

The consequences of air flow on the distribution of aqueous species during dielectric barrier discharge treatment of thin water layers

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Abstract

The desired outcomes of wet tissue treatment by dielectric barrier discharges (DBDs) strongly depend on the integrated fluences of reactive species incident onto the tissue, which are determined by power, frequency and treatment time. The reactivity produced by such plasmas is often expected to be proportional to treatment time due to the accumulation of radicals in the liquid over the tissue. However, one of the typically uncontrolled parameters in DBD treatment of liquids and tissue is gas flow, which could affect the delivery of plasma produced radicals to the tissue. Gas flow can redistribute long-lived, plasma produced gas phase species prior to solvating in the liquid, while not greatly affecting the solvation of short-lived species. Gas flow can therefore potentially be a control mechanism for tailoring the fluences of reactive species to the tissue. In this paper, we report on a computational investigation of the consequences of gas flow on treatment of liquid layers covering tissue by atmospheric DBDs by up to 100 pulses. We found that gas flow (through residence time of the gas) can control the production of gas phase species requiring many collisions to form, such as reactive nitrogen species (RNS). The resulting solvation of the RNS in turn controls the production of aqueous species such as $\text{NO}_{3\text{aq}}^-$ and $\text{ONOO}_{\text{aq}}^-$ (aq denotes an aqueous species). With the exception of O_3 and $\text{O}_{3\text{aq}}$, reactive oxygen species (ROS) are less sensitive to gas flow, and so OH_{aq} and $\text{H}_2\text{O}_{2\text{aq}}$ are determined primarily by discharge properties.

Keywords: dielectric barrier discharge, plasma–liquid interactions, atmospheric pressure plasma, flow dynamics, plasma chemistry

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric pressure dielectric barrier discharges (DBDs) provide disinfecting and therapeutic treatment of biological tissues by delivering radicals, photons, energetic ions and

electric fields [1–4]. Although the circuitry that delivers the voltage waveform to the DBD may be complex, the actual DBD devices which create the discharges used in biological applications are generally simple. The typical structure is a dielectric covered high voltage electrode operating in open air [5]. In the floating electrode configuration, the opposite electrode is the tissue being treated, usually less than a few mm away from the powered electrode. Other configurations, such

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as the surface micro-discharge (SMD), have both electrodes self-contained and independent of the tissue. In spite of the simplicity of these devices, control of the plasma produced reactants incident onto the tissue being treated can be challenging [6, 7]. The plasmas produce a variety of fluxes to the tissue, including ions, short- and long-lived radicals, and visible, UV and VUV photons. These species collectively react, making it difficult to independently deliver a single activating species to the tissue. The desired products for a specific treatment are typically delivered with by-products, which may have a counter-productive effects [8].

The delivery of reactant species to the tissue often occurs through an overlying liquid layer, which may be as simple as water or a saline solution, or as complex as a biological fluid [9–11]. Gas phase reactants produced by the DBD react with the liquid layer and transport as transformed reactivity to the underlying tissue. An approximate way to characterize this treatment is a dose or fluence (reactants cm^{-2}) delivered through the liquid layer to the underlying tissue. In the context of DBD treatment in ambient air, the dose or fluence is most typically affected by pulse-power format—voltage waveform and repetition rate.

An often uncontrolled parameter in DBD treatment of tissue and liquids is gas flow. The typical arrangement for DBD treatment of tissue, at least by floating electrode devices, is sustaining the discharge in ambient air without there being control on the flow of gas through the electrode-tissue gap, or even for humidity. There will likely be natural convection that occurs due to gas heating or ion-wind effects, however there is typically not controlled forced convection of air through the gap. As a result, any convection that does occur would usually be incidental and not controlled. At the other extreme, the SMD is often sustained in a closed volume without there being external flow, though there may be internal convection [12].

Gas flow could be an important method to control reactivity both in the gas phase and in the liquid. Such gas flow transports pristine (but possibly humid air) into the electrode-tissue gap, and transports products of the gap. Control resulting from gas flow originates from there being different reaction time scales. For example, the time scale required to produce ozone, O_3 , in air is only a few μs . O_3 is formed coincident with each discharge pulse and its formation is not significantly affected by gas flow. However, formation of significant densities of reactive nitrogen products (RNS), such as nitric acid, HNO_3 , requires many gas phase reactions occurring over many tens of ms (many discharge pulses). These times are long enough that gas flow which removes reactants from the gap can affect RNS formation. Gas flow also redistributes reactants generated by the discharge in space, which leads to another level of possible control. These spatial distributions of gas phase reactants then map onto spatially dependent solvation of reactants into the liquid.

In this paper, we report on the results from a 2D computational investigation of multiply pulsed DBDs in ambient air treating liquid covered tissue with a cross flow of humid air through the electrode-liquid gap. The liquid is a few hundred microns thick, consisting of water with dissolved O_2 .

A 100-pulse, 100 Hz negative discharge in humid air, and its afterglow were investigated. Plasma produced reactivity in both the gas and liquid phase, and the fluences onto the underlying tissue are discussed. We found that the redistribution of gaseous reactants directly affected the manner of solvation of reactants into the liquid. The gas flow can either redistribute rapidly solvating species or limit the rate of solvation of slowly solvating species by convecting the gas phase species out of the domain before solvation. The aqueous species can be divided into three groups. The first group containing, for example, OH_{aq} and $\text{H}_2\text{O}_{2\text{aq}}$, originate from nearly direct interaction of the plasma with the surface of the liquid during the discharge. (The subscript aq denotes an aqueous species.) These aqueous species are formed in the liquid before gas flow begins to influence the gas phase distributions of their precursors. The second group containing, for example, $\text{O}_{3\text{aq}}$ and $\text{N}_x\text{O}_{y\text{aq}}$, are strongly affected by the gas flow. The origin of these aqueous species are their gas phase analogues whose solvation rates are relatively small. Gas flow can convect the gas phase precursors far from the initial location of the plasma and eventually out of the domain, which then produces a plume of their solvation products. The final group containing, for example $\text{O}_{2\text{aq}}^-$, are indirectly affected by the gas flow. The consumption of $\text{O}_{2\text{aq}}^-$ by $\text{O}_{3\text{aq}}$ is a major loss, and so the spatial distribution of $\text{O}_{3\text{aq}}$ (directly a function of gas flow) affects the distribution of $\text{O}_{2\text{aq}}^-$.

We briefly discuss the modeling platform used in this investigation in section 2. In section 3, we discuss the consequences of gas flow on the production of radicals and charged species, with a comparison between several flow rates. Concluding remarks are presented in section 4.

2. Description of the model

The 2D plasma hydrodynamics model, *nonPDPSIM*, was used in this investigation. The incorporation of liquid species and the transport of species between the gas phase and liquid phase are described in [13, 14]. The manner of simulating multiple discharge pulses has been previously described in [14, 15]. The gas phase model, including the equations used to solve for the convective flow field and method of solution based on integration of Navier–Stokes equations, is described in [15]. With these previous descriptions, the model will be only briefly discussed here.

The basic model consists of an implicit integration of plasma transport equations for electrons, ions and charge densities, and Poisson's equation, on a 2D, unstructured Cartesian mesh. In a time slicing manner, integration of the plasma transport equations and Poisson's equation is followed by updates of neutral densities and the electron temperature. From a plasma and chemical kinetics perspective, the liquid phase is treated identically to and contiguously with the gas phase, albeit with different reaction mechanisms. The polarizability of molecules in the liquid phase is chosen to provide the appropriate dielectric constant. Neutral gas phase species enter into the liquid phase at rates limited by their Henry's Law equilibrium values. Ions and photons cross over into the

liquid unimpeded by the interface as their energies are typically much larger than surface potentials. Water vapor evaporates into the gas phase from a source at the surface of the liquid held at the saturated vapor pressure.

The duration of the plasma pulse is typically less than 15 ns whereas the interpulse period can be hundreds of μ s to tens of ms. Given this disparity in time scales, the plasma produced species appear to be instantaneously generated on a pulse-periodic basis. With these time scales, the following procedure was used to address multiple pulses. The full set of plasma transport and Poisson's equations are solved for the first discharge pulse, and the sources of the discharge produced species are recorded. After the voltage is removed and the plasma dissipates, Poisson's equation is no longer solved, and we compute the interpulse period enforcing charge neutrality. For the second and successive pulses, the sources functions from the first pulse are used to instantaneously generate a pulse of plasma produced species while continuing to integrate all transport and continuity equations. The resulting gas and liquid phase species densities are followed through the following interpulse period until the next pulse.

Similar to the models of plasma jets onto air or onto liquids described in [15, 16], a single set of compressible Navier–Stokes like equations are integrated for the laminar, convective flow field only in the gas phase with a no-slip boundary condition at the solid and liquid surfaces. The individual species then diffuse in the gas phase within the average flow field. All densities and velocities are directly computed at the mesh points of the unstructured mesh. The inlet boundary conditions for gas flow consist of specifying the fluxes perpendicular to the inlet plane of the components of humid air. The fluxes are uniform and at a pressure of 1 atm and temperature of 300 K. The outlet boundary condition is a specified pressure of 1 atm on the face of the outlet. A check is made on the normal velocity into the outlet and this velocity is required to be into the outlet. Due to the liquid layer being thin, we do not include convective flow in the liquid and transport is only diffusive. For sufficiently thin liquid layers, diffusion is a good approximation for reactant transport. For thick liquid layers, advection is likely the dominant transport mechanism [17].

Although the equilibrium concentrations of species in the gas and liquid are well described by Henry's law equilibrium concepts, the kinetics of these processes are less well known. It is clear that plasma produced gas phase reactants can quickly solvate into liquids and persist in the liquid for times much longer than the plasma exposure. For example Traylor *et al* [18] exposed water and phosphate buffered saline (PBS) to a surface-micro-dielectric barrier discharge sustained in air for 15 min or 3 h. After 2 d, they measured H_2O_2 concentrations of 10 μM in the water and 200 μM in the PBS. The latter persisted for 7 d.

