

Non-thermal plasma - liquid interactions and their environmental, biomedical, and agriculture applications

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Acknowledgments



EU NextGenerationEU



SLOVAK RESEARCH
AND DEVELOPMENT
AGENCY



European Space Agency



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Plasma applications
for smart and
sustainable agriculture



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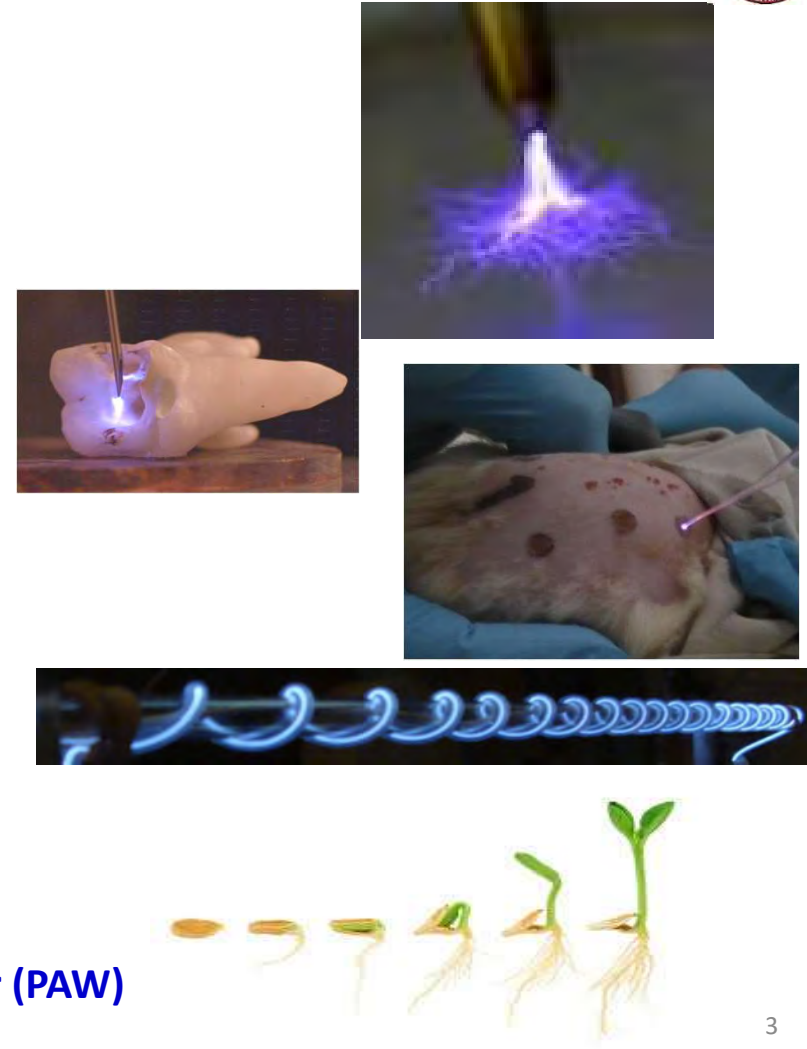
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Medicine

+ Slawomir Moritz, Proline Solutions, Austria



Background & motivation

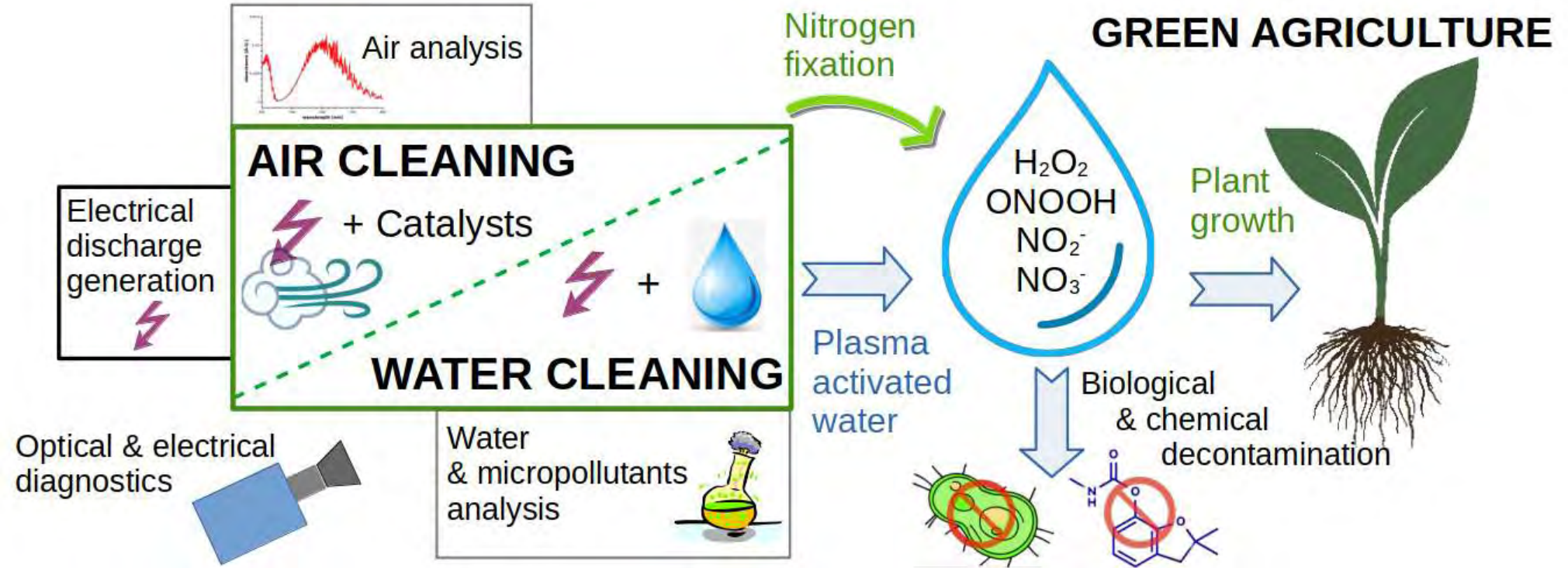
- **New biomedical - agriculture/food applications** of atmospheric pressure **low-temperature (cold) plasmas**
- **Decontamination / sterilization**
 - Water, surfaces, medical instruments, air, living tissues
 - Applicable for thermo-sensitive materials
 - Efficient on planktonic bacteria, spores, biofilms
- **Therapeutic effects** in tissues/cells – **Plasma medicine**
 - Dentistry (root canal, caries, tooth whitening)
 - Wound healing, skin diseases
 - Cancer treatment
- **Plasma agriculture and food applications**
 - Food decontamination (fruits/vegetables, nuts, juices, milk)
 - Enhanced seed germination, plant growth promotion
 - Nitrogen fixation
- **Direct plasma treatments** vs. **indirect** via **plasma-activated water (PAW)**





Motivation: plasma-liquid environmental applications

(our group research focus)



