## Кратка стручна биографија

Оливера Јовановић рођена је 12.08.1994. године у Београду. Физички факултет Универзитета у Београду уписује 2013. године, где 2017. године завршава основне академске студије, смер Примењена и компјутерска физика, са просечном оценом (9.18). Исте године уписује мастер академске студије на Физичком факултету. Мастер рад на тему,,Третман воде загађене пестицидима плазма млазом на атмосферском притиску за примену у пољопривреди" урадила је под менторством др Николе Шкора, вишег научног сарадника у Лабораторији за неравнотежне процесе и примену плазме Института за физику у Београду. Рад је одбранила септембра 2018. године на Физичком факултету Универзитета у Београду чиме завршва мастер студије са просечном оценом (10.00). У октобру 2018. године уписује докторске академске студије на Физичком факултету, смер Физика јонизиваног гаса и плазме. Положила је све испите са просечном оценом (10.00).

На седници Научног већа Института за физику одржаној 11.12.2018. стиче истраживачко звање Истраживач приправник. Оливера Јовановић је у радном односу у Институту за физику од децембра 2018. године. Била је ангажована на пројекту интегралних и интердисциплинарних истраживања ИИИ 41011 ("Примене нискотемпературних плазми у биомедицини, заштити човекове околине и нанотехнологијама") Министарства просвете, науке и технолошког развоја Републике Србије под руководством др Невене Пуач, у Лабораторији за неравнотежне процесе и примену плазме. Под руководством др Николе Шкора ради на темама везаним за третман течних узорака плазма млазом.

На Колегијуму докторских студија Физичког факултета одржаном 29.9.2021. године је одбранила тему докторске дисертације под називом "Плазма млаз са шиљастом електродом – карактеризација и примене у третманима течних узорака". За ментора докторске дисертације одређен је др Никола Шкоро.

Аутор је на једном раду у међународном часопису категорије (М23), има једно предавање са међународног скупа штампаног у изводу (М32), три саопштења са међународног скупа штампана у целини (М33) и девет саопштења са међународног скупа штампаних у изводу (М34).

#### Преглед научне активности

Оливера Јовановић се током свог досадашњег научног рада бавила проучавањем система плазма млаза са шиљастом електродом који ради на атмосферском притиску у области kHz фреквенција. Испитивала је његове карактеристике у контакту са течношћу и бавила се новим применама у областима плазма пољопривреде и биотехнологије. Досадашње истраживање било је фокусирано на експериментално проучавање особина оваквих пражњења и конкретну примену плазма млаза за третмане различитих течних узорака.

Први део истраживања био је фокусиран на детаљну карактеризацију извора плазме и пражњења на атмосферском притиску у контакту са течношћу. Урађена је електрична карактеризација система снимањем струјно-напонске карактеристике пражњења при различитим условима рада система. Коришћењем оптичке емисионе спектроскопије и технике брзог сликања ICCD камером идентификоване су реактивне врсте настале у гасној фази и снимљен је профил пражњења. У циљу успешне примене овог типа извора плазме у биолоији и плазма пољопривреди развијена је метода за прецизно мерење снаге која се ослобађа у пражњењу. Употребом комерцијалних сонди испитивани су ефекти који настају у течности услед изложености пражњењу и праћене су промене физичко-хемијских особина течности. Поред тога, у оквиру дијагностике течне фазе, развијена је спектрофотометријска и колориметријска мерења дугоживећих реактивних азотних и кисеоничних врста у третираном узорку. У зависности од тога да ли је узорак била чиста или загађена вода урађена су различита испитивања третираних узорака и одређени су механизми интеракције плазме са сваким типом узорка.

У оквиру активности које подразумевају интердисциплинарна истраживања остварена је сарадња са колегама из других институција:

- Технолошко-металуршки факултет Универзитета у Београду – испитивана је могућност употребе плазме у технологијама пречишћавања отпадних вода,

- Фармацеутски факултет Универзитета у Београду – испитивана је токсичност плазмом третиране воде у експериментима са пацовима,

- Институт за биолошка истраживања "Синиша Станковић" - проучаван је утицај плазмом третиране течности на раст и развој биљних ћелија.

## Списак објављених радова и других публикација

#### Рад у међународном часопису (М23)

**Olivera Jovanović**, Nevena Puač and Nikola Škoro, A comparison of power measurement techniques and electrical characterization of an atmospheric pressure plasma jet, Plasma Sci. Technol. (2022), <u>https://doi.org/10.1088/2058-6272/ac742b</u>

#### Предавање по позиву са међународног скупа штампано у изводу (M32)

**Olivera Jovanović**, Nevena Puač, Radmila Sandić and Nikola Škoro, Influence of plasma properties on reactive species in PAW, The 23rd Symposium on Application of Plasma Processes (XXIII SAPP), February 4. - 5. 2021., Bratislava, Slovakia, pp. 71-73

#### Саопштење са међународног скупа штампано у целини (МЗЗ)

N. Puač, N. Škoro, S. Živković, M. Milutinović, S. Jevremović, **O. Jovanović**, G. Malović and Z.Lj. Petrović, Plasmas for plant bio-engineering and in agriculture for resource recovery The 24th International Symposium on Plasma Chemistry (ISPC24), June 9. - 14. 2019., Naples, Italy, I-13

Nikola Skoro, Nevena Puac, **Olivera Jovanovic**, Gordana Malovic, Zoran Lj. Petrovic, Treatment of pesticide polluted water by atmospheric pressure plasma sources, The 11th International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy (ISNTP 11), 1. - 5. July 2018., Montegrotto Terme, Italy, O-22

**Olivera Jovanović**, Nikola Škoro, Nevena Puač, Zoran Lj. Petrović, Plasma Decontamination of Water Polluted by Pesticides for Application in Agriculture, The 29th Summer School and International Symposium on the Physics of Ionized Gases (SPIG 2018), 28. Aug - 01. Sep 2018., Belgrade, Serbia, pp. 242 - 245

#### Саопштење са међународног скупа штампано у изводу (М34)

Nikola Skoro, Nevena Puac, Amit Kumar, Olivera Jovanovic, Andjelija Petrovic, Uros Cvelbar, Zoran Lj. Petrovic, Atmospheric pressure plasma treatment and decontamination of water samples, 240th ECS Meeting, October 10-14, 2021., D05-1

**Olivera Jovanović**, Nevena Puač and Nikola Škoro, The effects of plasma discharge regime on production of reactive species in water, ISPlasma2021/IC-PLANT2021, March 7-11 2021, virtual symposium, 08P-34.

Nikola Škoro, Nevena Puač. Olivera Jovanović, Anđelija Petrović, Zoran Lj. Petrović, Creation and destruction of chemical species in liquids treated bv atmospheric pressure plasmas - from gas phase chemistry to bulk liquid, The 1st annual meeting of the COST Action CA18212 "Molecular Dynamics in the GAS phase" (MD-GAS 2020), February 18. – 21. 2020., Caen, France

N. Škoro, N. Puač, **O. Jovanović**, G. Malović, Z. Lj. Petrović, Plasma treatment of liquids and applications in agriculture, XXXIV International Conference on Phenomena in Ionized Gases (XXXIV ICPIG), July 14. – 19. 2019., Sapporo, Japan, TL-22, pp. 19 – 19

Nikola Škoro, Nevena Puač, **Olivera Jovanović** and Zoran Lj. Petrović, Influence of the atmospheric pressure plasma source configurations on the properties of treated liquid samples, The 46th European Physical Society Conference on Plasma Physics (EPS 2019), July 8. – 12. 2019., Milan, Italy, I1.304

Ivana V. Matić Bujagić, Svetlana D. Grujić, **Olivera J. Jovanović**, Nikola D. Škoro, Identification of malathion degradation n products produced by atmospheric pressure plasma, The 56th Meeting of The Serbian Chemical Society (56.SHD), June 7. – 8. 2019., Niš, Serbia, HZS P 1

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#### ACCEPTED MANUSCRIPT

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# A comparison of power measurement techniques and electrical characterization of an atmospheric pressure plasma jet

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#### Abstract

A growing interest in the investigation of atmospheric pressure plasma jets (APPJs) that operate in contact with liquid samples has been shown in the last two decades. In order to form a complete picture about such experimental system, it is necessary to perform detailed diagnostics of plasma jets as one step that will enable to adjust the system properties according to applications in different areas. In this work, we conducted a detailed electrical characterisation of a plasma system configuration used for water treatment. Helium plasma jet with a pin electrode powered by a continuous sine wave at the frequency of 330 kHz formed a streamer that was in contact with a distilled water sample. The electrical circuit allowed monitoring of electrical signals supplied to the jet and also to the plasma itself. Electrical characterisation together with power consumption measurements was obtained by using two different methods. The first method was based on the direct measurements of voltage and current signals, while in the second method we have used 'Lissajous figures'. We have compared these two methods when used for discharge power estimation and addressed their advantages and limitations. The results showed that both of these methods could be used to successfully determine power consumed by a discharge in contact with water but only when taking into account power dissipation without plasma.

Keywords: Atmospheric Pressure Plasma Jet, liquid target, power measurement, Lissajous figure.

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

# 1. Introduction

Over the past decades, non-equilibrium atmospheric pressure plasmas have been extensively investigated because they represent a powerful tool in various applications. In the treatment of

thermally sensitive and unstable materials, especially in bio-medicine, the key asset is plasma operating at room temperature [1–4]. Apart for biomedical applications, these plasmas are used in agriculture and water treatment technologies [5–10]. Nevertheless, in all cases, the potential of cold plasma was used to create specific particles and form a chemically active medium without additional chemical reagents.

APPJs are sources of non-equilibrium plasmas that can be made in various geometries and electrode arrangements. They usually consist of a dielectric tube, a powered electrode, that can be additionally isolated, and a grounded electrode. Depending on the geometry of the electrodes, operation frequency, power source and working gas, different types and modes of discharge can be generated. In all configurations, the discharge is created when the gas at atmospheric pressure is exposed to a strong electric field. These plasmas are called non-equilibrium owing to the different temperatures i.e. energies of the particles [11].

In the case of APPJs, the realized discharge can be a classical streamer or more diffuse discharge. Discharges generated by dielectric barrier discharge (DBD) devices can be spatially homogeneous and diffuse [11, 12] while those discharges generated by plasma jets are usually streamers or streamer-like discharges. The streamer discharge occurs after the streamer breakdown. The formed electrical field accelerates the charged particles providing energy to the plasma. The presence of an electric field causes the ionization in the gas gap and the formation of space charges at the head of the ionization wave. The field amplification owing to the space charge in the head leads to self-extending streamer discharge. Thus, after inception, the streamer propagation and properties depend on the system configuration, gaseous surrounding and the target. The energy of the fast-progressing streamer is mostly dissipated into the excitation of working gas [13, 14]. In case of APPJs this is demonstrated through the propagation of PAPS (Pulsed Atmospheric pressure Plasma Streamer) or, so called, 'plasma bullets' [15–17]. Streamers are also present in other types of plasma sources. When the discharge current is not limited they precede other types of discharge, such as sparks and lightning [18].

In several publications it has been investigated how the configuration of plasma jet system influences the properties of plasma. It has been shown that the efficiency of the power transfer process from the power supply to the plasma system determines the mode of the discharge [14, 19, 20]. For example, a comparison of two discharge regimes produced by different excitation sources

(direct current (DC)-pulsed and sine-wave alternating current (AC)) in the same single electrode plasma jet was reported. It was found that the excitation source determines discharge current, the length of plasma plume and plasma temperature [21]. The grounded electrode due to its capacitive nature can additionally lead to the energy loss influencing behavior of the plasma bullet, but at the same time it can increase local electric field that will result in lower voltages needed to sustain plasma [14]. Control of these plasma properties is essential when comes to plasma treatments.

Many studies have shown that an interaction coupling between plasma and the target exists in atmospheric pressure plasma systems. Target properties influence the discharge morphology and affect the creation of turbulence in the gas flow [22, 23]. In the presence of the liquid target, plasma heating leads to evaporation and changes in the composition of the surrounding atmosphere, modifying the physico-chemical properties of both the gas and liquid phases [24]. Studies of the influence of treatment conditions on water properties have shown that small changes in the distance and volume of liquid lead to changes in the concentrations of deposited reactive species [25, 26]. Therefore, an additional complexity is introduced in the plasma system with the liquid target. Exposure of aqueous samples to non-thermal plasma leads to changes in water properties, creating an acidic environment under certain treatment conditions, changing conductivity and redox potential, and creating reactive oxygen and nitrogen species (RONS) [27, 28]. Creating plasma-activated liquid with specific, predetermined properties and a certain content of reactive species provides huge application potential but, at the same time, is an extremely demanding task. Depending on the plasma jet configuration, type of the discharge and the energy released in the plasma, different reactions will occur in the gas phase (plasma) and the liquid [29]. One step towards better understanding of entangled relationship between characteristics of the plasma source, the discharge properties, and treated sample characteristics, is to carry out detailed diagnostics of the plasma jet. An important part of that includes investigation of the electrical parameters such as the efficiency of input power transfer to the source, power dissipation, and impedance of the whole system.