Based on these and similar observations, our working assumption is that plasma produced species solvate into the liquid with gas phase transport coefficients. The solvated species diffuse out of the liquid into the gas with liquid phase transport coefficients. Consider the gas phase species having density n_g adjacent to the liquid (Δx away) and its solvated

liquid phase partner having density n_l at the surface of the liquid with Henry's law equilibrium constant h . The flux from the gas into the liquid is,

$$\begin{aligned}\phi_{gl} &= \frac{D_g}{\Delta x} \left(1 - \frac{n_l}{n_g h} \right) (n_g - n_l), \quad n_l \leq n_g h \\ &= 0, \quad n_l > n_g h\end{aligned}\quad (1)$$

where D_g is the gas phase diffusion coefficient. In this expression, the gas phase flux solvating into the liquid goes to zero as the equilibrium concentration in the liquid is reached. The flux from the liquid into the gas is,

$$\begin{aligned}\phi_{lg} &= \frac{D_l}{\Delta x} \left(1 - \frac{n_g}{(n_l/h)} \right) (n_l - n_g), \quad n_g \leq (n_l/h) \\ &= 0, \quad n_g > (n_l/h)\end{aligned}\quad (2)$$

where D_l is the liquid phase diffusion coefficient. In this expression, the flux of solvated atoms entering the gas goes to zero as the equilibrium concentration in the gas is reached. For computational convenience to separate the reaction mechanisms for the gas and liquid phase, we have gas and liquid partners for each solvating species—for example, O_3 and O_{3aq} . The n_l and n_g in equations (1) and (2) are the sum of the partner species in the gas or liquid phase. When O_3 diffuses into the liquid, it is converted to O_{3aq} at a rate faster than any other process that might affect the densities of the partners. When O_{3aq} diffuses into the gas phase, a similar conversion is performed to O_3 .

The complete liquid reaction mechanism is discussed in [13]. A subset of the reactions is shown in table 1 and is discussed here. The water layer initially contains O_{2aq} at its equilibrium density with room air. With this dissolved O_2 , electrons solvating into the water will quickly attach to form O_{2aq}^- . Charge exchange of negative ions from the gas phase into the water also produce O_{2aq}^- . As the density of O_3 in the gas phase increases, the density of O_{3aq} increases by the solvation of O_3 . In the liquid phase, O_{3aq} can be also produced through O_{aq} reacting with dissolved O_{2aq} however the former channel dominates O_{3aq} production. The electron affinities of O_2 and O_3 are 0.48 eV and 1.96 eV, respectively [22]. Due to the larger electron affinity of O_{3aq} , electrons more likely attach to O_{3aq} to form O_{3aq}^- . O_{2aq}^- can charge exchange with O_{3aq} to form O_{3aq}^- .

OH_{aq} is mainly produced in significant amounts in the liquid through photolysis of H_2O_{aq} and by charge exchange of $\text{H}_2\text{O}_{aq}^+$ with H_2O_{aq} to form hydronium, $\text{H}_3\text{O}_{aq}^+$. OH_{aq} is also formed by solvation of OH from the gas phase. OH_{aq} is reactive and does not penetrate far into the water. In the absence of other species, OH_{aq} mutually reacts to form H_2O_{2aq} . In presence of $\text{N}_x\text{O}_{y\text{aq}}$ (i.e. NO_{aq} , NO_{2aq} , N_2O_{3aq} , N_2O_{4aq} and N_2O_{5aq}), OH_{aq} can react to form $\text{HNO}_{x\text{aq}}$ (i.e. HNO_{2aq} and HNO_{3aq}). H_2O_{2aq} preserves part of the reactivity of OH_{aq} and reacts with $\text{N}_x\text{O}_{y\text{aq}}$ with lower rate coefficients. During the repetitive DBD discharges, H_2O_{2aq} is produced in significant amounts, so the reactions with H_2O_{2aq} are important on a continuous basis.

NO is the initiating species for forming N_xO_y and their aqueous counter parts. Since NO is created in significant

Table 1. Selected aqueous reactions.

Reaction ^a	Rate coefficient ^a	Ref.
$e_{aq} + O_{2aq} \rightarrow O_{2aq}^-$	1.9×10^{10}	[19] ^b
$e_{aq} + O_{3aq} \rightarrow O_{3aq}^-$	1.9×10^{10}	[19] ^b
$O_{aq}^\bullet + O_{2aq} \rightarrow O_{3aq}$	3×10^9	[19] ^b
$O_{2aq}^- + O_{3aq} \rightarrow O_{2aq} + O_{3aq}^-$	5.5×10^9	[20]
$\bullet H_{aq} + O_{3aq} \rightarrow O_{2aq} + O_{3aq}^-$	1×10^{10}	[20]
$\bullet OH_{aq} + \bullet OH_{aq} \rightarrow H_2O_{2aq}$	5.5×10^9	[19]
$NO_{aq} + NO_{aq} + O_{2aq} \rightarrow NO_{2aq} + NO_{2aq}$	$2.3 \times 10^6 M^{-2} s^{-1}$	[20]
$NO_{aq} + NO_{2aq} + H_2O_{aq} \rightarrow HNO_{2aq} + HNO_{2aq}$	$2 \times 10^8 M^{-2} s^{-1}$	[20]
$NO_{aq} + \bullet OH_{aq} \rightarrow HNO_{2aq}$	2×10^{10}	[20]
$NO_{2aq} + \bullet OH_{aq} \rightarrow HNO_{3aq}$	3×10^{10}	[20]
$NO_{aq} + HO_{2aq}^\bullet \rightarrow HOONO_{aq}$	3.2×10^9	[20]
$NO_{2aq} + \bullet OH_{aq} \rightarrow HOONO_{aq}$	1.2×10^{10}	[20]
$NO_{2aq}^- + O_{3aq} \rightarrow NO_{3aq}^- + O_{2aq}$	5.0×10^5	[20]
$HNO_{2aq} + H_2O_{aq} \rightarrow H_3O_{aq}^+ + NO_{2aq}^-$	1.8×10^1	[21] ^c
$H_3O_{aq}^+ + NO_{2aq}^- \rightarrow HNO_{2aq} + H_2O_{aq}$	1.8	[21] ^c
$HNO_{3aq} + H_2O_{aq} \rightarrow H_3O_{aq}^+ + NO_{3aq}^-$	2×10^3	[21] ^c
$H_3O_{aq}^+ + NO_{3aq}^- \rightarrow HNO_{3aq} + H_2O_{aq}$	2×10^2	[21] ^c
$N_2O_{3aq} + H_2O_{aq} \rightarrow HNO_{2aq} + HNO_{2aq}$	1.1×10^4	[20]
$N_2O_{4aq} + H_2O_{aq} \rightarrow HNO_{2aq} + HNO_{3aq}$	8×10^2	[20]
$N_2O_{5aq} + H_2O_{aq} \rightarrow HNO_{3aq} + HNO_{3aq}$	1.2	[20]
$NO_{2aq} + NO_{2aq} + H_2O_{aq} \rightarrow HNO_{2aq} + H_3O_{aq}^+ + NO_{3aq}^-$	$1.5 \times 10^8 M^{-2} s^{-1}$	[21]
$NO_{2aq} + NO_{2aq} + H_2O_{aq} \rightarrow H_3O_{aq}^+ + NO_{2aq}^- + H_3O_{aq}^+ + NO_{3aq}^-$	$5 \times 10^7 M^{-2} s^{-1}$	[21]

^a Aqueous species have an 'aq' subscript. Rate coefficients have unit of $M^{-1} s^{-1}$ ($l \cdot mol^{-1} s^{-1}$) unless noted otherwise. ' $\bullet$ ' represents a free radical.

^b Approximated by analogy.

^c The rate coefficient is estimated according to thermodynamic hydrolysis in liquid water.

numbers only in the gas phase, the majority of $N_xO_{y,aq}$ production is associated with solvation from the gas phase. The solvation probabilities of the higher N_xO_y species are not well known [14]. In general, their solvation rates are small, and their residences times in the gas phase are on orders of milliseconds. Once in the liquid, $N_xO_{y,aq}$ either quickly reacts with OH_{aq} and H_2O_{2aq} , or slowly reacts with H_2O_{aq} , to form $HNO_{x,aq}$. Nitrogen acids, $HNO_{x,aq}$, depending on their acidity, either persist or hydrolyze to hydronium and their conjugate ions, $NO_{x,aq}^-$ ($NO_{2,aq}^-$ and $NO_{3,aq}^-$). Nitrous acid, $HNO_{2,aq}$ is a weak acid and only a few percent hydrolyzes, while $HNO_{3,aq}$ is a strong acid and nearly completely hydrolyzes. With O_{3aq} in the liquid, $NO_{2,aq}^-$ can be slowly oxidized to $NO_{3,aq}^-$.

3. Consequences of convective flow in DBD treatment of tissue

The geometry used in our investigation is shown in figure 1(a). The powered electrode at the top is covered by an insulator with a thickness of 0.1 mm and dielectric constant of 3.0. The air gap above the liquid layer is 2.0 mm. The tissue below the liquid and above the grounded electrode is treated as a dielectric material with a thickness of 5.0 mm and a dielectric constant of 6.0. The thin liquid layer covering the tissue is 200 μm thick and initially consists of water molecules ($3.22 \times 10^{22} cm^{-3}$) and dissolved oxygen (8 ppm). The liquid layer is computationally treated using the same algorithms as the air gap. The interface between the liquid and gas controls transport of species

between the two phases. For example, water naturally evaporates from the interface into the gas and to humidify the gas. Air flow enters from the left boundary and exits through the right boundary. The flow rate is varied from zero to 300 sccm. The incoming air is relatively dry, with a humidity of 2.9% (vapor pressure of 0.78 Torr or a mole fraction of water of 0.001). In this model, any mechanical deformation of the liquid layer is not accounted for. The entire computational domain is 8 mm wide and 5 mm deep. The unstructured computational mesh has 15389 nodes with spatial resolution ranging from 20 μm at the liquid surface to 0.2 mm at the far boundary.