- Direct plasma treatments - indirect plasma-activated water (PAW)



Plasma – water interaction

(A) Discharge directly in liquid (pulsed)

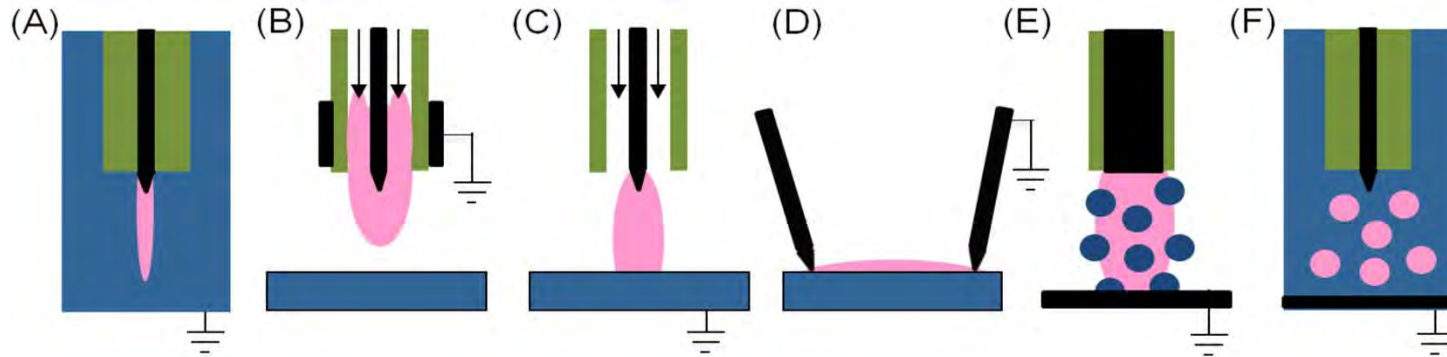
(C) Discharge with liquid electrode

(E) Plasma with dispersed liquid (aerosol)

(B) Plasma jet w/o direct contact with liquid

(D) Surface discharge over liquid

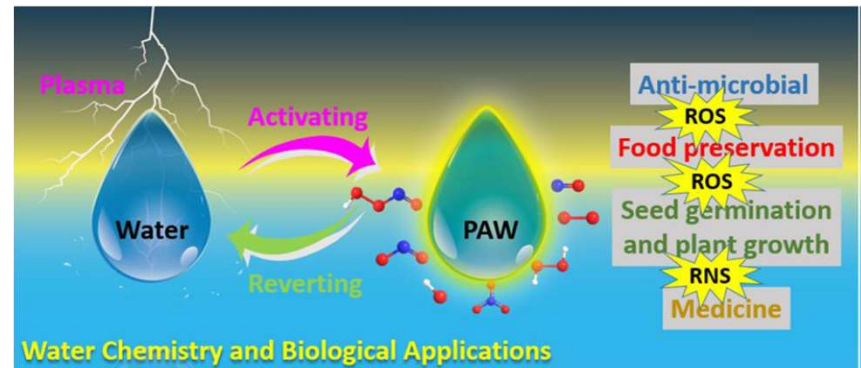
(F) Discharges in bubbles or foam



- P. J. Bruggeman et al.
Plasma-Liquid Interactions,
Plasma Sources Sci. Technol. 2016

- **Plasma-activated (treated / processed)
water / liquid (PAW / PAL)**

- Every PAW has different properties depending on the plasma parameters, gas and liquid composition, and exp. conditions



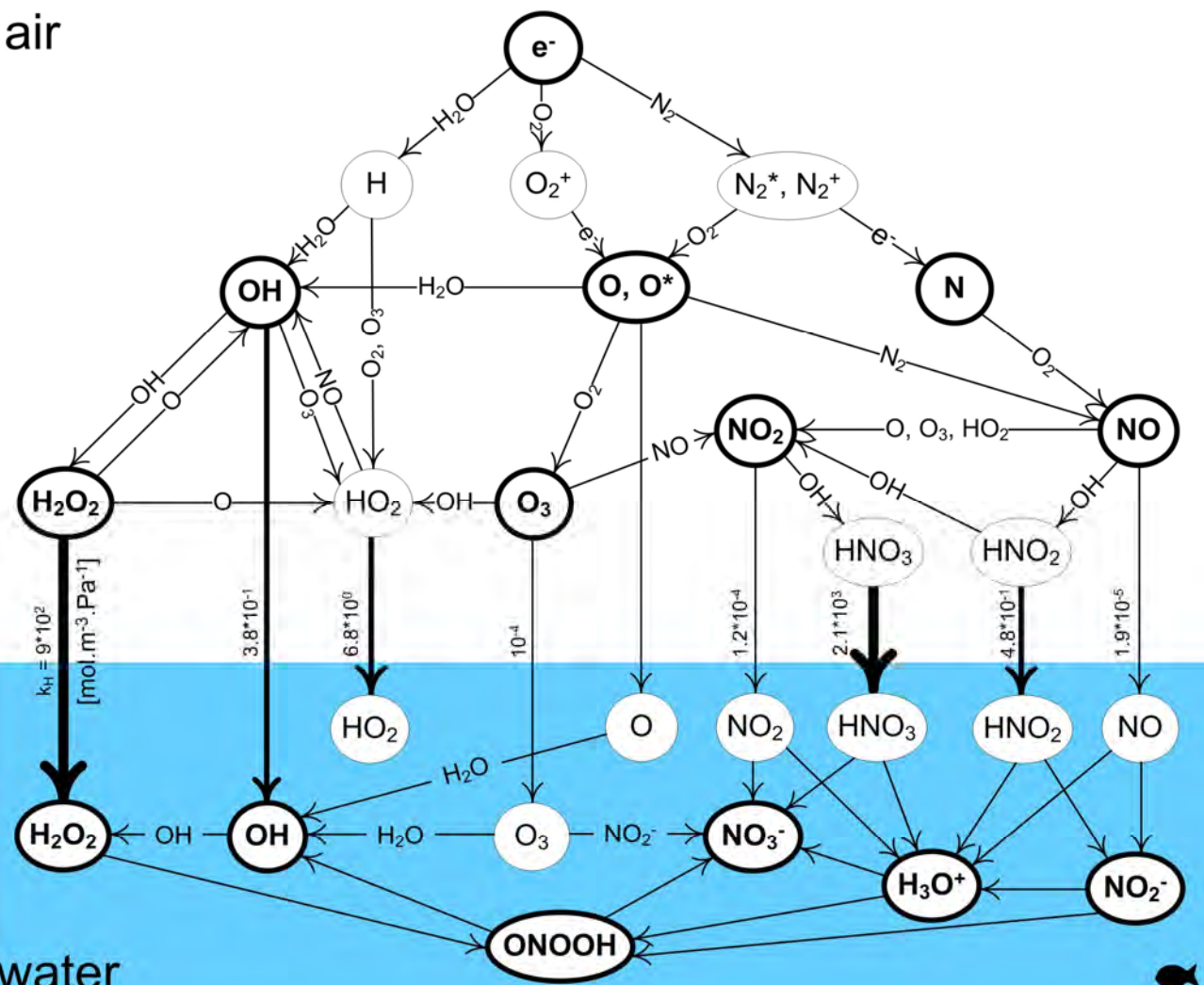
- R. Zhou et al J. Phys. D: Appl. Phys. 2020