In this study, we assessed in detail electrical characteristics of the He plasma jet operating against water target. The jet was supplied by a continuous sine high-voltage signal at the frequency of 330 kHz. The electrical discharge is generated in the gas phase above the liquid by applying the voltage at the pin electrode of the jet with distilled water serving as grounded electrode. The main

idea of the research was to perform proper determination of dissipated powers and evaluate typically used methods in plasma systems applied for water treatments. To estimate powers dissipated in the system, we employed two standard methods. In the first method, the power is calculated directly from the product of the measured time-varying current and voltage signals (V-I). The second method is based on measuring the voltage across a capacitor connected in a series with the grounded sample (Q-V).

These two methods, *V-I* and *Q-V*, as we named them here, are some of the most widely used power determination procedures. They have been extensively implemented in numerous plane geometry DBD configurations and several plasma jet systems including conventional plasma jet configurations supplied with both AC [30] and DC voltages [9, 31], driven by either a pulsed high-voltage signal [32] or continuous sinusoidal signal [33]. Furthermore, the input power and the discharge power have been estimated for diverse plasma jet arrangements such as hollow electrode APPJ [14, 34], kINPen [33], single-electrode jet [35], DBD jet [36] etc.

In recent years, a number of researchers have investigated cold plasma sources that interact with the targets of certain characteristics for a particular application. Plasma jet treatments are most commonly performed in secondary electrode configurations with a grounded or floating electrode. Two methods investigated in this work were used for power dissipation measurement in various plasma jet configurations for the treatment of biological materials and inactivation of bacteria [37, 38], biomedical application that include in vitro and in vivo treatments [39], producing of plasma activated (tap) water [40].

The research to date has tended to compare the differences between several measurement techniques for power determination only in the field of DBD plasma reactors [41–44]. However, as the Q-V method is mostly used with different DBD source configurations, there are few comprehensive analyses and comparisons of the two methods for pin-to-plate plasma jets [33, 35] operating with pulsed excitation. Although previous studies have investigated pin-to-plate configurations of plasma jet, there has been no study that we are aware of, which dealt with plasma jets interacting with liquid targets and driven by continuous sine wave. Therefore, the aim of this work was to assess the power consumption (at the target) of a high-frequency pin type plasma jet by using both *V*-*I* and *Q*-*V* methods and compare the obtained results.

# 2. Experimental setup and methods

#### 2.1. Plasma jet system

Figure 1 presents a schematic diagram of an experimental setup. Plasma source used in this experiment was a plasma jet designed to operate as a pin-electrode configuration at atmospheric pressure. It consisted of a cylindrical metal body (diameter 22 mm) and glass tube whose inner and outer diameters are 4 mm and 6 mm, respectively. A powered electrode was made of stainless steel wire with a diameter of 1 mm. It was covered with a ceramic insulating tube and placed along the glass tube axis. The sharpened tip of the wire protruded 3 mm from the ceramic insulation into the glass tube (see figure 1(b)). The powered electrode was connected to the high-voltage (HV) signal by a BNC connector positioned at the top of the metallic jet body. The second electrode was the target – a distilled water sample placed in a well of 6-well microtiter plate. The initial conductivity of water was 1.5 µS/cm (Hanna Instruments, HI76312 electrode, HI5521 controller). The plate was positioned below the tip of the powered electrode (see figure 1(b)). The volume of water sample in the well was 4 ml. The distance between the liquid surface and the wire tip was 10 mm in all measurements. The copper tape was attached at the outer bottom side of the well and grounded. The experimental setup, together with the positioning of the grounding tape, is a typical system which is used for plasma treatment of liquid samples. The setup on one side allows measurement of electrical signals while, on the other side, treated liquid is in contact only with the clean vessel so the chemical reactions are governed solely by the plasma-liquid interaction. Treatment of a liquid in contact with a copper tape showed that it produced additional chemical reactions and specific species in the liquid after the treatment [25]. Comparison between a setup where copper tape is inside the liquid sample or outside has been investigated for a similar system [29] showing rather small differences in the signals recorded in the grounded line. Also, working with the sine wave high voltage signal at high frequencies allows using different materials as a vessel for the samples.



Figure 1. Schematic representation of experimental setup (a) and enlarged view of the powered electrode and target placed below the tip of the electrode (b).

The plasma in the experiments was generated and controlled by using a commercial HV highfrequency power supply (T&C Power Conversion AG 0201HV-OS 140 W - 500 kHz with continuous sinusoidal signal with the frequency of 330 kHz. The power supply allows control of an output power (not output voltage or current) and measures the power forwarded from the device to the plasma system as well as the reflected power. The reflected power in all experiments was below 2 W. Due to several elements in the electrical circuit, there is a difference between the power measured at the source and the power delivered to the plasma. Since the power delivered to a discharge is a crucial parameter in the electrical diagnostics of a plasma jet, this indicates a need to measure current and voltage waveforms at the plasma jet itself. To monitor the instantaneously applied voltage waveforms at the power electrode we have used a HV probe (P6015A TEKTRONIX). The current waveforms were measured by using a current probe (Agilent N2783B) connected to the main line of the plasma jet (see figure 1(a)). To avoid an offset in the signal, the current probe was regularly demagnetized.

In the part of the electrical circuit containing the water sample we used two different approaches to measure the voltage and current waveforms. When utilizing the V-I method, the resistor of 1 k $\Omega$ 

resistance was connected in a series to the ground line of the electrical circuit (see schematic in figure 2). For the *Q*-*V* method (Lissajous figures) a capacitor was connected in series to the ground line of the electrical circuit (see schematic in figure 2). For these purposes, the capacitors had capacities of 0.8 nF and 10.3 nF. In both cases, the voltage drop across the elements placed in the ground line ( $v_G$ ) was measured by using a voltage probe (Agilent N2863B). The resistivity and capacitance of the used voltage probe are appropriate so it minimally perturbs the electrical circuit and influences the measurements. We used the Tektronix MDO3024 oscilloscope to record all waveforms.



Figure 2. The electrical circuit of the plasma jet system: v – applied alternating voltage at the powered electrode,  $v_{\rm G}$  - voltage in the ground line, *i*- current in the plasma jet main line, *i*<sub>G</sub> - current through the grounded line, *R* = 1 k $\Omega$ , *C* = 0.8 nF and 10.3 nF, *Z*<sub>NP</sub>- impedance of the plasma jet system configuration without plasma, *Z*<sub>P</sub> – impedance of plasma.

In all experiments He was used as a working gas with a fixed flow rate of 2 slm adjusted by a mass flow controller (Omega FMA5400/5500). The open-end geometry of the plasma jet enables the mixing of the He with the surrounding air. When plasma is ignited, the filamentary type discharge

operates in the gas mixture around the tip of the powered electrode. With the increase of the input power, the generated streamer propagates through the gap and for the most operating parameters it was touching the liquid sample.

## 2.2. The root mean square (RMS) values and V-I method

The electrical circuit (schematic in figure 2) allows monitoring of voltage and current instantaneous signals through the plasma jet main line and in the ground line. The waveforms of applied voltage v and current i through the plasma jet main line were plotted in figure 3.



Figure 3. Voltage and current waveforms obtained at the electrode in normal mode and average mode (16 cycles averaged). Waveforms were measured for applied peak-to-peak voltage of 5.5 kV, f = 330 kHz, and He flow of 2 slm. Electrical circuit configuration was with the resistor R = 1 k $\Omega$  in the grounded line. Half period of applied voltage ( $T/2 = \pi/f$ ) and phase difference ( $\Delta \varphi$ ) are noted in the plot.

The acquired time-dependent values of voltage and curent through the plasma jet main line, v(t) and i(t), and voltage drop across a resistor in the ground line  $v_G(t)$  were used for electrical characterisation and powers calculations. The root mean square values of the voltage and current were calculated in the following way:

$$V_{\rm RMS} = \sqrt{\frac{1}{nT} \int_0^{nT} \nu^2 \left(t\right) dt} \tag{1}$$

$$I_{\rm RMS} = \sqrt{\frac{1}{nT} \int_0^{nT} i^2(t) dt}$$
(2a)

$$I_{\rm G\_RMS} = \sqrt{\frac{1}{nT}} \int_0^{nT} i_{\rm G}^2 \,\mathrm{d}t \tag{2b}$$

where *T* is a period of the given signal and *n* is number of periods,  $i_G(t) = v_G(t)/R$  and *R* is the electrical resistance of the resistor in the grounded line.

In the *V-I* method, first the time-dependent powers delivered to the plasma jet and consumed by plasma were calculated as the product of voltage v(t) multiplied by the appropriate current, i(t) or  $i_G(t)$ . The average powers are then obtained as:

$$P_{\text{mean}} = \frac{1}{nT} \int_0^{nT} v(t) \cdot i(t) dt$$
(3a)

$$P_{\text{mean}_G} = \frac{1}{nT} \int_0^{nT} v(t) \cdot i_G(t) dt$$
(3b)

In all calculations as input data we used the waveform values obtained in avaraging mode. Comparison between two sets of data (obtained in normal and averaging mode) showed differences in calculated values less than 1% which is below experimental error. The phase differences ( $\Delta \varphi$ ) (see figure 3) between high voltage and other obtained signals were calculated in the following way:  $\Delta \varphi = (\Delta t/T) \times 360^{\circ}$ , where  $\Delta t$  is time period between points where both signals had zero values.

#### 2.3. *Q*-*V* method

Another method commonly used for electrical characterization and measurement of power consumed by plasma is based on a charge-voltage plot or Lissajous figure. For these measurements the capacitor was inserted in series with plasma jet and grounded line, so the same electrical charges formed in the discharge flow through the grounded target and the capacitor. By measuring the capacitor voltage, knowing the capacitance and assuming purely capacitive properties, the charge flow through the capacitor can be obtained. In the Lissajous figure, the area enclosed by the curve is equal to the energy dissipated per one period of applied voltage:

$$E = C \oint v(t) dv_{G} = \oint_{T} v(t) \frac{dQ}{dt} dt = \frac{P_{\text{mean}_{G}}}{f}$$
(4)

where *C* and  $v_G(t)$  are capacity and voltage across the additional capacitor (figure 2), v(t) is applied high-voltage signal, f = 1/T is the corresponding frequency, and  $P_{\text{mean}_G}$  is average power consumed by plasma [43, 45, 46]. In this work, the closed area of a Lissajous figure was obtained by the Polygon area function in the Origin software (Origin Lab Corporation, Northampton, MA, USA). A different approach to calculate the area inside the Lissajous figure can be found in [47].

To ensure that the influence of the capacitor on the whole system is minimal, the capacitance was chosen to be large compared to the equivalent capacitance of plasma jet, gas gap, and target. This difference is at least one order of magnitude. The second important property is the type of selected capacitor. It has been suggested that ceramic capacitors are preferred owing to their relatively low parasitic losses and accuracy in measurement of charge [48]. An additional advantage is that they are not polarized and may be safely connected to an AC source.

# 3. Results and discussion

#### 3.1. Instantaneous voltage and current

Before the onset of the plasma jet electrical measurements, the power supply has been set to operate at the frequency of 330 kHz with the lowest reflected power. The voltage and current signals were monitored for three different configurations of the ground line and in figure 4 we



show the waveforms for particular applied voltage. The measurement was performed without feed gas (Plasma OFF) and with the He flow of 2 slm (Plasma ON).



Figure 4. Voltage and current waveforms were measured for applied peak-to-peak voltage of 5.5 kV and frequency of 330 kHz. Dashed lines represent cases when the plasma was OFF, while full lines represent Plasma ON regime. In plots (a) and (e) Plasma ON and Plasma OFF signals overlap. (a) v - applied voltage at the electrode, (b)-(c) electrical circuit configuration with the resistor R = 1 k $\Omega$ : *i* - current in the plasma jet main line, *i*<sub>G</sub> - current through the grounded line, (d)-(e) electrical circuit configurations with capacitors:  $v_{G}$ - voltage across the 10.3 nF (blue line) and 0.8 nF (green line) capacitor.

