t = 0\text{hours}$, b) $t = 1.5\text{hours}$, c) $t = 3\text{hours}$, d) $t = 24$ and 48hours .

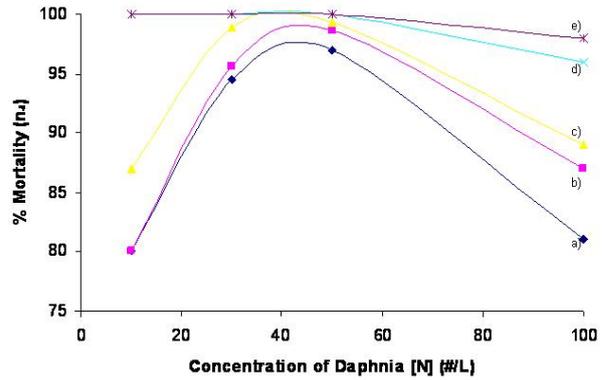


Fig. 6. Effect of Daphnia concentration on Daphnia mortality at varying time intervals. $V_{CH} = 2.98\text{-}3.04\text{kV}$, Gap distance = 0.5mm, $t_R = 10\text{min}$, $f_P = f(V_{CH})$. a) $t = 0\text{hours}$, b) $t = 1.5\text{hours}$, c) $t = 3\text{hours}$, d) $t = 24\text{hours}$, e) $t = 48\text{hours}$.

μsec period. Normally the discharge current is proportional to the plasma density and the concentration of active species, while the power injected is proportional to the pressure wave generated by discharges [5,6]. The pulse repetition rate was kept constant at approximately 0.2 Hz.

Corresponding pressure waves were measured in the inner wall of the apparatus, below the discharge electrode gap, as shown in Figure 3, the maximum pressure that can be reached is as high as 3 MPa. The period of the pressure wave after a single pulse was found to be more than 15 msec due to the reflection on the wall of multiple pressure waves. The mortality of plankton was related to body mass (g) and pressure rise (Pa-sec) as shown by Yelverton [8,29], hence, Figure 3 shows the effective pressure wave for the present *Daphnia* mortality with body mass below a few mg.

The effect of charging voltage and discharge electrode gap distances are shown in Figures 4 and 5, respectively, where time zero (0) refers to the moment 10 minutes after PAED treatment. In general, these figures show that the variation of discharge parameters significantly affected treatment efficiency as was originally predicted and this effect is shown to be non-monotonic. However, 100% mortality can be achieved 24 to 48 hours after treatment if discharge parameters was optimized. Figure 6 shows the effect of *Daphnia* concentration on treatment efficacy. These results show that plankton concentrations of > 50 animals/L may require a longer treatment time.

The mortality of zooplankton may depend on UV dosages, active species (such as OH, O_3 , etc.) concentrations, heat, and the pressure waves [30]. However, the reason for the minimum mortality with charging voltage (as shown in Figure 4) and discharge electrode gap distances (as shown in Figure 5) cannot be identified at this moment. Although the generated maximum pressure wave strength, UV intensities and active species concentrations in electrohydraulic discharges normally depend on the charging voltage, the electrode gap distances and water properties, the

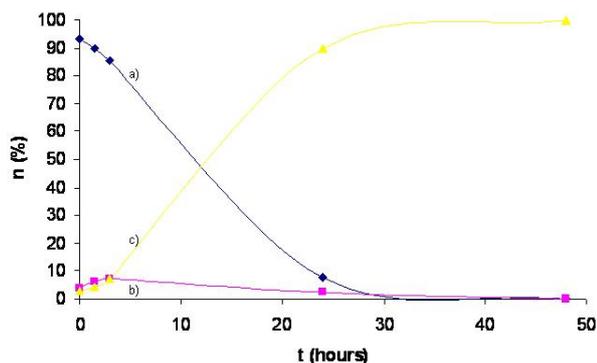


Fig. 7. Effect of a single PAED pulse on *Daphnia* mortality over time. $V_{CH} = 3.8kV$, Gap distance = 0.5mm, $N = 30$ *Daphnia*/L, $t_R = 6sec$. a) % living organisms, b) % dying organisms, c) % dead organisms..

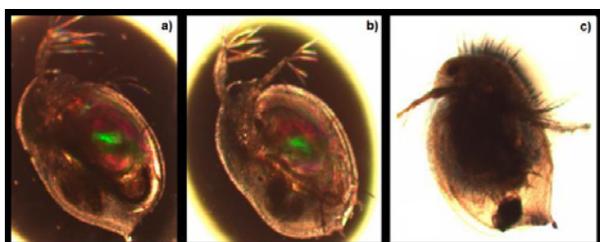


Fig. 8. *Daphnia* specimen, a) Fresh from tank, strong heart; b) Dying after 3.28kV, 0.5mm gap, 10 min treatment, weaker heart beat and antennae movement; c) Dead 24 hours after 1 pulse at $V_{CH} = 5.8kV$, Gap distance = 0.5mm

propagation of pressure waves, UV generation and active species transportation depend significantly on the reactor geometry, especially for the large volume reactor as used in the current experiments [6,8,30]. Based on the work by Yelverton [8], pressure rise in [Pa·s] vs body mass in mg characteristics seem to determine the mortality of small fishes. Hence, the effect of charging voltage on mortality may due to the volume-averaged pressure rise all over the reactor water, which may be minimum under our experimental conditions. Since the present experiments were limited to pressures measured at 4 locations across the reactor wall, only those general conclusions as outlined above can be presented at this time.

The effect of single pulse treatment for *Daphnia* is shown in Figure 7, where time zero corresponds to the time immediately after the single pulse PAED treatment was completed. This figure shows that the single pulse treatment did not result in immediate mortality, however the observations of the planktons themselves show an increasing physical damage after treatment, as shown in Figure 8. This damage may lead to increased mortality a few hours after treatment. Figure 8 also shows the differences seen in treated organisms. By observing the slowing down of the speed of the carapace contraction as well as organism movement, one could determine if an organism was dying.

With the short treatments used in the sets of experiments described herein, especially with single pulse treatments (less than 1 sec) in a large water-volume

reactor, UV generation with a rapid attenuation in water and insufficient radicals generated per unit volume under single pulse can be expected. Unlike UV inactivation for pathogens, zooplankton as used in this study cannot be killed with $0.08mW/cm^2$ level UV-B per pulse measured at the optical window position [28]. Temperature rise (less than 1 K) was also insignificant for single pulse treatments, hence it may be concluded that pressure wave plays the dominant role in the present case.

IV. CONCLUSION

Experiments were conducted to study the effect of PAED discharge for the mortality of *Daphnia*. The results show that exposure of zooplankton to 10-minute PAED treatment resulted in 84.7% mortality (mean of 10 trials) immediately after treatment, and 96.9% to 100 % after an additional 24 to 40 hours. Treatments with a single pulse or 1 minute treatment yielded lower mortalities. When looking at the total energy cost of these experiments, for the single pulse treatments, the energy cost is negligible for a 48 hour period (0.5 kJ per pulse per 3 L water) as compared with the continuous energy inputted to the system. The other proposed treatment system does not have any comprehensive values at this time. It is premature to estimate any realistic energy cost values before larger scale pilot tests are conducted.

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