Air-water plasma chemistry + transport into water



air



water

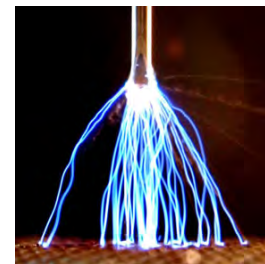
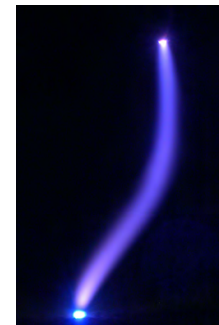
RONS - Reactive Oxygen
and Nitrogen Species



Outline

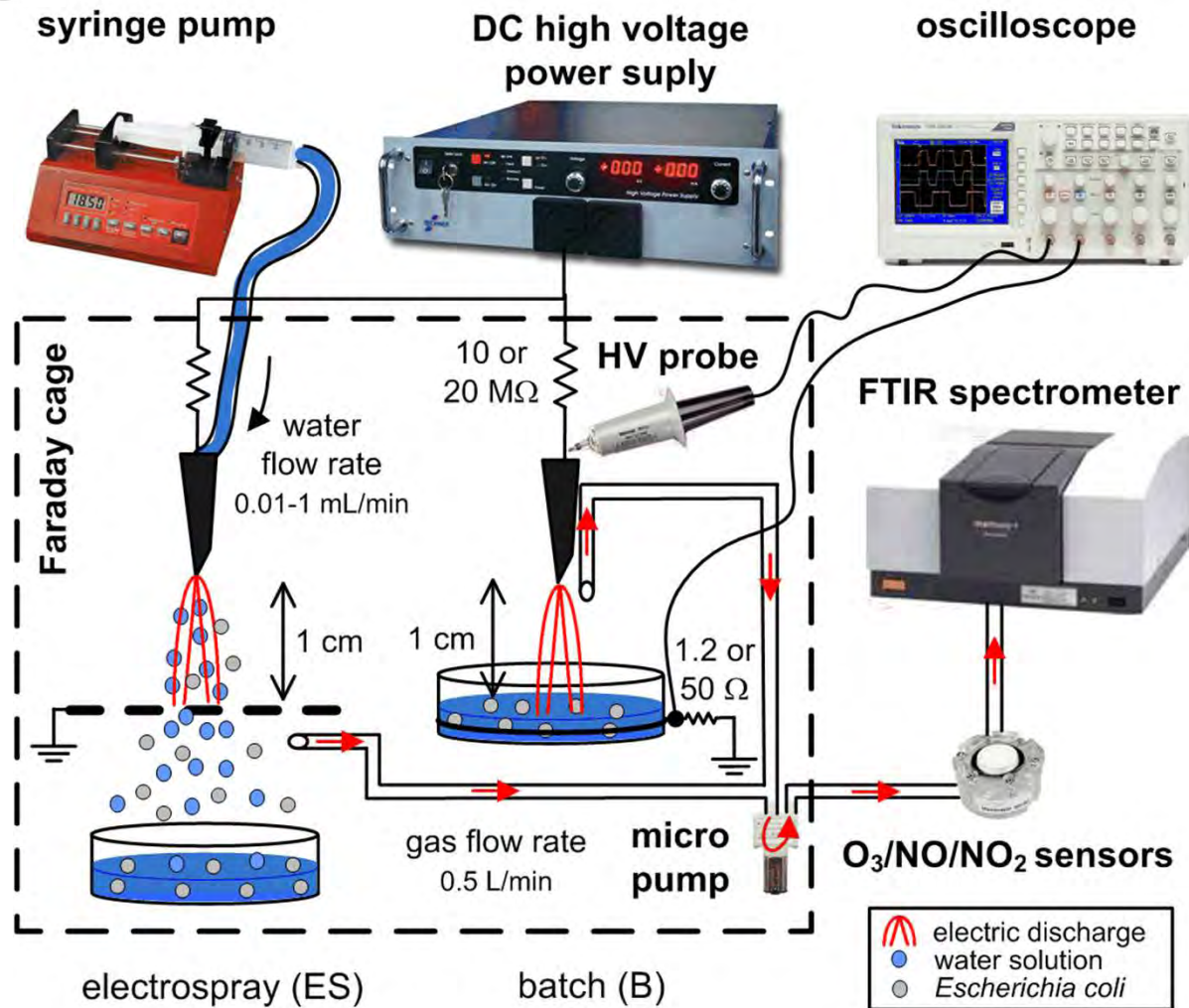


- Air discharges: O_3 vs. NO_x mode, OH radicals: plasma chemical processes; effects of power, flow rate, reactor
- Nitrogen fixation and fertilizers
- Transport of plasma reactive oxygen and nitrogen species into water bulk vs. microdroplets
- Air discharges with water: H_2O_2 and (H) NO_x formation in plasma-activated water
- Examples of biomedical/agro applications





Our cold plasma-liquid set-ups



Gas phase analysis:

NO , NO_2 , HNO_2 – electrochemical sensors, FTIR, UV absorption

O_3 – UV absorption (254 nm)

Aqueous phase analysis:

$\text{NO}_2^-/\text{NO}_3^-$: Griess reagent
→ azo product ($\lambda_{\text{max}} = 540 \text{ nm}$)

$\text{H}_2\text{O}_2 + \text{Ti}^{4+} \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O}_2 + 4\text{H}^+$
($\lambda_{\text{max}} = 407 \text{ nm}$)

O_3 : indigo blue reagent
($\lambda_{\text{abs}} = 600 \text{ nm}$)

ONOO^- : H_2DCFDA fluoresc. assay ($\lambda_{\text{ex}}/\lambda_{\text{em}} = 502/521 \text{ nm}$)