The plasma is produced by a voltage pulse of $-22 kV$ at 100 Hz upstream of the middle of the computational domain where a small cloud of neutral plasma is placed adjacent to the dielectric. The seed electrons have a density of $10^8 cm^{-3}$ and a diameter of 100 μm , values chosen not to affect the discharge characteristics. The electron density and ionization source during the discharge pulse are shown in figure 2. In this negative discharge, electrons are accelerated by the applied voltage in nearly a Townsend-like avalanche downward to the liquid surface within 3 ns. There is charging of the surface of the liquid and launching of a restrike positive ionization wave (IW) upwards towards the dielectric covered electrode. The restrike arrives by about 5 ns, which results in charging of the top dielectric.

The charging of the surface of the water and the top electrode produce surface ionization waves (SIWs) on both surfaces, and the discharge spreads over the liquid and the

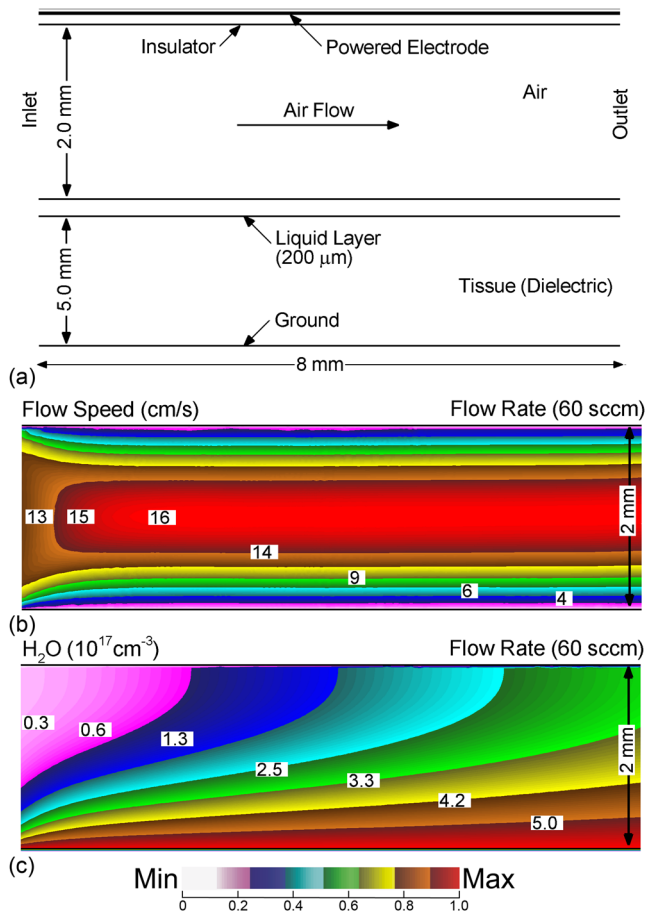


Figure 1. Conditions for the base case where the plasma interacts with a liquid layer covering tissue. (a) Schematic of the geometry. The total computational domain is 8 mm (wide) $\times$ 4 mm (high) $\times$ 5 mm (deep). Air flows in from the left boundary and exits through the right boundary. (b) Horizontal flow speed for 60 sccm flow rate of incoming air. (c) Density of water vapor for 60 sccm. The relative scale is noted on the color-bar.

dielectric surfaces. The SIWs on the bottom liquid surface and top dielectric surface fundamentally differ due to the disposition of electrons at the surface. As the volume IW strikes the liquid surface, electrons intersecting with the water are quickly solvated, which acts as a sink for gas phase electrons. The space charge and electric field which penetrate into the gas phase associated with the solvated electrons is small. This small penetration of the electric field from solvated electrons in turn reduces the intensity of the SIW which extends on the surface of the water. In contrast, as the restrike IW reaches the top dielectric, charging of the dielectric produces immobile charges which remain on the surface of the dielectric. The resulting electric field enhancement enables propagation of the SIW along its surface. Secondary electron emission also occurs at the dielectric surface, so the top dielectric can provide a source for electrons and help the spread of the discharge. The capacitance (F cm^{-2}) of the liquid is also larger than that of the top dielectric. The smaller capacitance of the dielectric more rapidly locally charges the surface, which then promotes spread of the SIW. (An IW striking a surface having infinite capacitance will not spread.) Note that the discharge spreading, both electron density and ionization source,

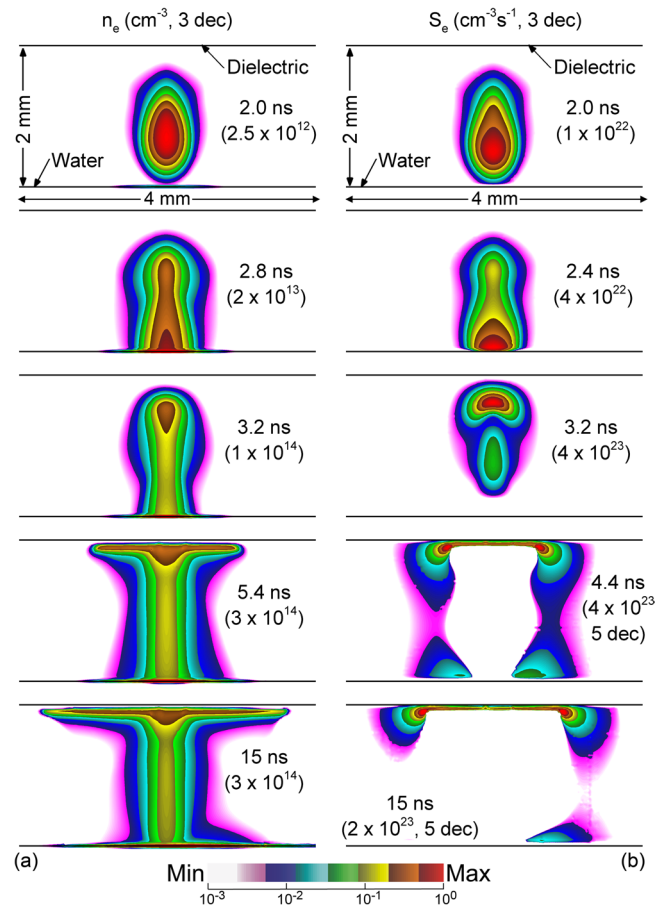


Figure 2. Time evolution of (a) electron density, n_e , and (b) electron impact ionization source, S_e , for a negative discharge operated at -22 kV for 10 ns over a $200 \mu\text{m}$ water layer. Only the gas gap is shown. The initial gas is 1 atm, $\text{N}_2/\text{O}_2/\text{H}_2\text{O} = 79.9/20/0.1$, and water evaporates from the surface. The contours for n_e and S_e are plotted on a log scale over three decades with maximum values shown at the top. Note the asymmetry in the surface ionization wave, more intense downstream due to the distribution of water vapor. The relative scale is noted on the color-bar.

near and on the liquid is asymmetric with there being greater spreading upstream. This asymmetry will be discussed below.

The horizontal gas flow speed is shown in figure 1(b). In the base case, air is flowed in through the left boundary at 60 sccm and pumped out through the right boundary where an atmospheric pressure is maintained. Since the flow is uniform at the inlet, there is a transient zone near the inlet where the boundary layer develops. With no-slip boundary conditions, the speed parallel to and at the surfaces is zero. As the boundary layer develops with the no slip condition, the flow speed in the center of the gap increases to conserve mass flux. With a flow rate of 60 sccm, the flow speed peaks in the middle of the gap at 16 cm s^{-1} , which is 0.16 mm ms^{-1} . During the interpulse period of 10 ms at 100 Hz, the flow distance is 1.6 mm which is a significant fraction of the total length of 8 mm.

The density of water vapor in the gas phase is shown in figure 1(c). The evaporation of water from the surface of the liquid is accounted for by holding the gas phase water density equal to the saturated vapor density at the surface of the water. Diffusion from the surface into the gas phase then occurs as

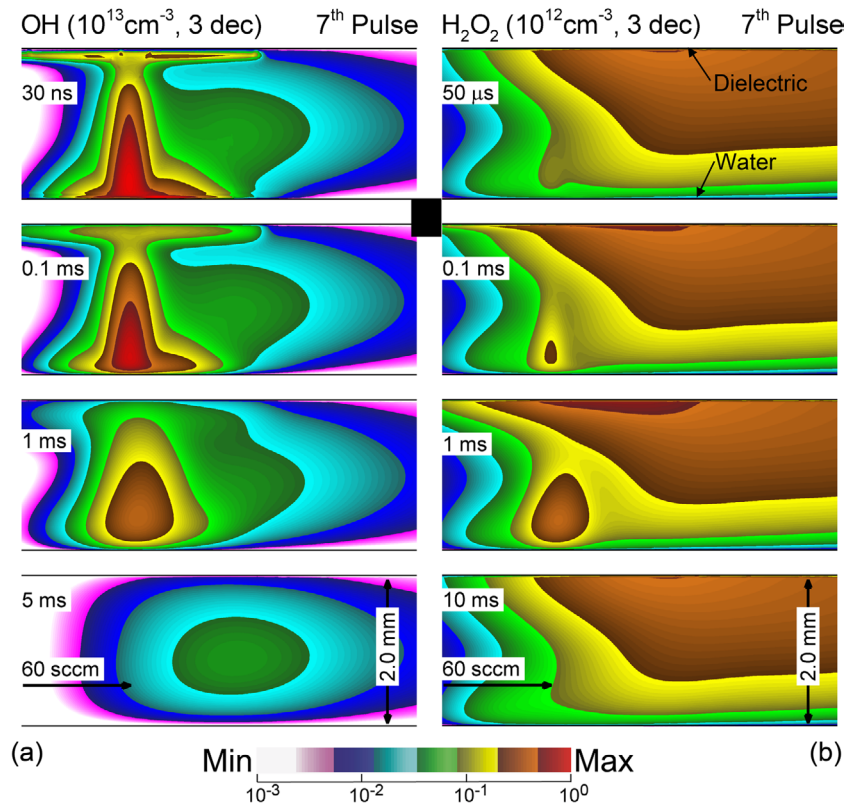


Figure 3. The evolution of (a) OH and (b) H_2O_2 densities in the gas gap for a flow of 60 sccm for the 7th pulse. The time is shown in each frame. The contours are plotted on a 3-decade log-scale with the maximum values noted in each frame. The relative scale is noted on the color-bar.

long as the local density of water is less than the saturated vapor density. At room temperature, the saturated water vapor density at the liquid surface is $5.5 \times 10^{17} \text{ cm}^{-3}$. In the absence of gas flow, the entire gap would eventually become saturated with water vapor. Under the influence of air flow, where the incoming partial pressure of water vapor is less than saturated, water vapor is blown downstream as it evaporates from the liquid surface. Along the surface of the liquid, the flow speed is small so that the density of water vapor is not significantly affected, and the air is nearly saturated with water vapor. Near the middle of the gap where the flow speed is maximum, convection transports the water vapor downstream in a plume. If the system was long enough, the water vapor would eventually fully fill the gap. However, here the non-uniform distribution of water vapor plays an important role in the generation of plasma produced radicals, such as OH and H_2O_2 .