The waveforms when the plasma was on are plotted by a full line while the dashed line shows the case without plasma (achieved without He flow). All presented signals were recorded with the applied peak-to-peak voltage of 5.5 kV. The waveforms in figures 4(a)–(c) are acquired in electrical circuit configuration with the resistor and represent averaged value of 16 acquired waveforms. The signals in figures 4(d) and (e) were obtained in electrical circuit configurations with capacitors by averaging 512 waveforms. Identical waveforms were obtained for the applied voltages v(t) (figure 4(a)) and currents i(t) (figure 4(b)) in configurations when two capacitors were inserted in the grounded branch of the circuit. Therefore, for simplicity, only one set of v(t) and i(t) signals are presented.

The high voltage signal applied to the plasma jet in the configuration with resistance R in the grounded branch of the circuit is shown in figure 4(a). It has a regular sinusoidal shape regardless of whether the plasma is ignited or not. Figure 4(b) shows the current i(t) obtained by current probe and flowing through the main line to the plasma jet. When there is no helium flow the obtained current signal is sinusoidal since the applied voltage is lower than the breakdown voltage in air. When the plasma is ignited, the current waveform is deformed from the sine wave and it has two peaks, one per each positive and negative half period of imposed voltage. The appearance of the peak in the current waveform is connected to the streamer type of the discharge. The observed deformation in the current waveform when discharge occurs has been found previously in other atmospheric plasma jet systems [15, 49–51]. It was the result of discrete propagation of the discharge outside the gas tube in a form of PAPS. In general, changes in the shape of the current signal occur because the current in plasma jet main line is superimposed to the displacement current. The displacement (capacitive) current can be measured directly when the tube is not filled with feed gas and there is no plasma.

The waveform of the current through the ground line  $i_G(t)$  is presented in figure 4(c). This is the discharge current that passes through the liquid target and a resistor connected in series to the ground. The difference between the waveform shape in the absence and presence of the plasma exists, but it is less noticeable than that in the case of current i(t). Related to the phase difference, the plasma off current waveforms i(t) and  $i_G(t)$  in figures 4(b) and (c) lead to the high voltage waveform by 85° and 88°, respectively. This points that the system is mainly capacitive (for pure capacitance the phase difference is 90°) with small deviation from 90° due to the inherent

resistivity of components of the electrical circuit and the plasma source. Deflection from 90° phase difference means we observe dissipation of the power even when plasma is not ignited. After the ignition of plasma these phase differences remain almost the same indicating that deposited power in plasma is small with the order of few watts. Voltages across two different capacitors are presented in figure 4(d) for C = 10.3 nF and in figure 4(e) for C = 0.8 nF. The voltages across 0.8 nF capacitor are in phase with the applied voltage independently of plasma being ignited or not, while in the case of 10.3 nF capacitor a small difference in voltage signals is visible.

#### 3.2. Volt-Ampere characteristics of the plasma jet

The volte-ampere *V*-*A* characteristics of the plasma jet with distilled water as the liquid target were presented in figures 5 and 6. By using the recorded waveforms for each selected operation point, the *V*-*A* characteristics were plotted as a function of the RMS current through the plasma jet main line (figure 5) and the RMS current through the target and ground line (figure 6).



Figure 5. *V*-*A* characteristics obtained at the plasma jet in presence (Plasma ON) and absence (Plasma OFF) of plasma for configuration with  $R = 1 \text{ k}\Omega$  in the grounded line. The *V*-*A* characteristics obtained when C = 0.8nF and C = 10.3nF were used in the electrical circuit are the same and not presented here to keep the clarity of the figure.

Both characteristics were recorded for the applied peak-to-peak voltages from 1.5 to 6 kV. The points were obtained by increasing the output power of the power supply. All measurements were performed in triplicate and observed differences in obtained values were not more than 7%. For all measurements as a target we used distilled water of the same initial conductivity because it was noticed that the conductivity of the liquid sample affects the power consumption [52, 53].

The *V*-*A* characteristic obtained at the plasma jet (figure 5) was recorded when the resistor was inserted in ground line of the electrical circuit. The characteristics that were the same within the error margins were obtained in the other two configurations of the electrical circuit (with capacitors C = 0.8 nF and C = 10.3 nF) and were not shown to keep the graph in figure 5 clear.

Increasing the power delivered to the plasma jet without plasma (triangles) results in a linear increase of both voltage RMS ( $V_{RMS}$ ) and current RMS ( $I_{RMS}$ ). With the gas flow, the discharge becomes visible at  $V_{RMS}$  of 0.5 kV and it first appears as a small bright point at the tip of the powered electrode. At  $V_{RMS}$  of 1.3 kV, a plasma filament forms and extends 2 mm from the electrode tip. The filament elongates with an increase of the input power. The discharge crosses the entire gap between the powered electrode and target, and streamer touches the water surface at  $V_{RMS}$  of 1.75 kV. As can be seen in figure 5, for currents above 30 mA and voltage above 1.75 kV the *V*-*A* characteristic measured with plasma on (inverted triangles) changes slope and it differs from the *V*-*A* characteristics obtained without plasma (triangles). A further increase in the output power of HV source (applied voltage  $V_{RMS} > 1.75$  kV) leads to more intense light emission from the plasma and to the change of colour. The streamer also begins to move on the liquid surface. For the highest applied voltages, it is observable that several short and thin filaments are adjoined in a streamer.

The V-A characteristics of the discharge plotted against the current in the grounded line  $I_{G_{RMS}}$ , shown in figure 6, were measured in the configurations with resistor  $R = 1 \text{ k}\Omega$  (figure 6(a)) and capacitor C = 10.3 nF (figure 6(b)). The pink and blue triangles show results for measurement when plasma is ignited, while the grey inverted triangles show results without plasma (without working gas flow).



Figure 6. *V-A* characteristics obtained for the current through the ground line  $I_{G_{RMS}}$  in the presence (Plasma ON) and absence (Plasma OFF) of plasma for the configuration with (a)  $R = 1k\Omega$  and (b) C = 10.3 nF in the grounded line. The *V-A* characteristic obtained when C = 0.8 nF was used in the electrical circuit is identical to the characteristic in (a). For better clarity of the figure it is not presented here.

The V-A characteristics presented in figure 6(a) shows linear dependence and there is no significant difference between the characteristics when plasma is ignited or not. When the capacitor C = 0.8 nF was inserted into the electrical circuit, the obtained V-A characteristic is similar to the characteristics presented in figure 6(a). However, the V-A characteristic obtained with capacitor C = 10.3 nF (figure 6(b)) has lower slope and departs from linear dependence at higher currents. The impedances of used capacitors can explain the observed difference. It can be assumed that the capacitor impedance is equal to the capacitive reactance  $X_c = \frac{1}{2\pi f C}$ , i.e. that resistance losses are negligible. Thus, the values of 597  $\Omega$  and 46  $\Omega$  are obtained for C = 0.8 nF and C = 10.3 nF, respectively. Comparing these results with the resistance of 1 k $\Omega$ , it is clear that the impedance of 0.8 nF capacitor is closer to 1 k $\Omega$  while the impedance of 10.3 nF capacitor differs by one and a half orders of magnitude from that value.

#### 3.3. Impedance of the plasma jet

In order to determine the impedance of the system, we have used a linear fitting of the plotted V- A characteristics obtained at the plasma jet. The total impedance of the plasma jet system  $\hat{Z}$  was obtained as the line slope of the calculated linear fit. It was calculated for both regimes – in the absence (Plasma OFF) and presence (Plasma ON) of plasma and for three different components in

the ground line of the electrical circuit. The equivalent circuit presented in figure 2 is very simple one and serves only for the estimation of the impedance of the used geometry (Plasma OFF) and of the discharge. These rough estimations of the jet system and plasma impedances are important when developing and/or choosing the appropriate power supply system. They present a load that will influence the work of the power supply, its output and optimal operating frequency. The plasma, which is highly non-linear system, will in most cases reduce the optimal operation frequency ('frequency pulling') of the power supply [54]. This means that output voltage can be reduced due to the exiting resonant state with the power supply transformer.

During the Plasma OFF regime, the complex impedance  $\hat{Z}$  can be considered as a series connection of the impedance  $\hat{Z}_{NP}$  and the impedance of the measuring element in the grounded line of the circuit – resistor or capacitor (see figure 2):

$$\hat{Z} = \hat{Z}_{\rm NP} + \hat{Z}_{R,C} \tag{5}$$

where all impedances are in complex form,  $|\hat{Z}_R| = R$ , and  $|\hat{Z}_C| = X_c = \frac{1}{2\pi fC}$  assuming that the contribution of the equivalent series resistance of the capacitor can be neglected.  $\hat{Z}_{NP}$  represents the equivalent impedance of the plasma jet system configuration without plasma, including capacitance of plasma jet configuration, target impedance, stray capacitance and parasitic resistance of cables and connections.

When the plasma is ignited (Plasma ON regime), plasma impedance is represented by  $\hat{Z}_{\rm P}$  in a parallel with the impedance  $\hat{Z}_{\rm NP}$  (figure 2). Plasma impedance is a complex system and it is beyond the scope of this work to estimate each of the components. After the plasma inception, the impedance  $\hat{Z}$  is given by:

$$\hat{Z} = \frac{1}{\hat{Z}_{\rm NP}} + \frac{1}{\hat{Z}_{\rm P}} + \hat{Z}_{R,C}$$
(6)

Table 1 shows the total impedances of the plasma jet system  $|\hat{Z}|$  obtained in the presence and absence of plasma. The impedances  $|\hat{Z}|$  obtained with three different configurations are in agreement with each other, with the difference smaller than 3%. This is expected since differences in the configurations were in the grounded line part. After the plasma is ignited, the total impedance is reduced by 10%.

Table 1. The total impedance of the plasma jet $ \widehat{Z} $ in Plasma ON and Plasma OF	FF states for
three different measuring elements in the ground line.	

Element in the	$ \hat{Z} $	(kΩ)	
ground line	Plasma ON	Plasma OFF	
$R = 1.0 \text{ k}\Omega$	54.2	59.0	Ń
C = 0.8  nF	54.3	59.8	
C = 10.3  nF	55.6	58.4	

## 3.4. Mean powers dissipated into the system A

In this part, we present and discuss two measured powers: the mean power delivered to the plasma jet -  $P_{\text{mean}}$  and the mean power consumed by plasma  $P_{\text{mean}}$  G, i.e., the power measured in the grounded line originating from the plasma and through the target. Additionally, a comparison of the results obtained using two standard methods, by integrating of current and voltage product (V-*I*) and by Lissajous figure method (*Q*-*V*) is presented.

The mean power delivered to the plasma jet  $P_{\text{mean}}$  was determined in all experiments regardless of which measurement element was inserted in the grounded line. The powers  $P_{\text{mean}}$  consumed with ignited plasma (red squares in plots) and without plasma i.e. feed gas (empty squares) were calculated by using the equation (3) and presented in figures 7 and 8.

Determination of the power  $P_{\text{mean}}$  without plasma has significance for determining the mean power delivered only to plasma since parasitic resistance in the system is included in power dissipation measured when the plasma is ignited. Therefore, to obtain the values delivered to the plasma itself  $(P_{\text{mean}}(\text{NET}))$ , the input power measured without He flow (Plasma OFF) was subtracted from the input power when the plasma was on (Plasma ON) for the same applied voltage value:

$$P_{\text{mean}}(\text{NET}) = P_{\text{mean}}(\text{Plasma ON}) - P_{\text{mean}}(\text{Plasma OFF})$$
 (7)

https://mc03.manuscriptcentral.com/pst The minimal uncertainty of both methods in our experiments was estimated to be 0.2 W for voltages below 1.5 kV given by power supply. In this range  $P_{\text{mean}}(\text{NET})$  is within this margin. It is found that the power  $P_{\text{mean}}(\text{Plasma OFF})$  increases nearly linearly with the applied voltage. Fitting a linear function to the obtained data points permits the determination of power losses for any applied voltage or current in the measured range. Comparing the dependences of  $P_{\text{mean}}$  on applied voltage  $V_{\text{RMS}}$  and on the current through the plasma jet  $I_{\text{RMS}}$  (see figure 8), it is clear that using either voltage or current as an independent parameter leads to the same power dependence.