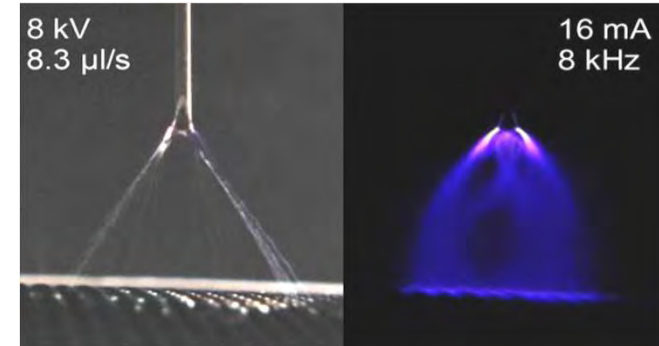
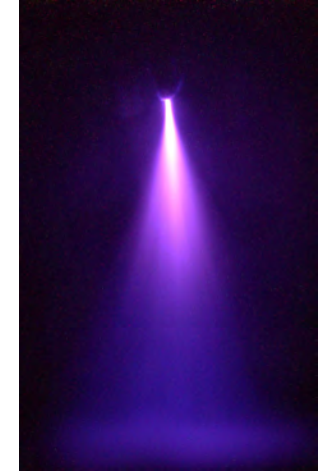
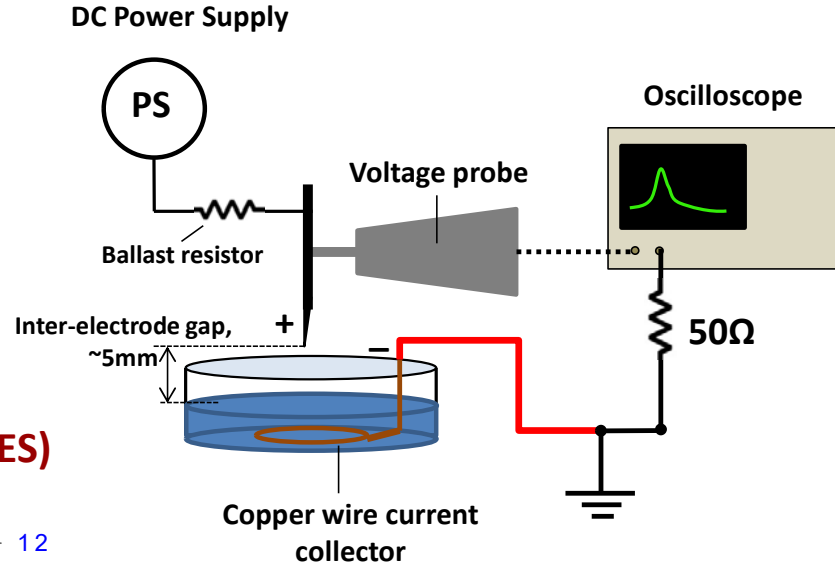
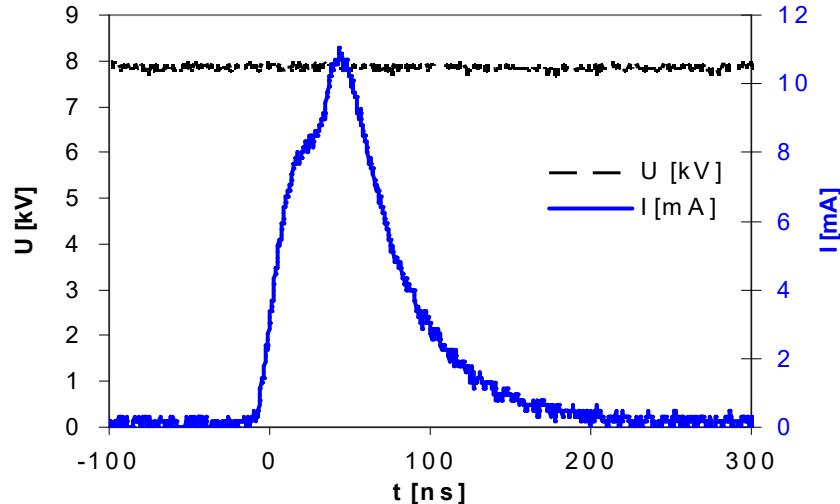
Antibacterial effects:

E. coli plate counting method



Streamer Corona Discharge (SC)

- Needle – plate, mesh, water electrodes
- Ambient air, $p = 1 \text{ atm}$
- $U = \text{const} \sim 5\text{-}10 \text{ kV}$,
- $I_{\text{mean}} \sim 10\text{-}200 \text{ mA}$, $I_{\text{max}} \sim 10\text{-}250 \text{ mA}$
- Pulses, $f \sim 5\text{-}20 \text{ kHz}$, $P \sim 0.1\text{-}1 \text{ W}$
- nonequilibrium cold plasma
- Easily combined with **water electrospray (ES)**



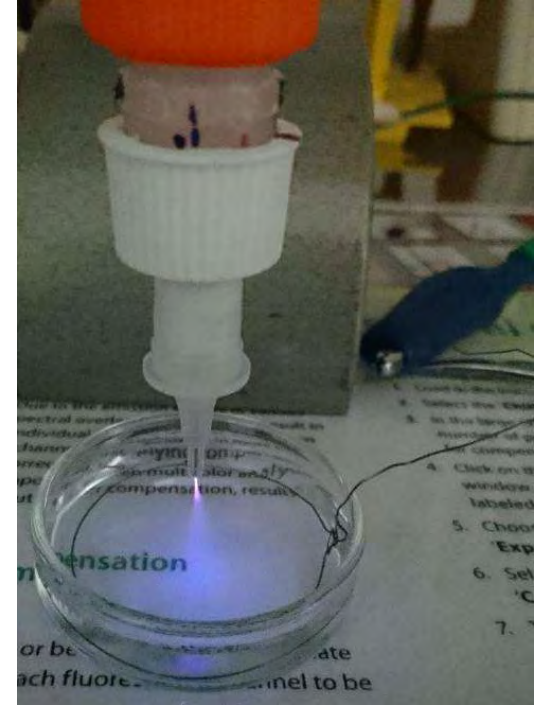
- B. Pongrac et al., *IEEE Trans. Plasma Sci.* 2011
- Z. Machala et al., *IEEE Trans. Plasma Sci.* 2008