The density of OH is shown in figure 3(a) for different times during the 7th pulse. For this length and flow speed, 7 pulses are sufficient to convect plasma produced species out of the system. OH is primarily produced by electron impact dissociation of H_2O vapor, and so its initial density follows the profile of the plasma streamer at 30 ns, shortly after the discharge pulse. The low density of OH downstream of the location of the plasma at 30 ns is the residual OH from prior pulses. The initial distribution of OH reflects both the location of the streamer and the distribution of the H_2O vapor. The OH density is larger near the top dielectric where the SIW spreads on its surface, and the OH density is larger near the water surface where the humidity is highest. A small asymmetry in

the initial distribution of OH produces more radicals on the downstream side of the plasma streamer due to the higher H_2O density downstream. This asymmetry in the distribution of water vapor is also apparent in the electron density and SIW shown in figure 2. After the discharge terminates, the OH density diminishes mainly through mutual reactions to produce H_2O_2 , shown in figure 3(b), and by solvation into the water. For times prior to about 0.1 ms, the flux of OH into the water is relatively small (indicated by the small gradient of OH at the surface of the water) since the density of OH_{aq} at the surface of the water is saturated. As the density of OH_{aq} at the surface is depleted by reactions at later times, solvation of OH from the gas phase increases. The convective flow is not apparent in redistributing the remaining OH density until about 1 ms. At this time, most OH has already reacted to form H_2O_2 or solvated into the water, and the air flow carries only residual OH downstream.

H_2O_2 is mainly produced in the afterglow of the discharge pulse through the mutual reaction of two OH radicals. For this reason, the OH-profile is imprinted into the initial profile of H_2O_2 every discharge pulse. The density of H_2O_2 reaches its maximum value when the OH is nearing depletion, at about 1 ms, and then is convected downstream. At 10 ms the majority of H_2O_2 has blown downstream. The H_2O_2 concentrates along the top insulator for several reasons. The first is that OH reaching the insulator recombines and returns to the gas as H_2O_2 . The second is that the flow speed slows to zero through the boundary as the insulator is approached. The third is that H_2O_2 is unreactive with the insulator in this model whereas

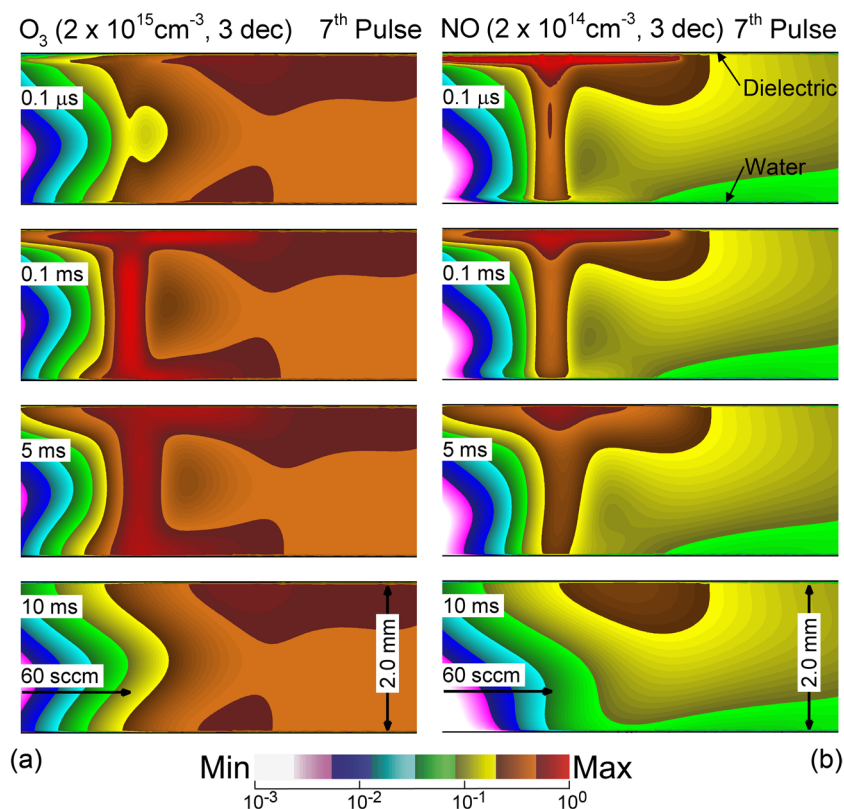


Figure 4. The evolution of (a) O_3 and (b) NO densities in the gas gap for a flow rate of 60 sccm for the 7th pulse. The time is shown in each frame. The contours are plotted on a 3-decade log-scale with the maximum values at the top. The relative scale is noted on the color-bar.

H_2O_2 solvates into the liquid, thereby reducing its density at the lower surface. H_2O_2 moderately accumulates on a pulse-to-pulse basis. Since H_2O_{2aq} is not fully saturated in the top layer of the water, H_2O_2 continues to solvate into the water throughout the pulse.

The density of O_3 during the 7th pulse is shown in figure 4(a). O_3 is primarily generated by O atoms, reacting with O_2 . O is produced by electron impact dissociation of O_2 in the plasma on a pulse-to-pulse basis. The reaction time for O atoms to produce O_3 is about 200 μs . The majority of O atoms produced in the discharge have formed O_3 by 0.1 ms prior to the convective flow redistributing the O_3 in the afterglow. Note that the O_3 initially produced following O atom production by dissociation of O_2 does not have the bell-shape of the OH at the surface of the water which is generated by electron impact dissociation of H_2O . Since the O_2 density is nearly constant as a function of height whereas the H_2O density is a function of height (larger near the water), there is more production of OH near the water. Initial production of O_3 is fairly uniform in the streamer. At 0.1 μs when O_3 begins to be generated from the fresh production of O atoms by the current pulse, the residual O_3 from the prior pulse is downstream of the location of the discharge. During the 10 ms afterglow, this plug of O_3 slowly reacts and flows downstream, and is replaced by the newly produced O_3 . The gradient of O_3 is small at the top surface since any quenching of O_3 produces an O atom which quickly regenerates O_3 . The gradient of O_3 is small at the surface of the water since the density of O_{3aq} is saturated due to its small Henry's law

constant. Since the rate of solvation of O_3 is small compared to OH, most of the O_3 is blown downstream where it slowly reacts with the increasing density of NO and NO_2 .

The density of NO during the 7th pulse is shown in figure 4(b). NO is mainly produced in the afterglow of the discharge pulse. Near the top insulator, the electron temperature is highest and so production of $N_2(A)$ and N atoms is largest, both of which are precursors for NO. Since NO does not react with the insulator and is caught in the slowly moving boundary layer, NO accumulates on a pulse-to-pulse basis near the top of the gap. On any single pulse, after 1 ms air flow begins to carry NO downstream before it gets solvated. Since NO only slowly solvates, a fairly uniform plume is generated.

The solvated densities of H_2O_{2aq} , NO_{2aq} and O_{3aq} in the liquid layer are shown in figure 5 after the 1st, 10th, 40th and 80th pulse. H_2O_2 solvates to form H_2O_{2aq} while OH solvates to form OH_{aq} relatively slowly. Photolysis of water by plasma generated UV directly in the liquid layer also produces OH_{aq} . As a result, the majority of OH_{aq} is produced directly under the discharge. The OH_{aq} mutually reacts to form H_2O_{2aq} within a few microseconds and within a few microns of the surface. As a result, after the first few pulses, H_2O_{2aq} reflects the production of OH_{aq} . H_2O_2 near the liquid surface can also solvate as the plume of H_2O_2 convects downstream. This solvation makes a relatively small contribution to the total production of H_2O_{2aq} but has important consequences. This small production of H_2O_{2aq} downstream occurs where the density of NO_{2aq} is also large, and so the H_2O_{2aq} downstream is largely consumed by reactions with NO_{2aq}^- .