Figure 7. Mean power delivered to plasma jet  $P_{mean}$  in presence (ON) and absence (OFF) of plasma as a function of applied voltage  $V_{RMS}$  for configuration with C = 0.8 nF in the grounded line. Power delivered only to plasma ( $P_{mean}$  (NET) points) is acquired by subtracting the values.

https://mc03.manuscriptcentral.com/pst



Figure 8. Mean power delivered to plasma jet  $P_{\text{mean}}$  in presence (ON) and absence (OFF) of plasma for configuration with  $R = 1 \text{ k}\Omega$  in the grounded line.  $P_{\text{mean}}$ (NET) points are acquired by subtracting the values. (a)  $P_{\text{mean}}$  dependence on applied voltage  $V_{\text{RMS}}$ , (b)  $P_{\text{mean}}$  dependence on the current through plasma jet main line  $I_{\text{RMS}}$ .

The obtained  $P_{\text{mean}}(\text{NET})$  as function of  $V_{\text{RMS}}$  is presented in the plot in figures 7 and 8 (star symbol). Figure 7 shows the power  $P_{\text{mean}}$  obtained in configuration with capacitor C = 0.8 nF, while figure 8 shows results measured in the arrangement with a resistor R. This power was found to be up to 6 W for the  $V_{\text{RMS}}$  range between 0.5 and 2 kV. In both figures 7 and 8, there is a jump in values  $P_{\text{mean}}(\text{NET})$  with the applied voltage above 1.5 kV (or  $I_{\text{RMS}}$  above 25 mA). This is the situation when the streamer reached and connected to the liquid target surface. By switching to that regime, the power  $P_{\text{mean}}$  jumps to higher values and continues to increase with increasing applied voltage.

In case of the measurement of power consumption by plasma,  $P_{\text{mean}_G}$ , we used two different methods (*V-I* and *Q-V*). With the serial resistor in the ground line (*V-I* method), the power  $P_{\text{mean}_G}$  was calculated by using equations (3) and (7). When a capacitor was connected in series with the grounded target, the *Q-V* method was employed. Figure 9 shows the dependence of the charge on the measurement capacitor on applied peak-to-peak voltage for capacitor C = 0.8 nF. Lissajous curves and the calculated deposited powers for three different input voltages of 5 kV, 5.5 kV, and 5.9 kV are presented.

The powers were calculated by using equation (4). Since both the applied voltage and the charge oscillate with the same frequency, a Q-V plot will form an ellipsoid Lissajous figure. The elliptical





Figure 9. Charge – voltage plot (Lissajous figure) and consumed power  $P_{\text{mean}_G}$  in the presence of plasma for three different applied peak-to-peak voltage (5 kV, 5.5 kV, 5.9 kV) and signal frequency of 330 kHz. A capacitor of 0.8 nF was used for measurement.

From the data in figure 9, it was apparent that the Lissajous loop retained the same shape and changed the slope (the line connecting points of minimum and maximum voltage) as the voltage changed. The centre of ellipse coincided with the coordinate system point of origin. Comparing the results for two different capacitors, it was found that the power measured using the 10 nF capacitor was slightly higher than the power estimated with 0.8 nF capacitor for the same applied voltage. The difference was around 23%, and it can be due to capacitor properties or plasma adjustment to different circuit elements [33].

Charge-voltage plots for states with and without plasma at the same applied voltage for 0.8 nF and 10.3 nF monitor capacitors were presented in figures 10(a) and (b), respectively. Our measurements show that the obtained Lissajous figure in the absence of plasma had a nonzero area, i.e. it was a very elongated ellipse. Usually, the curves obtained without plasma ignition the Q-V

 diagram are considered to be a straight line as it was assumed in the other studies with different plasma sources employed [42, 44]. The existence of the elongated ellipse when plasma is not ignited may be the result of technical issues such as defective wire connections or uncompensated probes [48]. In our case, these contingencies were checked and excluded. So, this power dissipation in Plasma OFF regime manifested the resistive losses present in the system, i.e. that a certain power was consumed in this part of the circuit even without plasma. This was observed also with Plasma OFF power values measured at the plasma jet (figures 7 and 8). Comparing the plots in figure 10, it can be seen that the power losses measured with 10.3 nF capacitor are one order of magnitude less than those in the case of 0.8 nF capacitor. In the case of high excitation signal frequency, the parasitic properties of the capacitor can have a significant value thus influencing the total impedance of the capacitor in the circuit [33, 41, 55]. This, in turn, influences determination of power, particularly in the Plasma OFF case.



Figure 10. Charge – voltage plot (Lissajous figure) and consumed power  $P_{\text{mean}_G}$  for applied peak-to-peak voltage of 5.5 kV and signal frequency of 330 kHz. Data in (a) green and (b) blue represent state with plasma and data in black (a) and (b) represent state without plasma (without He flow). Capacitors of (a) 0.8 nF and (b) 10.3 nF were used for measurements.

The Q-V plot in the absence of plasma has a shape of an elongated ellipse with the sharp turning point at maximum input voltage, meaning that charge and supplied voltage are in phase reaching the peak value at the same time. When the plasma is turned on, a Lissajous curve gains rounded end-points indicating additional resistive losses in the system. However, the waveforms of voltage

across the capacitor  $v_G(t)$  and high voltage v(t) remain in the phase for Plasma ON. Therefore, it can be assumed that the ignition of plasma does not lead to increase in impedance of an element of plasma jet system, which can change the phase between voltage signals. This analysis suggests that the power obtained with Plasma ON contains the total power consumed in the system. Thus, determination of the mean power consumed only by plasma,  $P_{\text{mean}\_G}$  (NET), has to follow a similar procedure used for the *V-I* method in equation (7): the power calculated from Plasma OFF Lissajous figure should be subtracted from power determined from Plasma ON Lissajous figure for the same applied peak-to-peak voltage.

In order to evaluate the two methods for the determination of the dissipated power, the dependence of the mean power consumed by plasma  $P_{\text{mean}_G}$  (NET) on  $V_{\text{RMS}}$  was plotted in figure 11 with values obtained with three different electrical elements in the grounded line.



Figure 11. Mean power consumed by plasma  $P_{\text{mean}_G}$  (NET) for three different measuring elements in the grounded line.

The power  $P_{\text{mean}\_G}$  (NET) ranges from 0 to 1.7 W for  $V_{\text{RMS}}$  between 0.5 and 2 kV. Compared to the results calculated for the power  $P_{\text{mean}}$ , we observed that less than 30% of  $P_{\text{mean}}$  is consumed by the plasma and forwarded through the grounded line. It can be seen in figure 11 that the power dependence on  $V_{\text{RMS}}$  calculated by the Lissajous figure (triangles) is in excellent agreement with those values obtained by the *V-I* method (squares). The error bars were estimated as standard errors

from three different measurements. In the  $V_{RMS}$  range from 0.5 to 1.1 kV, the calculated difference between powers measured in the presence and absence of plasma is close to zero. However, the plasma could be observed with the naked eye as a small bright region at the tip of the electrode even in this range of applied voltages. Therefore, these power values were lower than the sensitivity of the methods.

### 3.5. Difficulties in measurements of power

The most common problems in the power measurement are unwanted losses in the circuit that affect repeatability of the measurements. The losses in the plasma jet system occur due to the connections of the circuit elements, their quality i.e. characteristics, cables and also measuring equipment (especially when approaching high frequency range). In the ground line of the electrical circuit, we noticed that any change in connections such as the change of cables, connectors or a grounding technique will affect the measured values. To minimize the power losses and ensure reproducible results, the cables of appropriate length, connection and quality should be selected before measurement.

Several cautions need to be noted regarding the use of the Q-V method. The most common difficulties to pay attention to are: the selection of the appropriate type of capacitor, the use of proper cables for grounding the capacitor and the appearance of nodes or discontinuities in the curve.

Firstly, selection of an appropriate capacitor is considered as the most important part of the successful application of this method. It was found that the different types of capacitors with the same capacitance yield different results. The use of film capacitors has been found to lead to nonphysical results. When using a 10 nF metalized polyester (PET) capacitor, we measured more dissipated power when the plasma was OFF than when the discharge was ignited. In some cases when PET capacitor was used, we observed a self-intersecting loop in the part of the figure where charge and voltage change sign. The appearance of node points in the curve indicates different oscillation frequencies of the two signals – applied voltage and capacitor voltage. These findings suggest that PET capacitors should not be used in Q-V technique for power determination at least not with high-frequency signals.

The capacitor size should be chosen with respect to the plasma jet system capacitance, i.e. the capacitor should be selected that can store all the charge that has passed through the discharge during one half-cycle of the applied voltage. This can be fulfilled if the capacitor size is at least one order of magnitude higher than the plasma source capacitance. In this work, the capacitance size was selected to be three orders of magnitude greater than the plasma jet system capacitance.

As already mentioned, the connections in the grounded branch of the circuit greatly influence the repeatability of measurements. Small changes in the position of the cable between the grounded electrode and the monitor capacitor could cause changes in the inclination and width of the *Q-V* elliptic loop. A suitable cable which does not influence characteristics of Lissajous curve should be selected for the measurement.

Finally, despite its type and capacitance, every capacitor gives open loops. The Q-V plot is discontinuous because the curve after one period of applied voltage does not return to the starting point. That is, the charge and voltage values are different in points t = 0 and t = T. This feature of the Lissajous figure has already been observed for DBD plasma reactors [41, 56]. Despite this, the integration of the figure area is still possible, although there is a gap in the curve. This issue can be diminished when using high-resolution oscilloscope that provides waveforms with large number of points.

The main challenge with the use of the *V-I* method is resistor selection. It should be large enough to limit the discharge current. This is especially important in case of the low resistivity targets (conductive targets). An uncontrolled increase in discharge current can lead to a change in the type of discharge and then to heating and evaporation of the liquid target. However, the measurement resistor must be small enough to measure the voltage across the resistor with a voltage probe. Moreover, there are certain problems with using the *V-I* method when the pulsed power source is used in the experiment. In that case, when calculating the power, it is necessary to perform integration over the entire pulse duration period. Integration over one part of the period of the input signal which is shorter than the pulse duration, gives an inaccurate result for the power deposition as it could include only positive or negative part of the waveform oscillation. This would lead to an underestimation or overestimation of the measured power.

#### 

# 4. Conclusion

In this paper, we presented results of electrical diagnostics of the He plasma jet powered by continuous sine HV signal and operating in contact with a liquid sample. The main goals were to use data from systematically performed measurements of electrical parameters of such system for determination and comparison of mean power consumed by plasma  $P_{\text{mean}_G}$  obtained by using two different methods - *V*-*I* and *Q*-*V*. It must be emphasized that displacement current can be significant, especially in the case of atmospheric pressure plasma sources, and it needs to be taken into account. Since it is mainly result of the capacitive characteristics of the plasma systems it does not influence mean power deposited (consumed by) to the plasma. This is evoked by the fact that plasma jets in configuration with pin electrode are employed in different applications in contact with liquid target but without thorough investigation of power measurement techniques especially for the case of continuous wave power supply.

For that purpose, voltage and current waveforms were monitored and *V*-*A* characteristics of the plasma jet and the discharge were established. The phase difference between the current and voltage signal showed mainly the capacitive nature of the system, regardless of plasma presence in the system. As obtained *V*-*A* characteristics were linear, the data were used to determine the impedance of the whole system from the linear fitting of the plot. The impedance was almost the same regardless of the ground circuit configurations.

The mean power delivered to the plasma jet was determined by using the *V-I* method and found to be up to 6 W for  $V_{RMS}$  range between 0.5 kV and 2 kV. It was shown that plotting the power values using either voltage or current as an independent parameter results in the same power dependence.

The mean power consumed by plasma was determined by using two different methods. In both case when the capacitor was inserted in the ground line of the electrical circuit, an elliptical shape of the Lissajous figure was obtained. However, measured power observed with two different capacitors differs by 23%, suggesting slightly different adjustment of the plasma operating point due to the system conditions. Also, it shows that the properties of the capacitor should not be neglected when calculating the power delivered to the plasma as the capacitor should not be considered as an ideal element of the circuit. Nevertheless, this study has found that the discharge

power dependence on  $V_{\text{RMS}}$  calculated by the *V-I* method is consistent with those observed by the Lissajous figure (*Q-V* method).

Nevertheless, proper utilization of the power measurement method is necessary if one performs optimization of the energy efficiency of the plasma system. The mean power delivered to plasma calculated by both methods ranges from 0 to 1.7 W for  $V_{RMS}$  range between 0.5 kV and 2 kV. Therefore, this means that less than 30% of the power delivered to the plasma jet is consumed by the plasma.