“Corona pen” portable plasma source



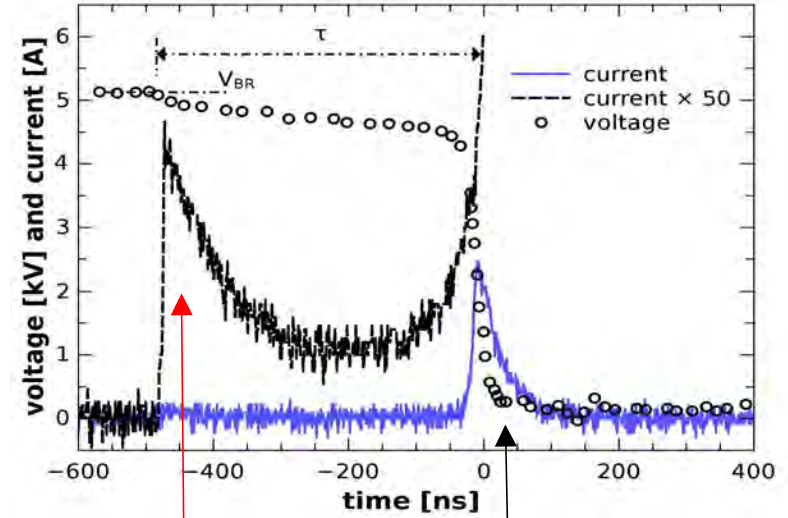
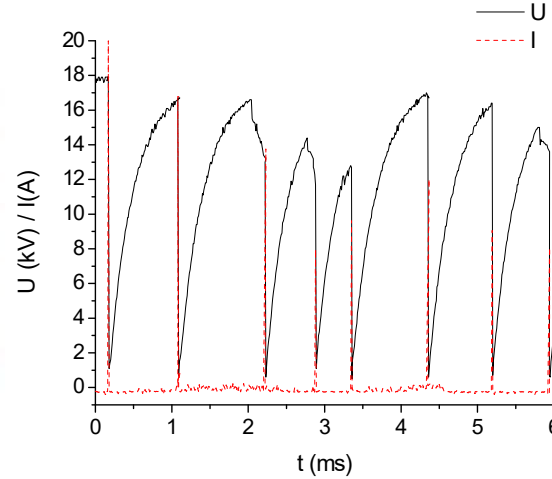
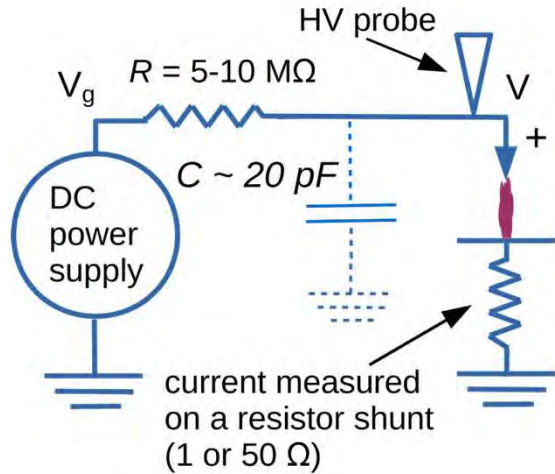
- Positive streamer corona – cold air plasma
- Average current ~ 100 mA, pulse frequency 5-30 kHz
- Safe, lightweight (<1 kg), portable, low-cost, optional on 12V battery power, low energy consumption ($P < 1$ W)
- **Antimicrobial effects** in ~ 1 min exposure
 - Tested on bacteria in water, biofilms, human skin wound healing,
- **Antitumor effects on cancer cells** (Direct and PAM, PAPBS)



- Z. Machala and D.B. Graves: *Trends Biotechnol.* 2018
- K. Trebulova et al. *Plasma process. Polym.* 2023



DC Transient Spark Discharge (TS)



streamer and spark phases of TS

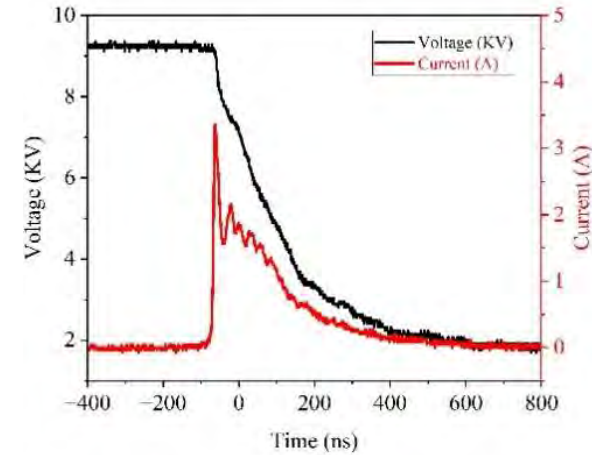
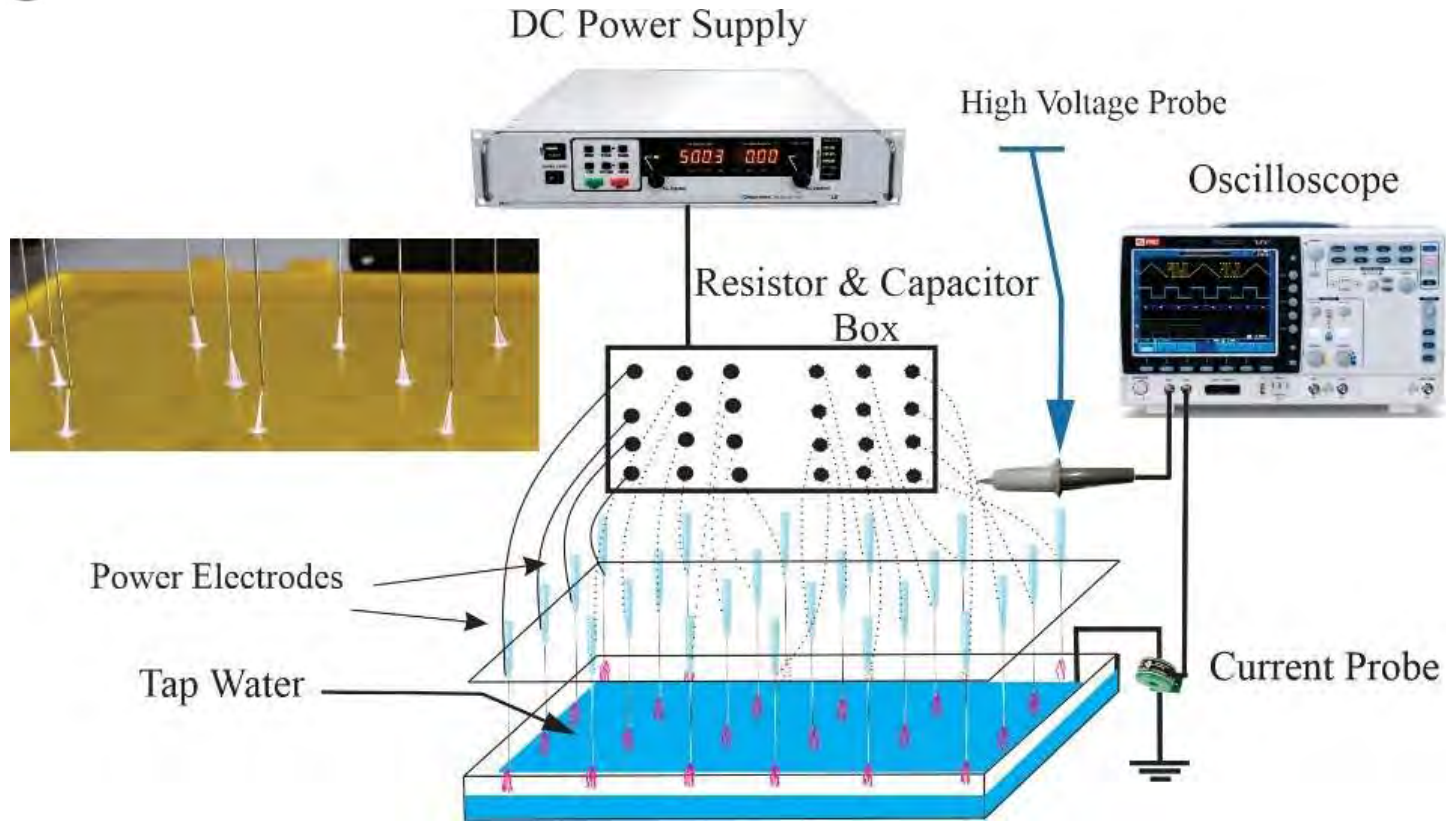