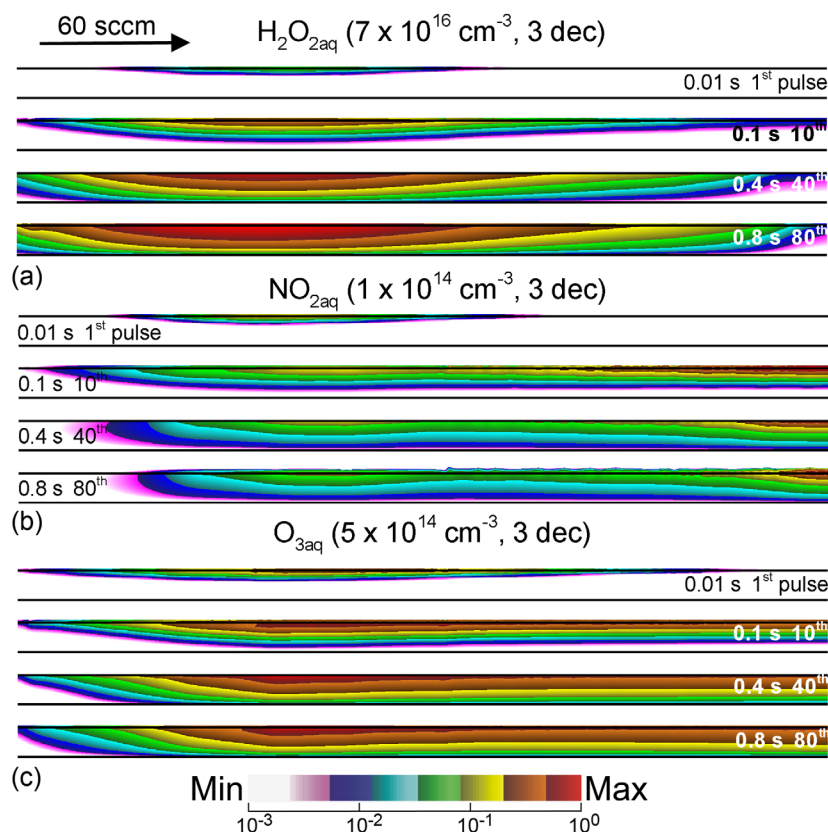


Figure 5. The time evolution of (a) $\text{H}_2\text{O}_{2\text{aq}}$, (b) $\text{NO}_{2\text{aq}}$ and (c) $\text{O}_{3\text{aq}}$ densities in the 200 μm water layer at the end of sequential discharge pulses (1st–80th pulse). The time and pulse number are shown in each frame. The contours are plotted on a 3-decade log-scale with the maximum values shown at the top of each frame. The relative scale is noted on the color-bar.

NO and NO_2 only slowly solvate into the water and slowly react in the gas phase. As a result, they convect downstream and survive to solvate downstream of the discharge. NO_{aq} rapidly reacts with OH_{aq} to form $\text{HNO}_{2\text{aq}}$, slowly reacts with $\text{H}_2\text{O}_{2\text{aq}}$ to form $\text{HNO}_{2\text{aq}}$ and reacts with $\text{O}_{2\text{aq}}^-$ to form $\text{NO}_{3\text{aq}}^-$. These reactions reduce the density of NO_{aq} to negligible values beyond the surface layer. $\text{NO}_{2\text{aq}}$ mutually hydrolyzes, which is a slow process, while rapidly reacting with OH_{aq} to form $\text{HNO}_{3\text{aq}}$. The density of $\text{NO}_{2\text{aq}}$ is therefore depressed in that portion of the liquid layer where the density of OH_{aq} is large at the surface. However, since NO_2 continually solvates into the liquid in the downstream plume, the density of $\text{NO}_{2\text{aq}}$ rebounds downstream where OH_{aq} does not reach.

O_3 has a slow to moderate rate of solvation so O_3 solvates under the discharge as well as solvating downstream from its plume. In the absence of organic molecules in the water, $\text{O}_{3\text{aq}}$ is relatively unreactive and so becomes saturated in the thin liquid layer. $\text{O}_{3\text{aq}}$ does charge exchange with $\text{O}_{2\text{aq}}^-$ to form $\text{O}_{3\text{aq}}^-$, a process that depletes $\text{O}_{2\text{aq}}^-$ as the density of ozone increases.

The solvated densities of $\text{H}_3\text{O}_{\text{aq}}^+$, $\text{NO}_{2\text{aq}}^-$ and $\text{NO}_{3\text{aq}}^-$ in the liquid layer are shown in figure 6 after the 1st, 10th, 40th and 80th pulse. $\text{NO}_{2\text{aq}}^-$ is initially produced by the hydrolysis of $\text{HNO}_{2\text{aq}}$ and the bimolecular reaction of $\text{NO}_{2\text{aq}}$. Neither HNO_2 nor NO_2 have large densities in the gas phase until several pulses have occurred. $\text{NO}_{2\text{aq}}^-$ then slowly increases its density downstream as its gas phase precursors increase their densities. $\text{NO}_{2\text{aq}}^-$ reacts with the increasing density of $\text{O}_{3\text{aq}}$

downstream to produce $\text{NO}_{3\text{aq}}^-$. Under the discharge where the density of $\text{O}_{3\text{aq}}$ increases on a pulse-to-pulse basis, $\text{NO}_{2\text{aq}}^-$ is eventually nearly completely consumed. Downstream the density of NO_{aq} at the surface is large which, through reactions with $\text{O}_{3\text{aq}}$, generates $\text{NO}_{2\text{aq}}^-$. So even though $\text{O}_{3\text{aq}}$ has a large density downstream which reacts with and consumes $\text{NO}_{2\text{aq}}^-$, the density of $\text{NO}_{2\text{aq}}^-$ manages to survive due to its larger production by hydrolysis of $\text{HNO}_{2\text{aq}}$. As a result, $\text{O}_{3\text{aq}}$ penetrates the liquid layer everywhere while $\text{NO}_{2\text{aq}}^-$ only accumulates downstream. The density of $\text{NO}_{3\text{aq}}^-$ extends from the location of the discharge where the plasma streamer hits the liquid fully downstream. $\text{NO}_{3\text{aq}}^-$ is mainly produced through hydrolysis of $\text{HNO}_{3\text{aq}}$, and so its density is higher along the liquid surface where HNO_3 solvates into the liquid, or $\text{HNO}_{3\text{aq}}$ is formed by reactions of OH_{aq} and $\text{NO}_{2\text{aq}}$.

The positive ions are dominated by $\text{H}_3\text{O}_{\text{aq}}^+$, which has a maximum density of nearly $5 \times 10^{16} \text{ cm}^{-3}$ after 100 pulses. As positive ions are solvated into the liquid, $\text{H}_2\text{O}_{\text{aq}}^+$ is formed first through charge exchange reactions. There is also a contribution from photoionization of $\text{H}_2\text{O}_{\text{aq}}$. $\text{H}_2\text{O}_{\text{aq}}^+$ quickly reacts with $\text{H}_2\text{O}_{\text{aq}}$ to produce $\text{H}_3\text{O}_{\text{aq}}^+$ and OH_{aq} . $\text{H}_3\text{O}_{\text{aq}}^+$ is more stable as the terminal positive ion. During this process, significant OH_{aq} is also produced. Although $\text{H}_3\text{O}_{\text{aq}}^+$ and $\text{O}_{2\text{aq}}^-$ are coincident under the discharge, a tail of $\text{H}_3\text{O}_{\text{aq}}^+$ extends downstream, whereas $\text{O}_{2\text{aq}}^-$ is located dominantly under the discharge where electrons

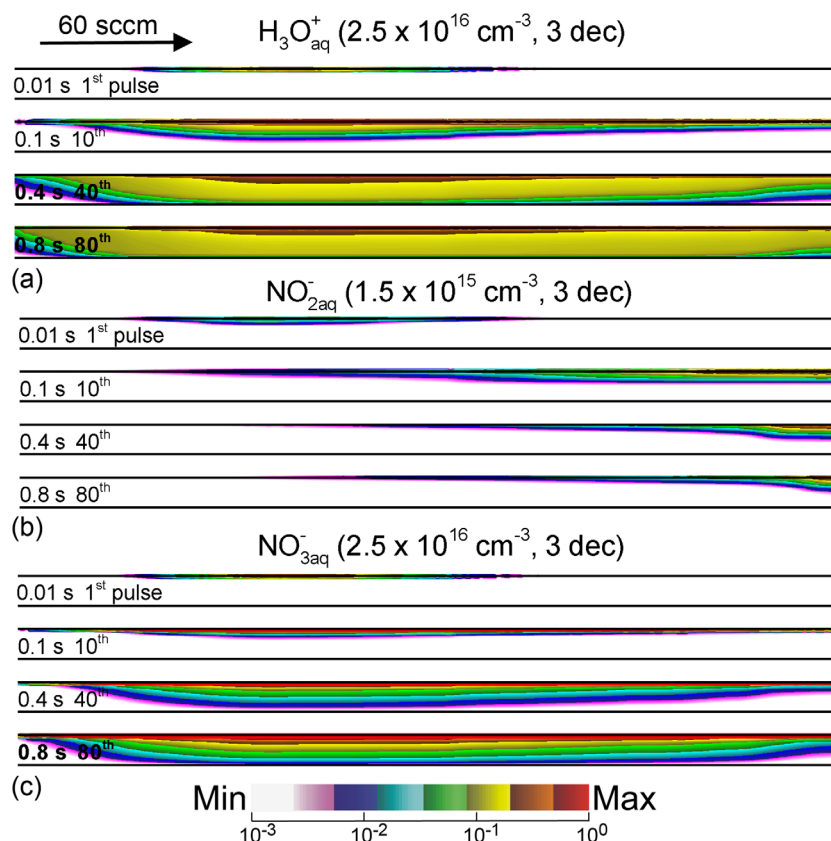


Figure 6. The time evolution of (a) $\text{H}_3\text{O}_{\text{aq}}^+$ (b) $\text{NO}_{2\text{aq}}^-$ and (c) $\text{NO}_{3\text{aq}}^-$ densities in the 200 μm water layer at the end of sequential discharge pulses (1st–80th pulse). The time and pulse number are shown in each frame. The contours are plotted on a 3-decade log-scale with the maximum values shown at the top of each frame. The relative scale is noted on the color-bar.

initially solvate. The persistence of $\text{H}_3\text{O}_{\text{aq}}^+$ downstream results primarily from the hydrolysis of nitrogen-oxides and acids from the gas phase plume that also extends downstream.