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# SAPPXXIII

# 23<sup>rd</sup> Symposium on Application of Plasma Processes

# Book of Contributed Papers

Virtual Meeting 4<sup>th</sup> and 5<sup>th</sup> February, 2021

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# INFLUENCE OF PLASMA PROPERTIES ON REACTIVE SPECIES IN PAW

#### Olivera Jovanović<sup>1</sup>, Nevena Puač<sup>1</sup>, Radmila Sandić<sup>1</sup>, Nikola Škoro<sup>1</sup>

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We have used a pin-type of atmospheric pressure plasma jet (APPJ) for treatment of distilled water samples and production of plasma activated water (PAW). Electrical characterization of the APPJ and plasma power measurements were performed in order to obtain information about stability of the treatment conditions, the plasma properties, and the influence of plasma parameters on PAW. In order to investigate the influence of working gas on the PAW chemistry, we have performed treatments with helium or argon streamer discharges. Diagnostics of treated liquid samples were carried out to evaluate the effectiveness of plasma treatment. Results show that chemically reactive gaseous environment of helium discharge favours the production of nitrates and nitrites. At the same time, the argon discharge produces an order of magnitude higher values of hydrogen peroxide and nitrates, but the amount of nitrites is quite low.

#### 1. Introduction

Cold atmospheric pressure plasmas have been intensively investigated over the past decade due to their great potential for various applications. In the area of plasma agriculture, gaseous plasma treatment of aqueous solutions has multiple advantages such as reduction or elimination of organic contaminants and antimicrobial effects [1, 2]. The exposure of water to plasma induces a number of reactions occurred in the gaseous phase and introduces reactive oxygen and nitrogen species (RONS) species in aqueous phases. The resulting "plasma-activated water" was shown to remain active long after the plasma is turned off [3]. Among the most commonly detected chemical species in PAW are hydrogen peroxide, nitrite and nitrate due to their relative stability. These reactive species play a key role in the reactions involving dissolved organic species in water and can effectively inactivate bacteria or microorganisms [4]. Proper and detailed diagnostics of plasma sources will help to achieve better understanding and establish the correlation between the plasma processes and the treatment effects which is of crucial importance for further applications. From the point of view of plasma physics, the central issue is to standardize the performance in RONS production. Here we will present the results of the influence of the type of the working gas used (He or Ar) on the production of RONS in PAW.

#### 2. Experimental setup

In the study, we assessed the performance characteristics of the pin-type configuration of an APPJ powered by a continuous high voltage signal at frequency 330 kHz and operated with He and Ar as working gases. Schematics of APPJ and experiment set up are provided in Fig.1. Determination of concentrations of three reactive species ( $H_2O_2$ ,  $NO_2^-$ ,  $NO_3^-$ ) in liquid and pH of treated aquous solution was performed. Plasma source consists of a metal cylindrical case, a glass tube with concentrically placed powered sharpened electrode. The copper tape at the bottom of the microtiter plate was connected to the ground through a 1 k $\Omega$  resistance for monitoring the discharge current flowing through the plasma. The electrical volt–ampere characteristics as well as the power consumption were analysed with electrical probes.


Fig. 1. Schematic overview of the experimental set up.

Two types of plasma treatments were done: with He as working gas with flow rate of 2 slm and Ar with flow rate of 1 slm. Treatment times were 5 and 10 minutes. The volume of treated samples placed in the wells of 6-well microtiter plate below the APPJ was 4ml. The distance between the water surface and wire was 10 mm in all treatments. In order to characterize PAW we used colorimetric methods for measuring the concentrations.

### 3. Results and Discussion

In Fig. 2. we show concentrations of long-lived reactive species obtained after 5 and 10 minutes treatment of water sample by a pin-electrode jet. We measured completely different concentrations of all reactive species depending on the working gas. By changing the working gas, concentrations of produced  $H_2O_2$  and  $NO_3^-$  in PAW are measured to differ by an order of magnitude. For both gases the results show an increase in concentration of  $H_2O_2$  and  $NO_3^-$  with treatment time. The amount of nitrite generated by He plasma is almost same after 5 and 10 min while in case of Ar plasma the concentrations of nitrite in liquid are negligible. This result may also reflect a significant difference in power dissipation under different feed gas composition.



Fig. 2. Concentrations of nitrite, nitrate, and hydrogen peroxide in PAW samples after 5 and 10 minutes treatments using He and Ar as working gases.

### 4. Conclusions

Plasma treatments of distilled water were done using an APPJ in a pin-electrode configuration. These experiments demonstrated that changing the working gas produced different amounts of measured reactive species in PAW while in both cases filamentary type of plasma was established. Correlating measurement of plasma parameters with liquid sample properties will enable to investigate influence of different plasma parameters on changes in the properties of treated samples. Furthermore, it will be important to explore the potential use of these samples for the particular application in plasma agriculture field.

### 5. Acknowledgments

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24<sup>TH</sup> INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY NAPLES (ITALY) JUNE 9-14, 2019

## **Final Program**

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### ISPC24 - 24<sup>TH</sup> International Symposium on Plasma Chemistry - Naples (Italy) June 9-14, 2019

	TUESDAY June 11, 2019 (afternoon)				
	<b>ROOM GALATEA</b>	<b>ROOM DIONE</b>	<b>ROOM PERSEIDE</b>		
14:00	Chairs Pietro Favia - Rony Snyders	Chairs Anton Nikiforov - Alessandro Patelli	Chairs: Javad Mostaghimi - Gervais Soucy		
	<i>Marc Böke</i> Separated effects of plasma species and post- treatment on the properties of barrier layers on polymers O-52 (4)	Bram Wolf Elucidating the role of gas dynamics in the vortex-confined microwave plasma on CO2 dissociation efficiency O-56 (2)	<i>Masasya Shigeta</i> To simulate turbulent thermal plasma flows for nanopowder fabrication I-12 (5)		
14:15	<i>Annaëlle Demaude</i> Easy synthesis of hybrid hydrophilic- hydrophobic patterned surfaces by atmospheric plasmas O-53 (4)	<i>Georgi Trenchev</i> Atmospheric pressure glow discharge: design improvement based on modelling and <u>experiments</u> O-57 (2)			
14:30	Huidong Hou Effect of Precursor Chemistry on the microstructure of Ba(Mg1/3Ta2/3)O3 during Hybrid Suspension/Solution Precursor Plasma Spraying O-54 (4)	<i>Françoise Massines</i> Dual frequency DBDs or how to design an	Vittorio Colombo Design-oriented modelling for the synthesis of Cu nanoparticles by a RF thermal plasma: impact of quenching solutions, radiative losses and thermophoresis O-60 (5)		
14:45	Shota Nunomura Defect generation and annihilation in hydrogenated amorphous silicon during plasma treatment O-55 (4)	atmospheric pressure plasma for surface treatment I-11 (2)	<i>Yasunori Tanaka</i> Effect of Alternating Gas Injection on Temperature Fields in Reaction Chamber using Inductively Coupled Thermal Plasmas for Nanoparticle Synthesis O-61 (5)		
15:00	Maria Adriana Creatore	Javad Mostaghimi Advantages of the New Conical Torch for ICP Spectrometry O-58 (2)	<i>Alexander Ustimenko</i> Plasma Treatment of Biomedical waste O-62 (5)		
15:15	Plasma-assisted atomic layer deposition of highly conductive HfNx layers I-10 (4)	<i>Efe Kemaneci</i> A zero-dimensional modelling of a coaxial surface wave discharge in oxygen diluted with hexamethyldisiloxane for the deposition of SiOx films O-59 (2)	<i>Tae-Hee Kim</i> Reproduction of cosmic dust analogues by non-equilibrium condensation in triple DC thermal plasma jet system O-63 (5)		
15:30	Refreshment break (30 min)				
	ROOM GALATEA				
16:00	Chair: Romolo Laurita				
	3 min poster pitches - Session II				
	POSTER AREA				
16:45 19:00	Parallel poster sessions (1-2-4-7-8)				

### Plasmas for plant bio-engineering and in agriculture for resource recovery

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**Abstract:** We have used different low-temperature atmospheric pressure plasmas for direct or indirect treatment of plant tissue. The plasma sources were characterised in detail by using optical emission spectroscopy, mass spectroscopy and electrical probes. The influence of the plasma treatments on the plant cells was investigated through enzyme response, development of calli and process of somatic embryogenesis. Also, the effect of plasma treated water and plasma decontaminated water was followed through the process of seed germination.

Keywords: plasma agriculture, plant calli, plasma decontamination.

#### 1. Introduction

In the last decade the atmospheric pressure plasma systems have been extensively used in biomedical application [1-3]. Their construction and development was governed by the type of application and by the type of biological system that is treated. In parallel another field of plasma applications was growing - plasma agriculture. The first experiments were done with the low pressure nonequilibrium plasmas and primarily in treatments of seeds [4, 5]. Due to the fact that most seeds, plants, plants cells etc. cannot withstand vacuum, the devices that are nowadays mostly used are operating at atmospheric pressure. In such system, for example, the rich plasma chemistry changes the coat of the treated seed resulting in changes in wettability, better water uptake, increased percentage and speed of germination [6-8]. At the same time the pathogens that can be found on the seed coat and can be responsible for low germination percentage or contaminated plant are also destroyed during the plasma treatments. Therefore, unlike the classical methods involving different chemicals, plasma treatments can have a double or even multiple impact on the treated seeds.

As with the mammal cells, the interaction of the chemical species created in plasma and the triggered mechanisms are of the outmost importance. In the world of plants this can be done through investigation of the plasma treatments of the plant calli. In biological research and biotechnology the plant callus (pl. calli) is induced from plant tissue and it forms growing mass of plant parenchyma cells. The influence of the plasma created reactive oxygen and nitrogen species (RONS) and their interaction with calli can be investigated through the response of the cell enzymes. Puač et al. have shown that the interactions of the plasma created RONS with the plant cells can have even a long term influence [9].

Apart from the plasma treatments where plasma is in direct contact with seeds or plant cells like calli, there is a large group of experiments that investigate the influence of plasma treated water (plasma activated water – PAW) on theses specimens. It was shown that PAW used for

imbibition of the different types of seeds increases germination percentage and on the molecular level changes the enzyme activity level.

Another very important topic is the possibility of reusage of the water contaminated by agricultural means (pesticides, fertilization, biological farm waste etc.). Here we will present the results of applications of atmospheric pressure plasmas in direct treatment of plant seeds and calli or treatment of clean or contaminated water.

# 2. Application of atmospheric pressure plasmas in treatments of plant tissue and water used in agriculture

We have used several types of nonequilibrium plasma systems that operate at atmospheric pressure for direct treatments of plant calli, for treatment of water in order to produce PAW and for treatment of water contaminated with pesticides.



Fig. 1. Daucus carota callus

Pin geometry plasma sources used for these applications operate in the range of frequencies from kHz to MHz. These devices were used with helium as working gas and He gas flow was kept constant at 1 slm and 2 slm depending on the application. All plasma systems were characterised in detail by optical emission spectroscopy, mass spectroscopy and by using electrical probes.

The direct plasma treatment of plant calli was used to investigate the plasma cell interactions and to follow the response of the plant tissue several hours and days after the treatment. Some of the samples that were used were taken from the model plants (like carrot cells – see Fig. 1.) and others from the plants that have an issue that needs to be overcome. For example callus of the yellow irises fall in the second group with its inability to enter the process of somatic embryogenesis (SE).

The direct plasma treatments of calli of *Daucus carota* were performed in order to investigate if the process of SE can be triggered even in the conditions where it is disabled. This means that the ratio of the growth hormones (in particular Auxin) in the culture medium is set to keep out the plant cells from going into SE. The results of such treatments are shown in Fig. 2. We can see that even in the conditions where SE cannot be initiated, plasma treatment triggered this process and the number of formed somatic embryos is higher with longer treatment time.



Fig. 2. Number of somatic embryos in *Daucus carota* callus for untreated and treated samples.

In case of water treatment, we have used clean distilled water and water contaminated by pesticides for creation of PAW. Both types of treated samples were then used for imbibition of seeds and investigation of effects on germination percentage and enzyme response. In order to determine the amount of active RONS species the PAW and decontaminated water samples were also characterised in detail by using spectrophotometry, total organic compound, dissolved oxygen, pH and conductivity measurements.

#### **3.**Conclusion

Nonequilibrium plasmas have shown a lot of potential in applications in biotechnology and agriculture. We have used several types of atmospheric plasma sources for treatments of plant calli or clean/contaminated water that was used for imbibition of seeds or watering of plants. All the plasma devices were characterised in great detail and optimised depending on the type of the sample and application. In the direct plasma treatment of plant calli it was determined that plasma species interacting with plant tissue can serve as a trigger for process of SE, even when this process is blocked or conditions unfavourable. When used in treatments of water, RONS created in plasma and deposited in PAW increased the germination percentage of the imbibed seeds. Also, in the case when this water was contaminated by pesticides it was found that plasma treatments reduced harmful effect.