- **Periodic streamer-to-spark transition**
– self-pulsing discharge
- Needle-to-plate, -mesh, water electrode
- Gas = air, 1 atm
- $U_{\max} \sim 12-18$ kV, $I_{\text{mean}} \sim 1-2$ mA,
 $I_{\max} \sim 2-30$ A, $P \sim 1-2$ W
- I-pulse duration **20-50 ns**, $f \sim 1-10$ kHz
- **nonequilibrium plasma**
- Can be combined with **water electrospray (ES)**

- Z. Machala et al., *IEEE Trans. Plasma Sci.* 2008
- Z. Machala et al., *J Phys. D: Appl. Phys.* 2000
- M. Janda et al., *Plasma Sources Sci. Technol.* 2011, 2012



Multineedle Transient Spark – scaled-up PAW production



- 21 needles - each with its own R and C, common liquid electrode 210 mL
- Batch or liquid flow system
- Typical PAW preparation: 1 ml / 1 min/ 1 needle/ 1 kHz/ 1 cm



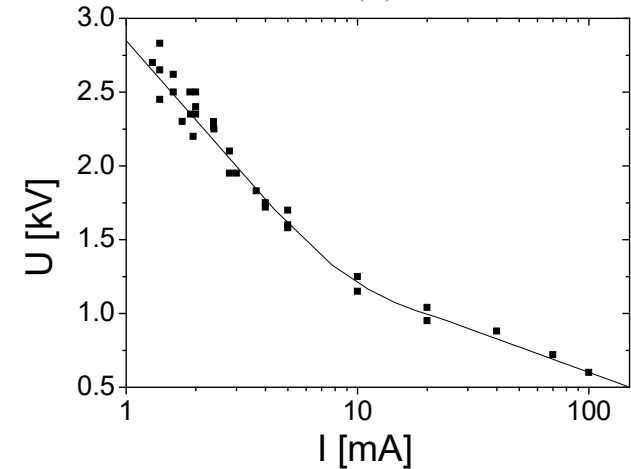
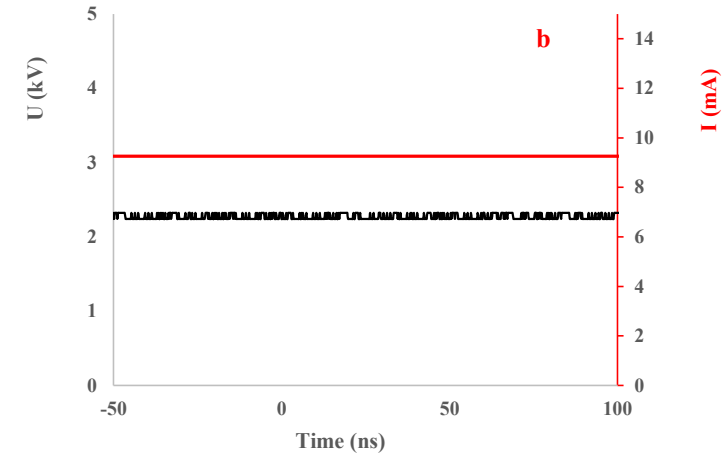
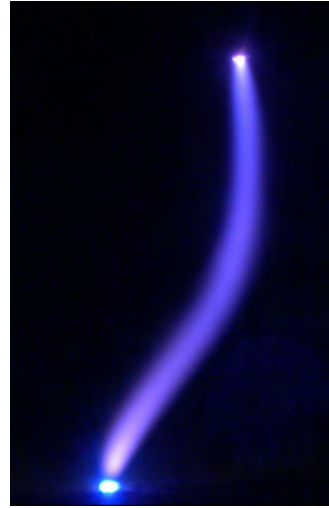
Glow discharge in air



- Ambient air, $p = 1 \text{ atm}$

Glow discharge (GD)

- Needle – plate, mesh, water electrodes
- pulse-less, $U = 1.7\text{-}2 \text{ kV}$, $I = 5\text{-}10 \text{ mA}$
 $P \sim 9\text{-}20 \text{ W}$
- Cathode fall $\sim 500 \text{ V}$ (water cathode, air)
- Diffuse character
- $n_e \sim 2 \times 10^{12} \text{ cm}^{-3}$
- $T_g \cong 1950 \text{ K}$, $T_e \sim 10,000 \text{ K}$
- nonequilibrium, yet relatively hot plasma



- Z. Machala et al., *J Phys. D: Appl. Phys.* 2000
- Z. Machala et al., *J. Advanced Oxid. Technol* 2004
- Z. Machala et al., *J. Molec. Spectrosc.* 2007

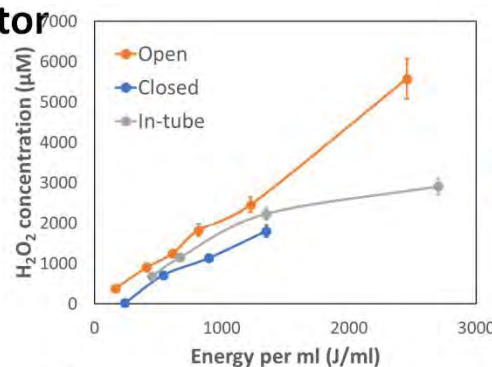
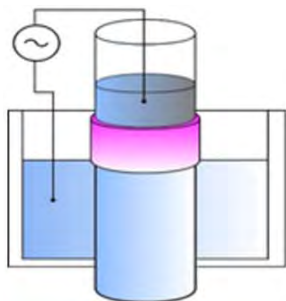


Surface DBD with liquid electrodes – catheter disinfection

- Cold plasma at the circumference boundary of air-liquid-dielectric tube
- Disinfection of catheters
- Hydrophilization of tube materials