The plasma produced aqueous species can be basically divided into two groups—less and more affected by the gas flow. Short-lived gas phase species, such as electrons, ions and OH, are produced coincidentally with the plasma streamer. After the discharge, they are either quickly solvated into the liquid or react in the gas phase before the air flow can redistribute their densities downstream. As a result, aqueous species that trace their origins to these short lived gas phase species appear where the plasma streamer hits the liquid. The long-lived gas phase species, such as O_3 and N_xO_y , are produced in the afterglow after the discharge pulses when the air flow plays a significant role in redistributing their densities. These species are blown downstream as they solvate into the liquid. As a result, aqueous species tracing their origins to these long-lived gas phase species appear from the streamer to downstream locations.

Gas residence time, here controlled by flow rate of the incoming air, to some degree can control the coincidence of short- and long-lived species in the gas phase, which is then imprinted in the liquid phase through solvation. At one extreme, in the absence of gas flow, short- and long-lived species are spatially coincident and, diffusion aside, will solvate and produce aqueous species at the same locations. Aqueous species that trace their origins to either short- or long-lived gas

phase species will be initially mixed and react. At the other extreme, very large gas flow rates will convect long-lived species away from the location of the discharge prior to their solvation into the liquid. In this case, aqueous species that trace their origins to either short- or long-lived gas phase species will be initially produced at different spatial locations.

The consequences of gas flow rate from 0 to 300 sccm on the distribution of reactive species in the gas phase and in the liquid were investigated. The axial speeds (as shown in figure 1(b)) have essentially the same spatial distributions with increasing flow rate with the exception of an increase in magnitude and an extension of the boundary layer downstream. The mid-gap speed at 15 sccm is 4 cm s^{-1} which produces a residence time 200 ms or a flow distance of 0.4 mm between pulses. At 300 sccm the mid-gap flow speed is 80 cm s^{-1} for a residence time of 10 ms and a flow distance of 8 mm (the full length) between pulses. Due to the lower speed in the boundary layers, species close to the surface will have longer residence times. However, at 300 sccm, plasma produced species outside the boundary layer can be convected out of the gap during a single inter-pulse period. Depending on the speed of solvation, the density of the aqueous species can be reduced significantly compared to the case of small flow rate.

A secondary influence of flow rate is on the distribution of water vapor in the gap. Since it takes a finite time for water vapor to diffuse into the gap, lower flow rates result in more uniformly distributed water vapor than higher flow rates, as shown in figure 7

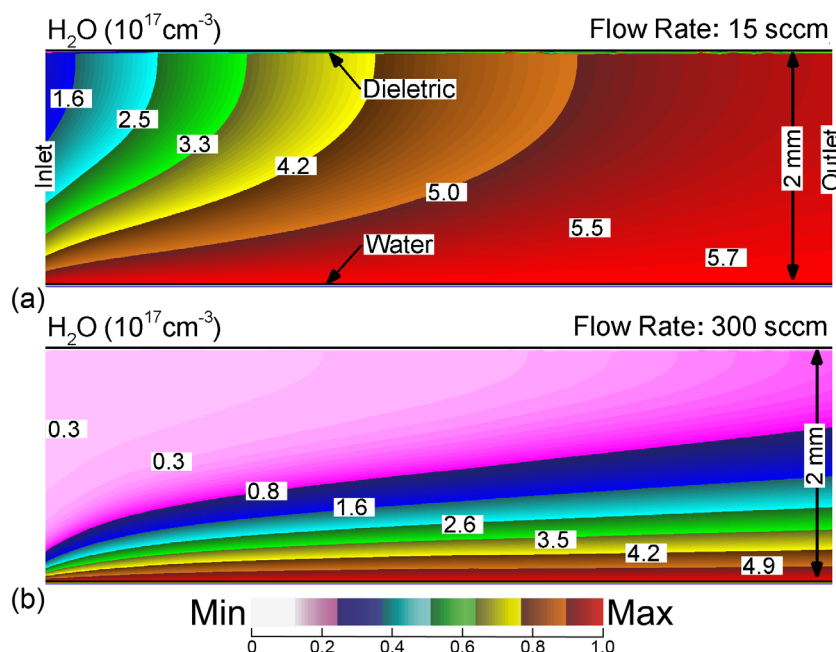


Figure 7. Water vapor density for flows of (a) 15 sccm and (b) 300 sccm entering from the left boundary and exiting through right boundary. The density of water vapor in the gap decreases with gas flow. The relative scale is noted on the color-bar.

for flow rates of 15 and 300 sccm. (See figure 1(c) for 60 sccm.) With an air flow of 300 sccm, water vapor is largely confined to the boundary layer where the flow speed is low. Without flow, the water vapor is nearly uniformly distributed in the gap.

The fluences of neutral species to the tissue after 0.4 s for flow rates of 0, 15, 60 and 300 sccm are shown in figure 8. Depending on the route for species to reach the underlying tissue, the fluences either vary strongly or do not vary with gas flow. For example, the fluence of $\text{O}_{3\text{aq}}$ to the tissue is shown in figure 8(a). For all practical purposes, the only source of $\text{O}_{3\text{aq}}$ is solvation of O_3 from the gas phase. As a result the density of $\text{O}_{3\text{aq}}$ is a sensitive function of gas flow. Without gas flow, the fluence of $\text{O}_{3\text{aq}}$ has a maximum value of $2.8 \times 10^{14} \text{ cm}^{-2}$, directly under the streamer. The distribution of $\text{O}_{3\text{aq}}$ then reflects diffusion of O_3 in the gas phase. With a low flow rate of 15 sccm, the maximum value of fluence is $3.3 \times 10^{14} \text{ cm}^{-2}$, slightly upstream from where the streamer hits on the liquid layer. Even at this low flow rate, there is redistribution of O_3 in the gas phase. The fluence also extends upstream by the spatial extent that the SIW spreads on the surface of the water. The fluence of $\text{O}_{3\text{aq}}$ extends downstream as the gas flow extends a plume of O_3 downstream. With increasing gas flow, the profile of the fluence of $\text{O}_{3\text{aq}}$ to the tissue significantly changes as the location of peak value shifts downstream. At 60 sccm, the maximum fluence is reduced to $1.2 \times 10^{14} \text{ cm}^{-2}$, and its tail downstream increases to $8 \times 10^{13} \text{ cm}^{-2}$ as the more rapid gas flow produces a plume of $\text{O}_{3\text{aq}}$ from the upstream to downstream. There is less fluence upstream as O atoms are themselves convected downstream prior to forming O_3 . The end result is that the fluence of $\text{O}_{3\text{aq}}$ is fairly uniform downstream. This uniformity comes at the cost of dose. At 300 sccm the O_3 is so rapidly convected out of the domain that even the density of $\text{O}_{3\text{aq}}$ is reduced downstream. The spatially integrated fluence of $\text{O}_{3\text{aq}}$ decreases with increasing gas flow which progressively

convects more $\text{O}_{3\text{aq}}$ out of the domain. In the end, the effect of gas flow on the fluence of $\text{O}_{3\text{aq}}$ depends on the production pathways for $\text{O}_{3\text{aq}}$ and its rate of solvation. O_3 is produced nearly exclusively in the gas gap with a long enough lifetime that gas flow can redistribute its density. The solvation rate of O_3 is relatively slow and $\text{O}_{3\text{aq}}$ reflects the time average density of O_3 above the liquid, a value that can be controlled by gas flow.

Different from $\text{O}_{3\text{aq}}$, $\text{H}_2\text{O}_{2\text{aq}}$ is an example of a species produced in the volume of the discharge and which solvates relatively quickly, or is produced by a discharge generated species which solvates moderately quickly, in this case, OH. The fluence of $\text{H}_2\text{O}_{2\text{aq}}$ to the tissue is shown in figure 8(b) for flow rates of 0–300 sccm. In spite of the increase in flow rate, the spatial distribution of the fluence of $\text{H}_2\text{O}_{2\text{aq}}$ does not appreciably change until a flowrate of 300 sccm. For flow rates up to 60 sccm, the maximum fluence is $1.8\text{--}2.5 \times 10^{15} \text{ cm}^{-2}$ near the location where the streamer strikes the liquid. $\text{H}_2\text{O}_{2\text{aq}}$ is dominantly produced in the liquid. OH_{aq} is generated by OH produced by the streamer and which directly solvates into the liquid, by charge exchange of $\text{H}_2\text{O}_{\text{aq}}^+$ with $\text{H}_2\text{O}_{\text{aq}}$, and by photolysis of $\text{H}_2\text{O}_{\text{aq}}$, all of which occurs in the direct vicinity of the streamer. OH_{aq} then quickly forms $\text{H}_2\text{O}_{2\text{aq}}$. H_2O_2 is also formed in the gas phase in the discharge through similar pathways and the solvation rate of H_2O_2 is large, and so that the majority of H_2O_2 solvates into liquid before being blown downstream except for the highest flowrate. Therefore, the fluence of $\text{H}_2\text{O}_{2\text{aq}}$ peaks under the plasma streamer. The spatial extent of $\text{H}_2\text{O}_{2\text{aq}}$ is partly determined by the spatial extent that the SIW that spreads on the surface of the water.