Acknowledgments: Supported by MESTDRS III41011 and ON171037.

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# Treatment of pesticide polluted water by atmospheric pressure plasma sources

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**Abstract**. In this work we present a method for purifying water contaminated with pesticides for further application in agriculture. For this purpose, a needle-type atmospheric pressure plasma jet (APPJ) was used, with electrode powered by a high voltage signal at frequency 330 kHz. We have used He as working gas with flow rate 2 slm. The solution of pesticide Malathion in distilled water was treated as contaminated sample. Optical emission spectroscopy was performed during liquid sample treatment. Pollutant concentrations in the samples were analysed and parameters of the chemical kinetics were obtained. Malathion destruction is described with the first order reaction. Then, the samples were used for radish seed imbibition. The results have shown that the plasma decontaminated water treatments have positive effect on germination of radish seeds.

### 1. Introduction

For more than a decade cold atmospheric pressure plasma have been successfully used in various types of biomedical treatments [1-3]. Studies performed within this field proved that non-equilibrium plasma is very versatile and efficient medium with complex dependence between its properties and controlling parameters as well as the interaction between plasma and treated surfaces. Research in the new field of plasma agriculture, which brings novel applications for APP, in the first place should study the key mechanisms underlying particular application in order to understand and control new processes [4]. One of the most important issues of modern agriculture is water pollution due to immense use of pesticides.

Thus, in our study we investigate application of cold atmospheric pressure plasma source for decontamination of water containing dissolved pesticide. Here, as an initial step, we present results of employment of atmospheric pressure plasma jet (APPJ) for the decontamination of aqueous solutions of pesticide Malathion.

### 2. Experimental

In Fig. 1 we show a schematic diagram of our experimental setup. Plasma source used for treatments is an atmosphere pressure plasma jet (APPJ) which consists of a metal cylindrical case, glass tube, with the inner and outer diameters of 4 mm and 6 mm, respectively, with

concentrically placed powered electrode. The electrode was made of stainless steel wire with the diameter of 1 mm. The end of the wire is sharpened and it is extending for 3 mm from the ceramic insulation into the glass tube. A commercial high voltage RF generator working at frequency of 330 kHz is used as a power source. In all treatments He was used as a working gas with flow rate of 2 slm. The experimental setup is similar to the one described in [5].



Fig. 1 Schematic overview of the experimental set up.

The samples containing Malathion were treated in the wells of 6-well microtitter plate. The volume of treated solution of Malathion in the well was 4 ml and initial concentration was 500 ppm in distilled water. Treatment times were 5 and 10 minutes. At the bottom of the micro titter plate copper tape is glued and connected to the ground through a 1 k $\Omega$  resistance for monitoring the current passing through the plasma. The distance between the surface of the liquid in the plate and wire was 10 mm. Optical emission spectroscopy is performed by using a UV-VIS lens positioned above the microtitter plate (as shown in Fig. 1), a fiber and spectrometer (Shamrock 750). Analysis of the liquid samples are accomplished in HPLC measurements, determining the area below the peak corresponding to Malathion.

### 3. Results and Discussion

In order to study the pollutant degradation process induced by plasma we performed characterization of plasma and liquid samples that are treated with the APPJ. Monitoring of the current through the plasma allowed us to continuously check the treatment conditions. Since we had the values of  $I_{RMS} = 5 \ \mu A$  in all treatments, we had stable plasma conditions. To reveal what kind of excited species we produce in plasma, we employed optical emission spectroscopy measurements. The lens was positioned in such way that its viewing angle contained the plasma plume and the interface volume between plasma and the liquid surface.



Fig. 2 Optical emission spectrum of APPJ with 2 slm of He as working gas recorded while operating against water sample contaminated with 500 ppm of Malathion.

In Fig. 2 we show emission spectrum taken at treatment conditions in wide range of wavelengths – from 290 nm to 800 nm. The spectrum is recorded in time-integrated manner with exposition time of 500 ms. Lines with the highest intensities are designated in the plot. Overall, the highest intensity lines belong to excited Nitrogen molecules, particularly the Second Positive System (SPS). Then, the lines of the First Negative System (FNS) of Nitrogen ion follow in the intensity scale. Strong Oxygen atom line at 777 nm is also visible suggesting the existence of high concentration of Oxygen atoms. These atoms are produced in the plasma is several dissociation channels [6]. Therefore, both atomic Oxygen species and probably some Nitrogen species are present in the plasma above the liquid [7]. Three He lines are also visible although their intensity is much lower in comparison to Nitrogen and Oxygen lines. Low-intensity OH (A-X) band (306-309 nm) can be also found in the spectrum. This band originates mostly from excited OH radicals formed after molecules of water vapour dissociation [8].

Fig. 3 shows data of measured Malathion decomposition in liquid samples treated by the APPJ. The initial concentration in these measurements were  $C_0=10$ ppm and the evaluation of concentrations C after treatments of 1 min, 5 mins and 10 mins was performed from the chromatographic peak area of Malathion peak. In Fig.3b) the relative concentration values are plotted in semi-logarithmic scale and fitted with linear fit. Therefore, Malathion destruction process can be defined with the first order reaction with R<sup>2</sup>=0.989. From the fit we obtained parameters of the chemical kinetics k=0.5 min<sup>-1</sup> and T<sub>1/2</sub>=1.4 min.



**Fig. 3** Change in the relative concentration of Malathion after different treatment times: a) in linear scale of concentrations, b) in semi-logarithmic scale with linear fit (red line).

Treated contaminated water samples were used for imbibition of radish seeds. The 40 seeds were placed in Petri dishes and they were imbibed with 2 ml of liquid per Petri dish (5 cm in diameter). The dishes with the seeds were left in a room with constant temperature and with day-night cycle. For the control samples, we used seeds imbibed with distilled water and solution of Malathion (500ppm). All experiments were done in triplicate.



**Fig. 4** Mean values of radish seeds germinated after 18 hours of imbibition with different water samples. dH2O – distilled water, distilled water contaminated with 500 ppm Malathion, MD5 – contaminated water treated 5 minutes, MD10 – contaminated water treated 10 minutes.

In Fig. 4 we show histograms of mean value of germinated radish seeds (left hand-side axis) and germination percent (right hand-side axis) 18h after seed imbibition. Comparison between control groups showed that the number of germinated seeds imbibed with distilled water is almost twice as higher than the number of seeds germinated after imbibition by Malathion solution. As for the seeds imbibed with plasma decontaminated water, we can see the positive effect of longer plasma treatment of water polluted by Malathion. More precise, the results on plasma treated samples show that in this case duration of treatment of water polluted by Malathion significantly affects germination. While the set imbibed with solution treated for 5 mins is almost the same as the Malathion sample with the germination below 40%, the sample treated for 10 mins has the germination of almost 60%, i.e. the value which is 1.5 times higher. However, even after 10 mins of plasma treatment these seeds still have germination lower than 70% which is the value obtained with seeds imbibed with distilled water. Nevertheless, it is clear that seeds imbibed with plasma treated samples have higher germination percent than the seeds imbibed with contaminated water.

### 4. Conclusion

We conducted a research aiming to explore the possibility of utilization of atmospheric pressure plasma for decontamination of water polluted with organic pollutants. As the first step, we choose to target pesticide Malathion dissolved in distilled water. The liquid samples were treated by Helium APPJ while performing electrical and optical diagnostics. The optical emission spectrum showed existence of nitrogen and oxygen reactive species and small concentrations of OH radicals. Measurements of pollutant concentrations before and after treatments showed that destruction process can be fitted with first order reaction. Finally, radish seeds were imbibed with plasma treated samples. Results of germinated seeds compared to the case of seed imbibition with Malathion polluted water. This proves that plasma treatments can purify water and cause decomposition of pollutant molecules to the extent suitable for the plasma treated water to be reused for plant cultivation. However, in order to achieve efficient process, one need to investigate decomposition mechanisms triggered by plasma treatment and the influence of treated solution on seed physiological processes.

### Acknowledgments

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29<sup>th</sup> Summer School and International Symposium on the Physics of Ionized Gases

Aug. 28 - Sep. 1, 2018, Belgrade, Serbia

# **CONTRIBUTED PAPERS** &

### ABSTRACTS OF INVITED LECTURES, TOPICAL INVITED LECTURES, PROGRESS REPORTS AND WORKSHOP LECTURES

Editors: Goran Poparić, Bratislav Obradović, Duško Borka and Milan Rajković



Vinča Institute of Nuclear Sciences



Serbian Academy of Sciences and Arts

### CONTRIBUTED PAPERS & ABSTRACTS OF INVITED LECTURES, TOPICAL INVITED LECTURES, PROGRESS REPORTS AND WORKSHOP LECTURES

of the 29<sup>th</sup> Summer School and International Symposium on the Physics of Ionized Gases

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### 2. EXPERIMENTAL SETUP

The Fig. 1 shows a schematic diagram of the experimental setup. Plasma source was an atmosphere pressure plasma jet which consists of a metal cylindrical body, glass tube, with the inner and outer diameters of 4 mm and 6 mm, respectively, and concentrically placed electrode with ceramic insulation. The electrode was made of stainless steel wire with the diameter of 1 mm. The end of the wire (powered electrode) is sharpened and it is protruding for 3 mm from the ceramic insulation into the glass tube. As power source we have used a commercial high voltage RF generator working at frequency of 330 kHz. In all experiments He was used as a working gas with flow rate of 2 slm.



Figure 1. Schematic overview of the experimental set up.

The samples containing Malathion were treated in the wells of 6-well microtiter plate. The volume of treated solution of Malathion in the well was 4 ml and initial concentration was 500 ppm in distilled water. Treatment times were 5 and 10 minutes. At the bottom of the micro titter plate we glued copper tape that was connected to the ground through a 1 k $\Omega$  resistance. The distance between the surface of the liquid in the plate and wire was 10 mm.

### **3. RESULTS AND DISCUSSION**

Treated solutions as well as distilled water and Malathion contaminated solution were used for the imbibition of maize and radish seeds in Petri dishes, with 12 and 40 seeds, respectively in each dish. The seeds were imbibed with 2 ml of liquid per Petri dish (5 cm in diameter). The dishes with the seeds were

left in a room with constant temperature and with day-night cycle. All experiments were done in triplicate.

For the control samples, we used seeds imbibed with distilled water and solution of Malathion (500ppm). Histogram shown in Fig. 2 presents mean value of germinated maize seeds four days after imbibition. Comparison between control groups showed that number of germinated seeds imbibed with distilled water is more than twice higher than number of seeds germinated after imbibition by Malathion solution. As for the seeds imbibed with plasma decontaminated water, we can see the positive effect of plasma treatment of water polluted by Malathion. The number of germinated seeds watered with the solutions treated for 5 minutes and 10 minutes is higher 1.5 times than in the untreated Malathion solution. Mean values in both sets of seeds imbibed with decontaminated water are the same (around the value 5) within the error bar. Nevertheless, it is still lower than the control group imbibed with distilled water where the mean value is 7.3.



**Figure 2.** Mean values of maize seeds germinated after 4 days of imbibition with different water samples.  $dH_2O$  – distilled water, distilled water contaminated with 500 ppm Malathion, MD5 – contaminated water treated 5 minutes, MD10 – contaminated water treated 10 minutes.

Similar results are obtained in the case of germination of radish seeds. Fig. 3 shows mean values of germinated radish seeds 18 hours after imbibition. In this case, values in control groups with  $H_2O$  and 500ppm Malathion have difference of 1.75 times. However, the results on plasma treated samples show that in this case duration of treatment of water polluted by Malathion significantly affects germination. While the set imbibed with solution treated for 5 mins is almost the same as the Malathion sample (mean value around 15.5), the sample treated for 10 mins has the value which is 1.5 times higher.



**Figure 3.** Mean values of radish seeds germinated after 18 hours of imbibition with different water samples.  $dH_2O$  – distilled water, distilled water contaminated with 500 ppm Malathion, MD5 – contaminated water treated 5 minutes, MD10 – contaminated water treated 10 minutes.

### 4. CONCLUSION

Results of germination of seeds imbibed with plasma decontaminated water showed increase in number of germinated seeds compared to the case of seed imbibition with Malathion polluted water. This proves that plasma treatments can purify water and cause decomposition of pollutant molecules to the extent suitable for the plasma treated water to be reused for plant cultivation. However, in order to achieve efficient process, one need to investigate decomposition mechanisms triggered by plasma treatment and the influence of treated solution on seed physiological processes.