Tap water – weak buffer
Power 5 – 20 W

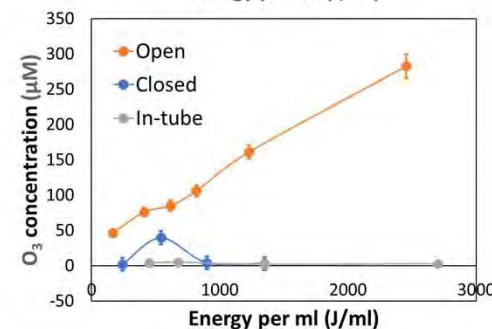
Plasma outside tube / open reactor



PAW: High H_2O_2 , high O_3 , high NO_2^-

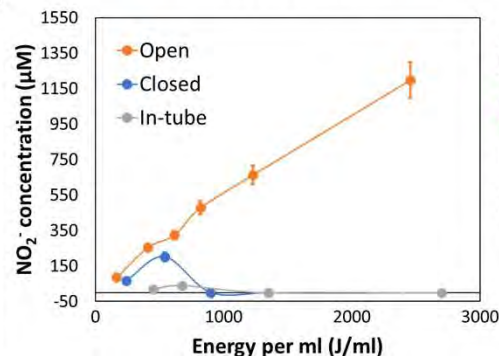
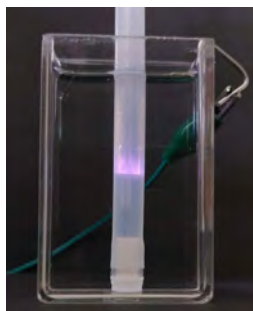
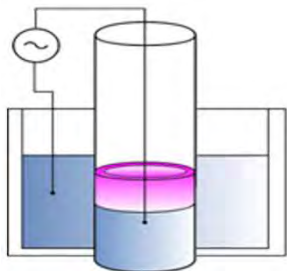
Peroxone process at pH > 5.5:
 $\text{H}_2\text{O}_2 + 2 \text{O}_3 \rightarrow 2 \text{OH} + 3 \text{O}_2$

Plasma outside tube / closed reactor



PAW: Low H_2O_2 , low O_3 , low NO_2^-

Plasma inside tube / closed reactor



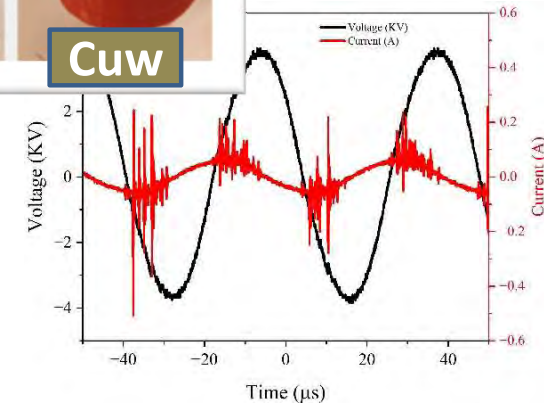
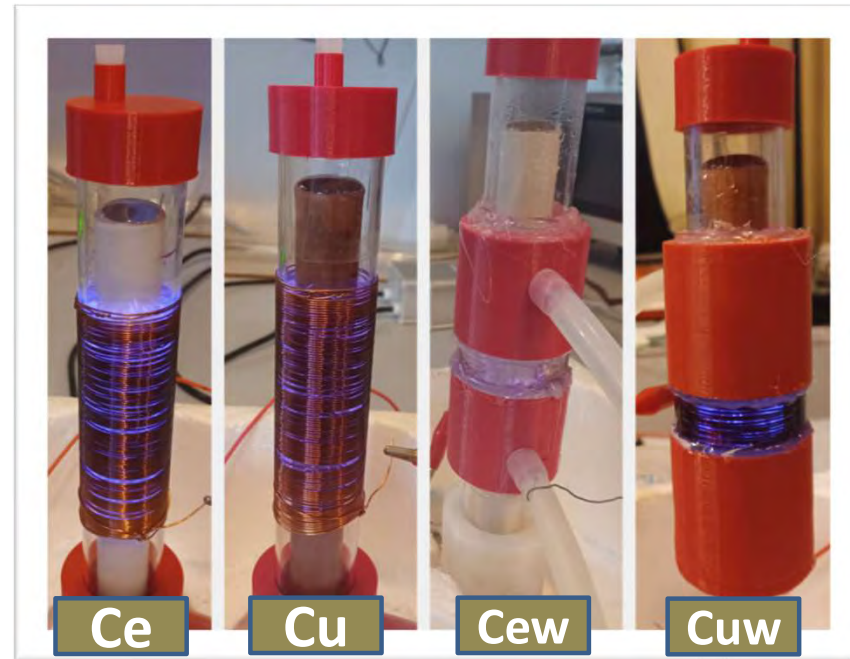
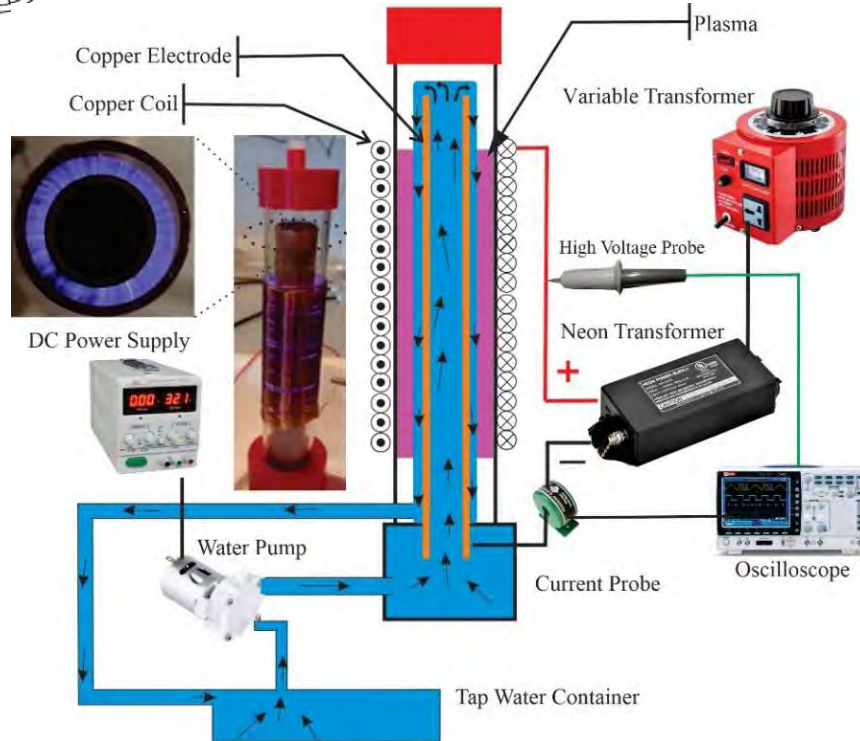
PAW: Medium H_2O_2 , very low O_3 and NO_2^-

Increased evaporation to the limited volume → higher H_2O_2

- O. Galmiz et al., *J Phys. D: Appl. Phys.* 2016
- O. Galmiz et al., *Plasma Sources Sci. Technol.* 2025