The fluences of a third class of species are affected not only by the gas flow but also by reactions. For example, the fluence of $\text{NO}_{2\text{aq}}$, shown in figure 8(c), is produced by both solvation from the gas phase and reactions in the liquid. With

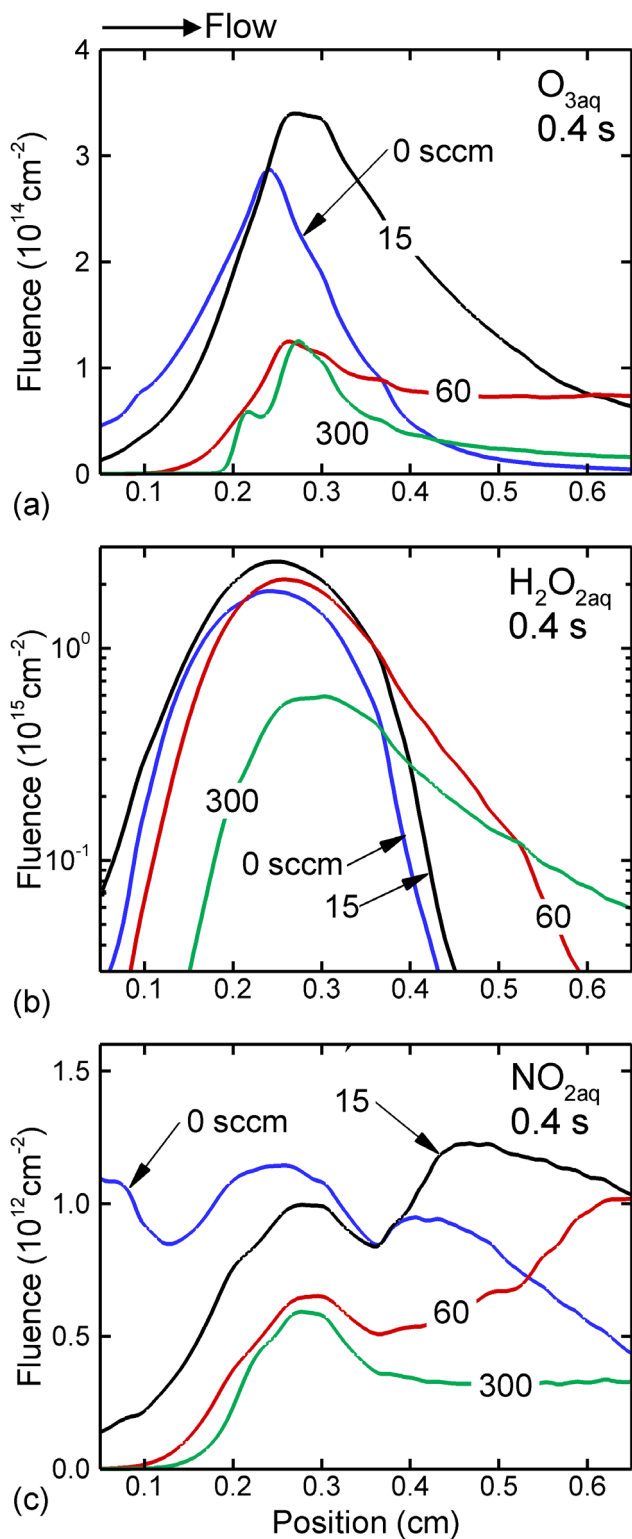


Figure 8. Fluences of neutral species onto the tissue underlying the 200 μm water layer integrated over 40 pulses with different gas flow rates (0–300 sccm). (a) $\text{O}_{3\text{aq}}$, (b) $\text{H}_2\text{O}_{2\text{aq}}$ and (c) $\text{NO}_{2\text{aq}}$.

increasing gas flow, the plume of NO_2 extends downstream providing a source of $\text{NO}_{2\text{aq}}$, spreading beyond the location where reactions with ROS would deplete its density. The increase in gas flow therefore produces a larger fluence of $\text{NO}_{2\text{aq}}$ downstream.

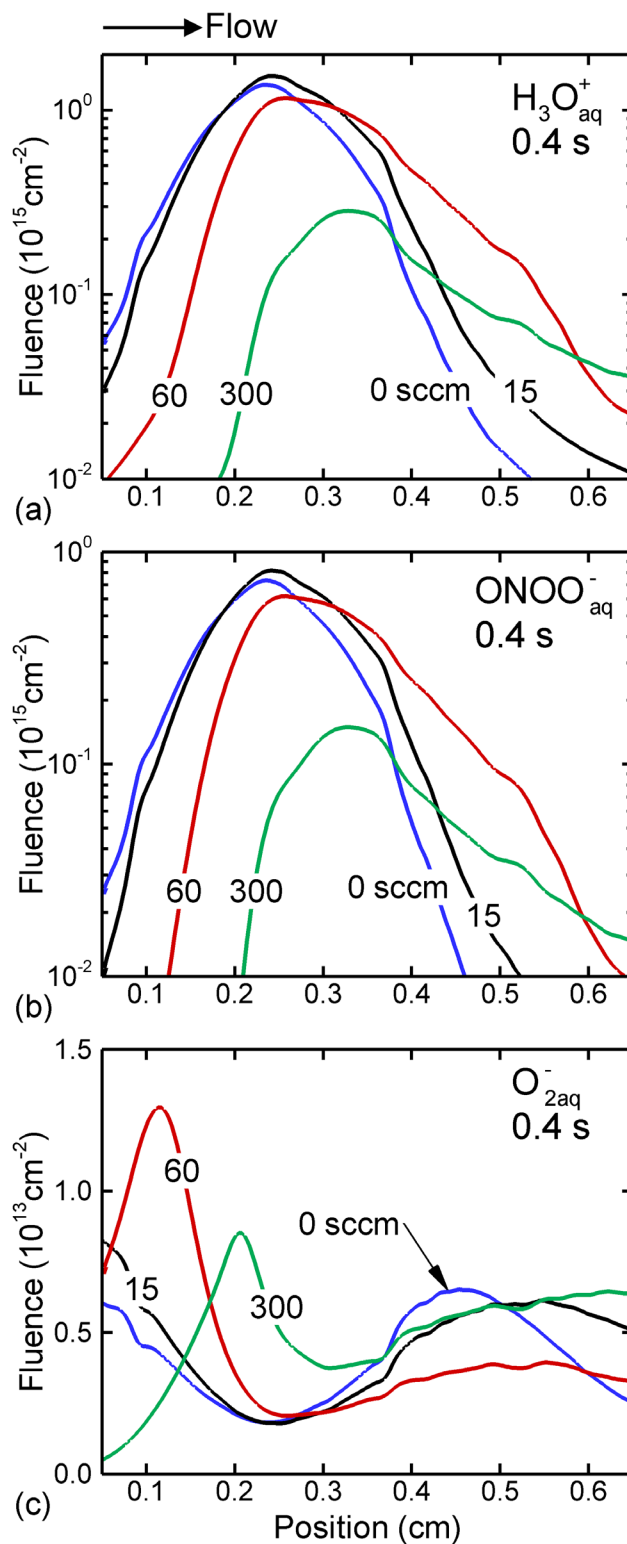


Figure 9. Fluences of ions onto the tissue underlying the 200 μm water layer integrated over 40 pulses with different gas flow rates (0–300 sccm). (a) $\text{H}_3\text{O}_{\text{aq}}^+$, (b) $\text{ONOO}_{\text{aq}}^-$ and (c) $\text{O}_{2\text{aq}}^-$.

The fluences to the tissue of the charged species $\text{H}_3\text{O}_{\text{aq}}^+$, $\text{ONOO}_{\text{aq}}^-$ and $\text{O}_{2\text{aq}}^-$ are shown in figure 9 after 40 pulses. The fluence of $\text{H}_3\text{O}_{\text{aq}}^+$ peaks under the plasma streamer with a tail to the downstream. Fluences generally decrease with flow

rate. $\text{H}_3\text{O}_{\text{aq}}^+$ is mainly produced through charge exchange and hydrolysis of RNS. When positive ions produced by the plasma streamer strike the liquid, they solvate and charge exchange with $\text{H}_2\text{O}_{\text{aq}}$ to form $\text{H}_3\text{O}_{\text{aq}}^+$. These reactions occur mostly under the plasma streamer. In the other pathway, $\text{N}_x\text{O}_{y\text{aq}}$ reacts with OH_{aq} , $\text{H}_2\text{O}_{2\text{aq}}$ and $\text{H}_2\text{O}_{\text{aq}}$ to form the nitrogen acids $\text{HNO}_{2\text{aq}}$, $\text{HNO}_{3\text{aq}}$ and HOONO_{aq} , which then hydrolyze to form $\text{H}_3\text{O}_{\text{aq}}^+$, $\text{NO}_{2\text{aq}}^-$, $\text{NO}_{3\text{aq}}^-$ and $\text{ONOO}_{\text{aq}}^-$. As the flow rate increases, the precursor gas phase N_xO_y species are convected downstream and out of the domain, thereby decreasing nearly all sources of $\text{H}_3\text{O}_{\text{aq}}^+$ that trace their origins to hydrolysis.

The spatial distributions of the fluences to the tissue of $\text{ONOO}_{\text{aq}}^-$ and of $\text{NO}_{3\text{aq}}^-$ are similar to that of $\text{H}_3\text{O}_{\text{aq}}^+$, decreasing with flow rate under and near the plasma streamer with a tail that increases with flow rate. $\text{ONOO}_{\text{aq}}^-$ is produced by hydrolysis of ONOOH_{aq} which is produced by reactions of OH_{aq} with $\text{NO}_{2\text{aq}}$ and $\text{HO}_{2\text{aq}}$ with NO_{aq} . (The hydrolysis of ONOOH_{aq} has branchings to both $\text{ONOO}_{\text{aq}}^-$ and $\text{NO}_{3\text{aq}}^-$, which explains their similar profiles.) The former reaction dominates and so the spatial extent of $\text{ONOO}_{\text{aq}}^-$ is determined by the spatial extent of OH_{aq} . $\text{NO}_{2\text{aq}}$ originates from gaseous NO and NO_2 , whose distributions are strongly affected by the gas flow. With low gas flow, $\text{NO}_{2\text{aq}}$ is mostly formed under and near the plasma streamer. With high gas flow, $\text{NO}_{2\text{aq}}$ is formed less under the plasma streamer and more in the downstream. The density of NO_2 decreases with flow rate due to convection out of the domain. As a result, the fluence of $\text{ONOO}_{\text{aq}}^-$ decreases with flow rate under and near the plasma streamer while increasing with flow rate downstream. This trend continues until the highest flow rate of 300 sccm when the precursors are blown out of the domain before solvating.