### Acknowledgements

This research is supported by the Serbian Ministry of Education, Science and Technological Development under project numbers ON171037 and III41011.

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### Atmospheric Pressure Plasma Treatment and Decontamination of Water Samples (invited)

N. Skoro, N. Puac, A. Kumar, O. Jovanovic, A. Petrovic (Institute of Physics Belgrade), U. Cvelbar (Jozef Stefan Institute), and Z. L. Petrovic (Serbian Academy for Sciences and Arts, School of Engineering, Ulster University)

### Abstract Text:

As water scarcity becomes widespread concern in many countries, new approaches for water processing are being considered. In order to have the potential to be applied in the industry, these new methods should be primarily environmentally friendly and with low-energy consumption. Employment of non-equilibrium plasma for water treatment entirely satisfies these two points and therefore makes plasma a good candidate. Non-equilibrium (or cold) plasma at atmospheric pressure has so far been successfully used in various applications related to biology and medicine. Plasma rich-chemistry environment produced at room atmosphere with ambient temperature enabled treatment of cells, plants, bacteria, tissues etc. with aims ranging from destruction of pathogens to healing or enhancing the growth in biological systems. Therefore, these applications clearly point out that plasma sources can deliver broad spectrum of treatment conditions.

The latest research direction related to plasma and liquid treatment is plasma agriculture where different approaches for application of plasma in agricultural processes are investigated. Within these novel research area we investigate two possible applications: for the treatment of clean water samples for the production of plasma activated water (PAW); and for decontamination of polluted water containing organic micro pollutants (OMPs). PAW in comparison to clean water is rich in reactive oxygen and nitrogen species (RONS) and this proves to be an important asset when applied to seeds and plants. We showed that germination and plant growth can be enhanced when PAW is applied for seed imbibition and plant watering. On the other hand, the presence of reactive oxygen species in plasma and inside the treated water samples (especially droplets or aerosols) induces the decomposition of different molecules of OMPs. We demonstrated ability of plasma decontamination for several different organic molecules, such as decomposition of Malathion in atmospheric pressure plasma jet with high efficiency, and also for some chemicals used as chemical warfare surrogates. Apart from direct treatment of polluted samples by plasma, we have investigated a possibility of using PAW as a decontamination chemical to decompose organic dye Acid Blue 25 dissolved in water. Along the line of plasma agriculture research we combined the effects of two plasma applications in the plasma processing of agricultural waste water for reuse in irrigation. The experimental results showed that pesticide-containing polluted water can be decontaminated and at the same time enriched with RONS that positively influence germination of maize and radish.

These successful applications unfold many questions related to the plasma properties, plasma gas and liquid phase chemical reactions, an entangled connection between plasma produced reactive species and their chemical interactions with organic molecules in water. In order to make a detailed insight into the treatment process, we performed comprehensive diagnostics of the plasma and of the liquid samples. Our results provide information about electrical and optical plasma properties and make connection with physical parameters of the liquid sample (pH, electrical conductivity). We used colorimetric methods to determine RONS in the treated liquids. To acquire information about plasma-induced decomposition and obtain by-products in the treated samples we performed liquid chromatography coupled with mass spectrometry. All these results provide important knowledge on plasma water treatments and represent another step towards understanding which are the best parameters for treatment monitoring and techniques for up-scaling plasma devices to treat large amounts of water.

Acknowledgement: This study was partially supported by NATO SPS 984555, projects ON141037 and III 41011 of MESTD Republic of Serbia and H2020-MSCA-ITN 812880 Nowelties.

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08P-12	A Home-Made Langmuir Probe for Time-Resolved Measurement on HIPIMS Copper Deposition <sup>12</sup> Kam-Hong Chau, <sup>34</sup> Yoshinobu Kawai, <sup>2</sup> Chi-Wai Kan, <sup>13</sup> Jia-Lin Syu, <sup>13</sup> Yen-Chun Liu, <sup>13</sup> Ying-Hung Chen, <sup>3</sup> Chen-Jui Liang and <sup>13</sup> Ju-Liang He <sup>1</sup> Feng Chia University <sup>2</sup> The Hong Kong Polytechnic University <sup>3</sup> Feng Chia University <sup>4</sup> Kyushu University
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### The effects of plasma discharge regime on production of reactive species in water

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### 1. Introduction

Knowledge of the composition of active species generated in low temperature plasmas is of crucial importance for new biomedical and chemical applications [1]. Plasma activated water (PAW) is a major area of interest within the field of plasma agriculture. A number of researchers have reported that PAW, containing mainly species. wide variety reactive have of applications such as increasing the germination percentage of treated seeds, decontamination and sterilization of food products etc. PAW can also ecological alternative method be an for fertilization, decontamination and modification of soil [2].

Here we will present the electrical characterization and optical emission spectroscopy (OES) of an atmospheric pressure plasma jet (APPJ) that can operate in two different discharge regimes and it is employed for treatments of water samples and PAW production.

### 2. Experimental Setup

Plasma treatments of distilled water were carried out using an APPJ in a pin-electrode configuration with different flow rates of He as working gas.

The water samples were placed below APPJ powered by a continuous kHz sine signal and treated for 5, 10 and 20 min. OES of the plasma above the sample surface was performed during water treatment. To assess concentrations of long lived reactive species formed in the liquid phase we used a colorimetric method.

### 3. Results and Discussion

Fig. 1. presents concentrations of long lived reactive species existing in PAW after 20 min

treatment. In case of helium flow of 1 slm plasma plume was formed in air above the water sample (histogram left side). The right side of histogram shows results for regime when plasma was in contact with water (He 2slm). As can be seen from the Fig. 1. there was a significant difference in hydrogen peroxide concentrations, but almost same amount of nitrogen reactive species was acquired.



Fig. 1 Concentrations of hydrogen peroxide, nitrate and nitrite in PAW samples treated for 20 minutes for two different He flow rates.

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### **Book of Abstracts**

### 1st annual meeting of the MD-GAS COST Action

organized in the framework of the COST Action CA18212 "Molecular Dynamics in the GAS phase"



18<sup>th</sup> - 21<sup>st</sup> February 2020 Caen, France

### About MD-GAS

Emerging highly advanced ion-beam traps and storage rings combined with synchrotrons, Xray facilities, and high performance computers offer completely new ways to study Molecular Dynamics in the GAS phase (MD-GAS). Cryogenic traps and rings will allow studies of decay and reaction processes involving molecular ions in well-defined conformations and in single or narrow ranges of quantum states.

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09:40-10:00	High radiative cooling rates of small clusters	P Ferrari
10:00-10:20	The stability of the smallest carbon cluster dianion: $C_7^{2-}$	P Najeeb
10:20-11:00	Coffee break	
11:00-11:30	Working Group 3 Kick off Meeting - M. Alcamí	
11:30-12:00	Ion-collision induced reactivity in molecular clusters	P. Rousseau
12:00-12:30	Gas-phase molecules through the lens of time-resolved photoelectron spectroscopy	A. Ponzi
12:30-13:00	Interaction of low energy electrons with biomolecules and clusters of biomolecules	J. Kocisek
13:00-14:30	Lunch at the GANIL restaurant	
14:30-15:00	Highly charged helium nanodroplets	M. Gatchell
15:00-15:30	<i>Creation and destruction of chemical species in liquids</i> <i>treated by atmospheric pressure plasmas - from gas</i> <i>phase chemistry to bulk liquid</i>	N. Skoro
15:30-16:00	Resonant Inelastic X-ray scattering of chloromethanes	M. Zitnik
16:00-16:30	Elastic electron scattering on molecules in the gas phase in the middle energy range	J. Maljković
16:30-17:30	Coffee break	
16:30-17:30	Laboratory visit	
19:00-21:30	Conference diner - Café Mancel, le Château Ducal, Caen	

### CREATION AND DESTRUCTION OF CHEMICAL SPECIES IN LIQUIDS TREATED BY ATMOSPHERIC PRESSURE PLASMAS - FROM GAS PHASE CHEMISTRY TO BULK LIQUID

### N. Škoro<sup>(a)1</sup>, N. Puač<sup>(a)</sup>, O. Jovanović<sup>(a)</sup>, A. Petrović<sup>(a)</sup>, Z. Lj. Petrović<sup>(b)</sup>

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Large number of recent studies are investigating operation of cold atmospheric pressure (CAP) plasmas in contact with liquids. This is a continuation of the research related to biomedical applications where CAP has proved its excellent potential for sterilization and cleaning of both living tissues and inorganic materials from pathogenic microorganisms [1]. Applications of CAP use chemically reactive gaseous environment that contain reactive oxygen and nitrogen species such as •OH, •NO, H2O2, NO2-, NO3-, HNO3 etc. These species produced in CAP, which is in contact with the liquid, can penetrate and react with molecules in a bulk liquid modifying its physical and chemical properties [2]. This interaction goes through the interfacial region located between the gaseous plasma and a bulk liquid where many important processes involving short-lived species occur. As a result, the treated liquid is activated or, in case of polluted water, decontaminated by plasma [3]. However, in many cases specific plasma-liquid interactions behind the achieved positive results are elusive due to unknown processes in the interfacial region.

Here we will present results of laboratory-scale studies using different plasma source configurations that aim to induce decontamination of polluted water and/or activation of clean water. In all experiments we used plasma jets powered by a continuous kHz signals with the liquid samples placed below the jets. We will show results of detailed plasma diagnostics as well as measurements of basic physico-chemical properties of treated samples in order to reveal the influence of the plasma treatment. Special attention will be devoted to the possibility of assessing reactions in the interfacial region in order to clarify important reactions which exist in the particular treatments.

Acknowledgement: This work is supported by projects ON171037 and III41011 of the MESTD, Republic of Serbia.

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### Plasma treatment of liquids and applications in agriculture

<u>N. Škoro<sup>1</sup></u>, N. Puač<sup>1</sup>, O. Jovanović<sup>1</sup>, G. Malović<sup>1</sup>, Z. Lj. Petrović<sup>1,2</sup>

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As recent investigations in non-equilibrium atmospheric pressure plasma field are directed towards different applications in biology, agriculture and food industry, many new challenges emerge. In this work we aim to examine properties of a plasma treated water and its further influence on biological samples within the scope of plasma agriculture applications of atmospheric pressure plasma jets. We used two configurations of plasma jets for treatments of pure distilled water and water contaminated with dissolved pesticides. The jet parameters were varied and we measured physico-chemical properties of the treated liquid samples. Moreover, we used the treated samples for imbibition of commercially used plant seeds and then investigated their germination.

#### 1. Introduction

With expansion of the field of non-equilibrium low temperature plasmas to atmospheric pressure sources, their application domain has grown immensely. In the last 20 years, development of new plasma sources operating at atmospheric pressure has been mostly related to the new biomedical applications such as wound healing, cancer treatment as well as sterilization and treatment/production of biocompatible materials [1,2]. Since low temperature plasmas are environmentally friendly and the active gaseous environment is at room temperature, recent investigations are directed towards different aspects of plant biology, agriculture and food industry [3].

Although investigations in these fields so far proved that there is a great potential for application of atmospheric pressure plasma (APP) sources, what also became known is that complexity of the processes in the whole plasma-treated target system is immense thus making a large obstacle in studying the mechanisms of interaction between plasma and target of interest.

#### 2. Results and Discussion

In this work we aim to examine results of a plasma treatment of liquid and its further influence to biological samples within the scope of plasma agriculture applications. Treatments of pure distilled water and water contaminated with dissolved pesticides were performed by using a plasma jet. In the study we used two configurations of APP jets powered by a continuous kHz signal and operated with He and Ar as working gases. After the procedure. we established physico-chemical properties of the liquid sample, e.g. by measuring concentrations of nitrite ions, nitrate ions and hydrogen peroxide by using a colorimetric method.



Fig. 1. Reactive species concentration in water sample contaminated with 500 ppm of Malathion after 5 mins treatment by pin-electrode jet.

In Fig. 1 we show concentrations of reactive species obtained after 5 min treatment of Malation spiked water sample by a pin-electrode jet. Depending on the working gas, H<sub>2</sub>O<sub>2</sub> concentrations differ by an order of magnitude while nitrites and nitrates show completely different behaviour. Therefore, it is obvious that changing the working gas produced different reactive species in the liquid. This proved to be of great importance since the treated samples were used for imbibition of commercially used plant seeds and a follow-up of their germination process. Within the framework of plasma agriculture, changes in the properties of treated liquid samples could play essential role when successful and efficient treatment of pure or contaminated water is expected. Moreover, as reactive species produced in the plasma treatment are also biologically significant molecules important for functioning of plant cells their mutual balance is also important. Therefore, the influences of plasma parameters, properties of plasma treated sample and of the biological target are all intertwined in particular plasma treatment. Only a detailed knowledge of all parameters and mechanisms could provide a prosperous result for the particular application in plasma agriculture field.

*This research has been supported by MESTD Republic of Serbia, under projects III41011 and ON171037.* 

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# 46th EPS Conference on Plasma Physics (EPS 2019)

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Milan, Italy 8-12 July 2019

Part 1 of 2



### 11.304 Influence of the atmospheric pressure plasma source configurations on the properties of treated liquid samples

Monday, July 8, 2019 6:00 PM (30 minutes)

See the full abstract here http://ocs.ciemat.es/EPS2019ABS/pdf/I1.304.pdf

In recent years, expansion of non-equilibrium plasma applications is directed towards plasma sources operating at atmospheric pressure that are used for treatment of liquids. Usually, different applications involving liquid targets have different aims and, as precondition for all these applications, it is important to make the plasma processes as efficient as possible in every specific case. Therefore, these tasks are demanding due to the complexity of plasma chemistry, which depends on the type of plasma source and is further tangled by the presence of liquid target. Here we will present results of a laboratory-scale study aiming to make comparison between different plasma source configurations and to reveal their influence on treated pure and contaminated water samples. Two-level approach is necessary: on one side one should characterize the plasma used for treatments while, on the other side, properties of the liquid samples should be obtained. Detailed discharge diagnostics involving optical emission spectroscopy and electrical characterisation will provide information on plasma conditions for particular source. Emission spectrum provide information on excited species produced in the gas phase. Measurement of electrical signals allow to calculate power input provided to the system and thus establish a parameter describing the plasma. Additionally, certain physicochemical properties of the treated liquids (pH, dissolved Oxygen content, conductivity, total organic carbon content in contaminated samples etc.) will be obtained allowing to cross reference data with plasma characterization and give an insight into interaction chemistry of the specific plasma source used for liquid treatment. Results regarding the influence of different plasma source configurations to the treated liquid will be presented in the context of possibility of applications in the field of plasma agriculture (PAW, water decontamination etc.).

pppo

Presenter: ŠKORO, N. (EPS 2019) Session Classification: LTPD Srpsko hemijsko društvo



### 56. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA

# KRATKI IZVODI RADOVA

56<sup>th</sup> MEETING OF THE SERBIAN CHEMICAL SOCIETY

**Book of Abstracts** 

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### HZS P 1

# Identifikacija degradacionih produkata malationa nastalih primenom plazme na atmosferskom pritisku

Hemija životne sredine / Environmental Chemistry

<u>Ivana V. Matić Bujagić</u>, Svetlana D. Grujić, Olivera J. Jovanović\*, Nikola D. Škoro\* Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Karnegijeva 4, Beograd \*Institut za fiziku, Univerzitet u Beogradu, Pregrevica 118, Beograd

U ovom radu opisan je razvoj instrumentalne metode za određivanje proizvoda degradacije organofosfatnog pesticida malationa. Za razgradnju malationa u cilju dekontaminacije poljoprivrednih otpadnih voda koje se potom mogu ponovo koristiti za zalivanje, primenjen je izvor plazme na atmosferskom pritisku - plazma mlaz. Polazni rastvor malationa i uzorci tretirani plazma mlazom su analizirani korišćenjem LTQ XL linearnog jonskog trapa, kao masenog spektrometra. Na osnovu rezultata MS<sup>n</sup> analize odabrane su reakcije fragmentacije dobijenih degradacionih produkata malationa. Uz tečno-hromatografsku analizu, ove reakcije su zatim korišćene za identifikaciju i praćenje malationa i odabranih produkata degradacije u tretiranim uzorcima. Kao dominantni produkti razgradnje identifikovani su dietil-2-merkaptosukcinat (m/z 229), kao i malaokson (m/z 315) koji se dalje degraduje u dimetilfosfonat (m/z 111). Takođe je utvrđeno postojanje degradacionih proizvoda (m/z 127, 273 i 293) koji su prisutni u manjem obimu. Na osnovu dobijenih rezultata predložen je put razgradnje malationa i nastanak degradacionih prozvoda.

Zahvalnica: Ovaj rad je finansijski podržan od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekti: ON 172007, ON 171037 i III 41011).

# Identification of malathion degradation products produced by atmospheric pressure plasma

<u>Ivana V. Matić Bujagić</u>, Svetlana D. Grujić, Olivera J. Jovanović<sup>\*</sup>, Nikola D. Škoro<sup>\*</sup> Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade \*Institute of Physics, University of Belgrade, Pregrevica 118, Belgrade

This paper describes the development of an instrumental method for determination of degradation products of organophosphate pesticide malathion. For degradation of malathion, an atmospheric pressure plasma jet was applied, for the purpose of decontamination of agricultural wastewater, which can then be re-used for watering. Initial malathion solution and samples treated with atmospheric pressure plasma were analyzed using the LTQ XL linear ion trap as a mass spectrometer. Based on the results of MS<sup>n</sup> analysis, fragmentation reactions of obtained malathion degradation products were selected. Using liquid chromatography, these reactions were then used to identify and track malathion and selected degradation products in the treated samples. The dominant degradation products were identified as diethyl-2-mercaptosuccinate (m/z 229), and malaoxon (m/z 315), which further degrades to dimethyl phosphonate (m/z 111). Additional degradation products (m/z 127, 273 and 293), present to a lesser extent, were also determined. Based on the obtained results, the pathway of malathion degradation and formation of degradation products was proposed.

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Abstract: S01.00027 : Tracing Plasma Produced Atomic and Molecular species from Plasma into the Liquid and Living tissue for various applications

 

Preview Abstract

 Abstract >

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Nevena Puac (Institute of Physics, University of Belgrade Serbia)

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Significant effects observed in applications of atmospheric pressure non-equilibrium plasmas have been shown to be due to the effect of plasma produced atomic and molecular reactive species. Some of those species are the ones acting as signaling agents initiating response of the living cells. At the same time, albeit in larger numbers, they may be chemical agents that can damage or dissociate unwanted living organisms, human cells or chemical agonts that can damage or dissociate unwanted living organisms, human cells or chemical agonts that can damage or enzymes regulations and molecular physics starting from their formation, their passage into living cells and the passage into living cells or the reaction of cells that they invoke. Two exampless will be the long term changes in enzymes regulating hydrogen peroxide in plasm cells and destruction of malation, a pesticide used in agriculture that may be a model of more lethal weapons of mass destruction. Finally we shall illustrate how presence of those active species in plasma treated water affects the germination of seeds. -/abstract-Authors Zoran Lj Petrovic, Nikola Skoro, Suzana Zivkovit/(c), Milica Milutinovic, Olivera Jovanovic, Nenad Selakovic,

# 8<sup>th</sup> Central European Symposium on Plasma Chemistry

26<sup>th</sup> to 30<sup>th</sup> May 2019, Gozd Martuljek, Slovenia

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## Production of reactive species in pure and polluted water treated by atmospheric pressure plasma

### O. Jovanović (1), N. Škoro (1), N. Puač (1) and Z. Lj. Petrović (1, 2)

(1) Institute of Physics, University of Belgrade, Belgrade, Serbia

(2) Serbian Academy of Sciences and Arts, Belgrade, Serbia

Recent studies deliver wider knowledge on the role and significance of reactive oxygen and nitrogen species (RONS) that lead to their new chemical and biological applications and, at the same time, make a demand for development of new methods to generate them. Numerous research show that atmospheric pressure plasma can be used to efficiently produce numerous aqueous reactive species in plasma treated water. In the studies involving the influence of plasma treated water on biological samples researchers demonstrate that hydrogen peroxide as well as nitrite and nitrate play an important role in biological effects. Therefore, it is suggested that quantitative analysis of the above species should be related to the plasma source characterization in terms of the evaluation of the biological activity of liquids treated with atmospheric pressure plasma source.

In this work we have used an atmospheric pressure plasma jet to produce nitrate and nitrite ions and hydrogen peroxide in liquid samples. The plasma source used in the experiments was a pin-electrode jet with He as working gas with different flow rates. The treatments of pure distilled water and water contaminated with dissolved pesticides were performed. The liquid samples were placed below the plasma source powered by a continuous kHz signal and treated for different treatment times. After treatments, the physicochemical properties of the treated samples were measured. Additionally, we measured concentrations of nitrite ions, nitrate ions and hydrogen peroxide generated by the discharge plasma in exposed water solutions. This was done by using a colorimetric method with test strips. The chemical analysis of aqueous solutions after treatments show that creation of RONS in pure and polluted water is different, i.e. that the treated liquid composition is affecting the RONS production. The existence of hydrogen peroxide and nitrite ions was observed in all samples, but nitrate ions were detected only in clear treated water. Additionally, results show that increase in concentrations of nitrite ions and nitrate ions depends on the duration of the treatment.

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# 7TH INTERNATIONAL CONFERENCE ON PLASMA MEDICINE



JUNE 17-22, 2018



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# Book of Abstracts

ICPM7 June 18-22, 2018 Drexel University Philadelphia

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# Atmospheric pressure plasma decontamination of water polluted by organophosphates used in agriculture

N. Škoro<sup>1</sup>, N. Puač<sup>1</sup>, O. Jovanović<sup>1</sup>, G. Malović<sup>1</sup>, Z. Lj. Petrović<sup>1,2</sup>

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In biomedicine, atmospheric pressure plasmas (APP) have proved their excellent potential for sterilization and cleaning of both living tissues and inorganic materials from pathogenic microorganisms [1]. Moreover, large number of recent studies are investigating operation of APP in contact with liquids. Results show that chemically reactive gaseous environment produced by plasma sources can influence and modify physical and chemical properties of liquids [2]. As a result of the knowledge acquired in previous studies the investigation of APP now widens to a new emerging research field - plasmas in agriculture, where novel applications for APP appear.

Nowadays, one of the biggest environmental problems is water pollution with contemporary agriculture techniques as one of the main sources causing the pollution of surface waters. Organic micropollutants, originating from immense use of pesticides in agriculture production, require special chemical or biological treatments for water purification, again using environmentally hazardous substances. Our idea is to employ APP for decontamination of water polluted by pesticides, which is by now successfully used is warfare applications [3]. As a first step, we conducted a study on decontamination of water samples polluted with different pesticides, i.e. organophosphate compounds, by using an atmospheric pressure plasma jet (APPJ) operating with He as working gas. The plasma jet was powered by a continuous kHz signal source. Liquid samples placed below the APPJ were treated for different duration times, different sample volumes and different water contamination levels. Optical and electrical characterization of the APPJ was performed in order to obtain information about stability of the treatment conditions and the plasma properties. Before and after the treatment liquid samples were analyzed by spectrophotometric techniques, high performance liquid chromatography (HPLC) and liquid chromatography coupled with mass spectrometry (LC-MS) in order to follow degradation of organophosphates. Significant and efficient degradation of pesticides is noticed in all cases and appearance of degradation products is observed in the liquid sample. Thus, we could also evaluate toxicity of produced byproducts. From measurements of parent molecule degradation we established dependence of the decontamination efficiency on treatment time. Having in mind the possibility of reuse the decontaminated water in agriculture, we also investigated the influence of treated water on seed germination.

This work was supported by projects ON171037 and III41011, MESTD, Serbia.

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На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

### УВЕРЕЊЕ

**Јовановић (Јанко) Оливера**, бр. индекса 2018/8015, рођена 12.08.1994. године, Београд, Савски венац, Република Србија, уписана школске 2021/2022. године, у статусу: самофинансирање; тип студија: докторске академске студије; студијски програм: Физика.

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## У*В Е Р Е Њ Е*

### Оливера Јовановић

име једної родишеља Јанко, ЈМБГ 1208994715252, рођена 12.08.1994. їодине, Беоїрад, ойшшина Беоїрад-Савски Венац, Рейублика Србија, уйисана школске 2013/14. їодине, дана 27.09.2017. їодине завршила је основне академске сшудије на сшудијском йроїраму Примењена и комйјушерска физика, у шрајању од чешири їодине, обима 241 (двесша чешрдесеш један) ЕСПБ бодова, са йросечном оценом 9,18 (девеш и 18/100).

На основу наведеног издаје јој се ово уверење о стеченом високом образовању и стручном називу Дипломирани физичар.

Декан Проф. др Јаблан Дојчиловић



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# У*ВЕРЕЊЕ*

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Датум	Продекан за науку Физичког факултета	
29.09.2021	Curjegueslel	•
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