The fluence to the tissue of $\text{O}_{2\text{aq}}^-$ is shown in figure 9(c). Unlike other ions, the fluence of $\text{O}_{2\text{aq}}^-$ increases with flow rate. $\text{O}_{2\text{aq}}^-$ is formed through electron attachment and charge exchange, and so its initial formation tends to peak under the plasma streamer. The spatial extent of $\text{O}_{2\text{aq}}^-$ is in part determined by the extent of the SIW. In the liquid, $\text{O}_{2\text{aq}}^-$ further charge exchanges with $\text{O}_{3\text{aq}}$ to form $\text{O}_{3\text{aq}}^-$. In spite of a small rate coefficient, charge exchange with $\text{O}_{3\text{aq}}$ is still significant due to the moderate density of $\text{O}_{3\text{aq}}$. In the absence of gas flow, reactions of $\text{O}_{2\text{aq}}^-$ with $\text{O}_{3\text{aq}}$ dominantly occur in the vicinity of the streamer. As O_3 is progressively blown downstream with higher flow rate, the density of $\text{O}_{3\text{aq}}$ in the vicinity of the discharge decreases (and particularly upstream of the where the streamer strikes). The depletion of $\text{O}_{2\text{aq}}^-$ by reactions with $\text{O}_{3\text{aq}}$ is less and so more $\text{O}_{2\text{aq}}^-$ is able to diffuse through the liquid to reach the underlying tissue.

4. Concluding remarks

During DBD treatment of biological surfaces using air plasmas, and wet surfaces in particular, gas flow is typically not actively controlled. Gas flow has the potential to not only affect production of gas phase species but also their solvation into the liquid and the subsequent reaction of aqueous species. DBD produced

species with a cross gas flow of humid air were computationally investigated in the context of plasma tissue treatment of wet tissue. The species produced in the gas phase are redistributed by the gas flow, which both redistributes their solvation into the liquid and reduces their residence time, the latter of which particularly affects production of RNS. Depending on their production pathways, the aqueous species and their fluences are then indirectly affected by flowrate. Those species which are formed at the liquid surface during the discharge, such as OH_{aq} and $\text{H}_2\text{O}_{2\text{aq}}$, are weakly affected by gas flow. Those aqueous species which result from gas phase precursors formed in the gap during the afterglow, such as $\text{N}_x\text{O}_{y\text{aq}}$ and $\text{O}_{3\text{aq}}$, are strongly affected by the gas flow. The precursor species are convected by the gas flow downstream, producing a plume of solvation products downstream. The reactions attributed to these species can be regulated with gas flow. With a high flow rate, these species are depleted in the gas phase which then reduces their solvation into aqueous species. Another class of species, for example $\text{O}_{2\text{aq}}^-$, can be indirectly affected by gas flow. The initial production of $\text{O}_{2\text{aq}}^-$ is dominantly due to the attachment of solvated electrons to $\text{O}_{2\text{aq}}$ and is nearly insensitive to flow rate. However, the depletion of $\text{O}_{2\text{aq}}^-$ is dominated by reactions with $\text{O}_{3\text{aq}}$, which in turn is a sensitive function of flow rate (lower with increasing flow). So $\text{O}_{2\text{aq}}^-$ is sensitive to flow through its depletion by $\text{O}_{3\text{aq}}$.

The dependencies of aqueous species on flow rate discussed here are, to some degree, an extreme case. The plasma discharge strikes in the same location and only a single streamer was investigated. In practice, the location of the streamer may vary and the plumes from multiple streamers will likely overlap. The details of flow rate control of aqueous species will critically depend on these details and configurations. For example, Sakiyama *et al* [23] performed experiments and modeling of a surface microdischarge apparatus sustained in stagnant humid air in a sealed container. They found a transition between ROS dominated reactants to RNS dominated reactants with increasing exposure of the gas to the discharge. The exposure time is analogous to flow rate in an open system—low flow rate maps to long exposure time. A defining experiment to investigate the potential of this using flow rate to regulate the distribution of reactants in the gas and liquid phase would be a single DBD-like streamer striking the same location on a stagnant liquid, while controlling cross-flow of the gas across the liquid surface. Measurements of gas phase species leaving the gap at the end of the liquid as a function of gas-flow rate would determine the importance of residence time. Simultaneous measurements of the liquid phase activation would be correlated to the gas phase species. Such control of production of aqueous species in DBDs through gas flow is a relatively unexplored opportunity.

Acknowledgments

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References

- [1] Scholtz V, Pazlarova J, Souskova H, Khun J and Julak J 2015 Nonthermal plasma—a tool for decontamination and disinfection *Biotechnol. Adv.* **33** 1108
- [2] Babington P, Rajjoub K, Canady J, Siu A, Keidar M and Sherman J H 2015 Use of cold atmospheric plasma in the treatment of cancer *Biointerfaces* **10** 029403
- [3] Brehmer F et al 2015 Alleviation of chronic venous leg ulcers with a hand-held dielectric barrier discharge plasma generator (PlasmaDerm® VU-2010): results of a monocentric, two-armed, open, prospective, randomized and controlled trial *J. Eur. Acad. Dermatol. Venereol.* **29** 148–55
- [4] Balzer J, Heuer K, Demir E, Hoffmanns M A, Baldus S, Fuchs P C, Awakowicz P, Suschek C V and Oplander C 2015 Non-thermal dielectric barrier discharge (DBD) effects on proliferation and differentiation of human fibroblasts are primary mediated by hydrogen peroxide *PLoS One* **10** e0144968
- [5] Weltmann K-D, Kindel E, von Woedtke T, Hähnel M, Stieber M and Brandenburg R 2010 Atmospheric-pressure plasma sources: prospective tools for plasma medicine *Pure Appl. Chem.* **82** 1223
- [6] Baldus S, Schröder D, Bibinov N, Schulz-von der Gathen V and Awakowicz P 2015 Atomic oxygen dynamics in an air dielectric barrier discharge: a combined diagnostic and modeling approach *J. Phys. D: Appl. Phys.* **48** 275203
- [7] Laurita R, Barbieri D, Gherardi M, Colombo V and Lukes P 2015 Chemical analysis of reactive species and antimicrobial activity of water treated by nanosecond pulsed DBD air plasma *Clin. Plasma Med.* **3** 53
- [8] Kong M G, Kroesen G, Morfill G, Nosenko T, Shimizu T, van Dijk J and Zimmermann J L 2009 Plasma medicine: an introductory review *New J. Phys.* **11** 115012
- [9] Yagi I, Ono R, Oda T and Takaki K 2014 Two-dimensional LIF measurements of humidity and OH density resulting from evaporated water from a wet surface in plasma for medical use *Plasma Source Sci. Technol.* **24** 015002
- [10] Matthe R, Bende C, Schlüter R, Koban I, Bussiahn R, Reuter S, Lademann J, Weltmann K-D and Kramer A 2013 Antimicrobial efficacy of two surface barrier discharges with air plasma against *in vitro* biofilms *PLoS One* **8** e70462
- [11] Lukes P, Dolezalova E, Sisrova I and Clupek M 2014 Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: evidence for the formation of peroxyxynitrite through a pseudo-second-order post-discharge reaction of H₂O₂ and HNO₂ *Plasma Source Sci. Technol.* **23** 015019
- [12] Pavlovich M J, Chang H W, Sakiyama Y, Clark D S and Graves D B 2013 Ozone correlates with antibacterial effects from indirect air dielectric barrier discharge treatment of water *J. Phys. D: Appl. Phys.* **46** 145202
- [13] Tian W and Kushner M J 2014 Atmospheric pressure dielectric barrier discharges interacting with liquid covered tissue *J. Phys. D: Appl. Phys.* **47** 165201
- [14] Tian W and Kushner M J 2015 Long-term effects of multiply pulsed dielectric barrier discharges in air on thin water layers over tissue: stationary and random streamers *J. Phys. D: Appl. Phys.* **48** 494002
- [15] Norberg S A, Johnsen E and Kushner M J 2015 Formation of reactive oxygen and nitrogen species by repetitive negatively pulsed helium atmospheric pressure plasma jets propagating into humid air *Plasma Sources Sci. Technol.* **24** 035026
- [16] Norberg S A, Tian W, Johnsen E and Kushner M J 2014 Atmospheric pressure plasma jets interacting with liquid covered tissue: touching and not-touching the liquid *J. Phys. D: Appl. Phys.* **47** 475203
- [17] Lindsay A, Anderson C, Slikboer E, Shannon S and Graves D 2015 Momentum, heat, and neutral mass transport in convective atmospheric pressure plasma–liquid systems and implications for aqueous targets *J. Phys. D: Appl. Phys.* **48** 424007
- [18] Traylor M J, Pavlovich M J, Karim S, Hait P, Sakiyama Y, Clark D S and Graves D B 2011 Long-term antibacterial efficacy of air plasma-activated water *J. Phys. D: Appl. Phys.* **44** 472001
- [19] Maddena K P and Mezyka S P 2011 Critical review of aqueous solution reaction rate constants for hydrogen atoms *J. Phys. Chem. Ref. Data* **40** 023103
- [20] NDRL/NIST Solution kinetics database (online) (available: <http://kinetics.nist.gov/solution/>)
- [21] Pandis S N and Seinfeld J H 1989 Sensitivity analysis of a chemical mechanism for aqueous-phase atmospheric chemistry *J. Geophys. Res. Atmos.* **94** 1105
- [22] Berkowitz J, Chupka W A and Gutman D 1971 Electron affinities of O₂, O₃, NO, NO₂, NO₃ by endothermic charge transfer *J. Chem. Phys.* **55** 2733
- [23] Sakiyama Y, Graves D B, Chang H-W, Shimizu T and Morfill G E 2012 Plasma chemistry model of surface microdischarge in humid air and dynamics of neutral species *J. Phys. D: Appl. Phys.* **45** 425201