Fountain DBD with liquid electrode

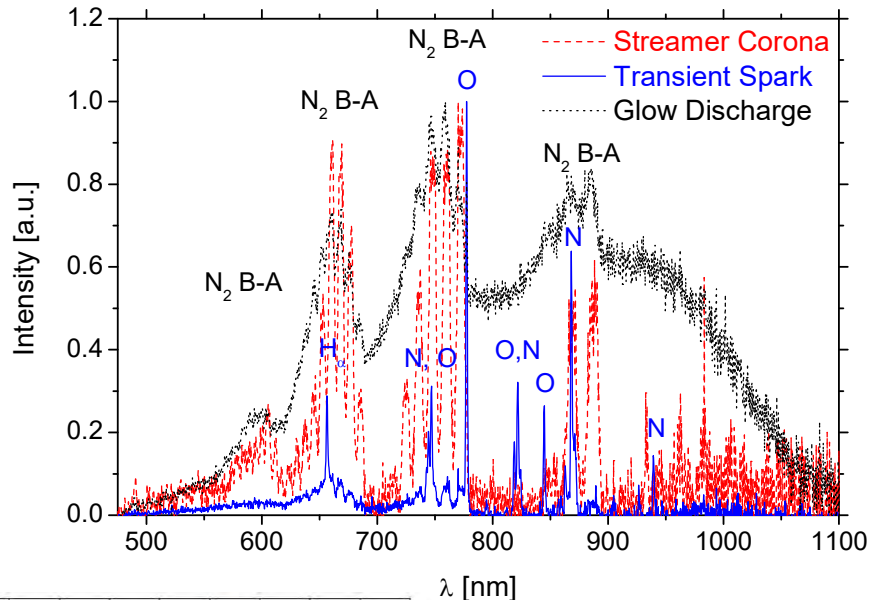
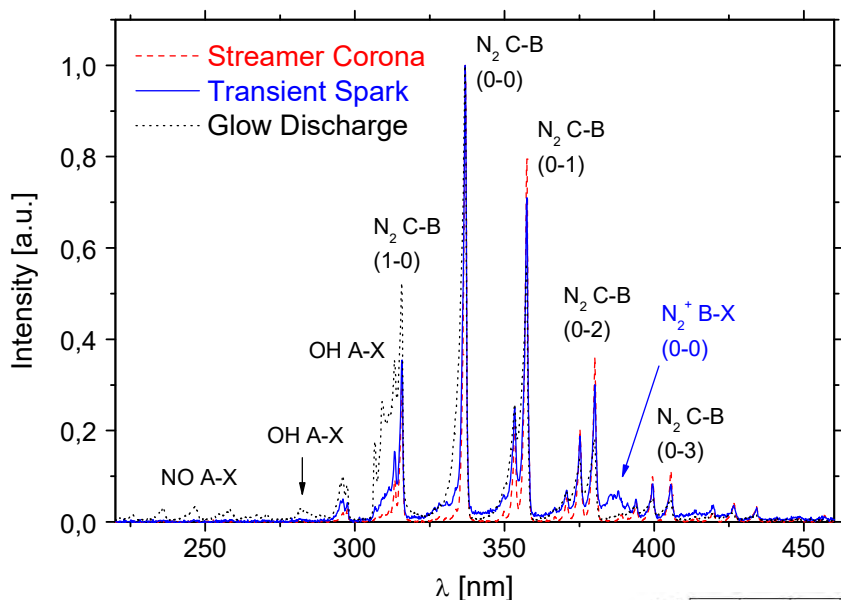


- Metal/ceramic inner tube with water film
- Glass/quartz outer tube
- Circulating water (large volume, typ. 1L)
- PAW production for bio-decontamination and seed germination
- RONS production depends on central electrode material (plasma power and number of microdischarges), and outside water cooling

- S. Kooshki et al., *Env. Technol. Innov.* 2023
- S. Kooshki et al., *J. Water Proc. Eng.* 2024



Identification of RONS by Optical Emission Spectroscopy

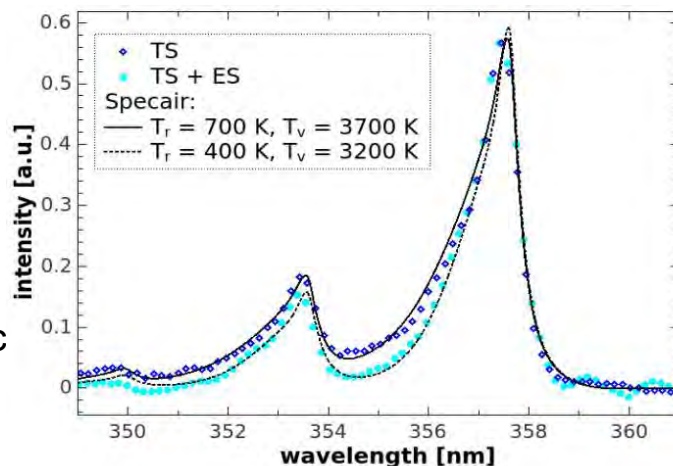


Molecular systems:

- N_2 ($C^3\Pi_u - B^3\Pi_g$), N_2 ($B^3\Pi_g - A^3\Sigma_u^+$); N_2^+ ($B^2\Sigma_u^+ - X^2\Sigma_g^+$)

Atomic lines:

- **H, O, N, OH** radicals – dissociations due to energetic electrons

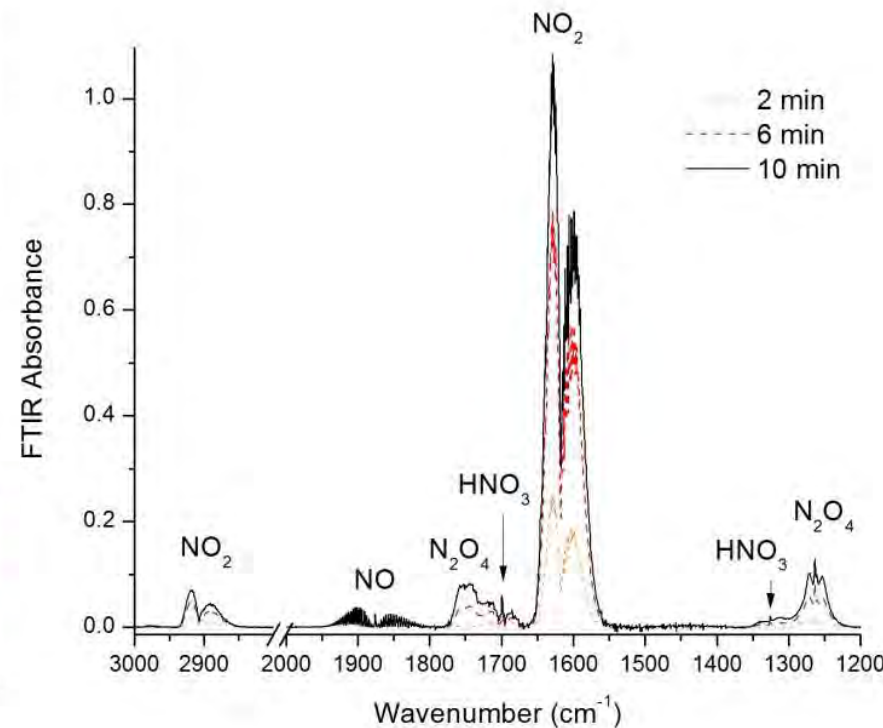
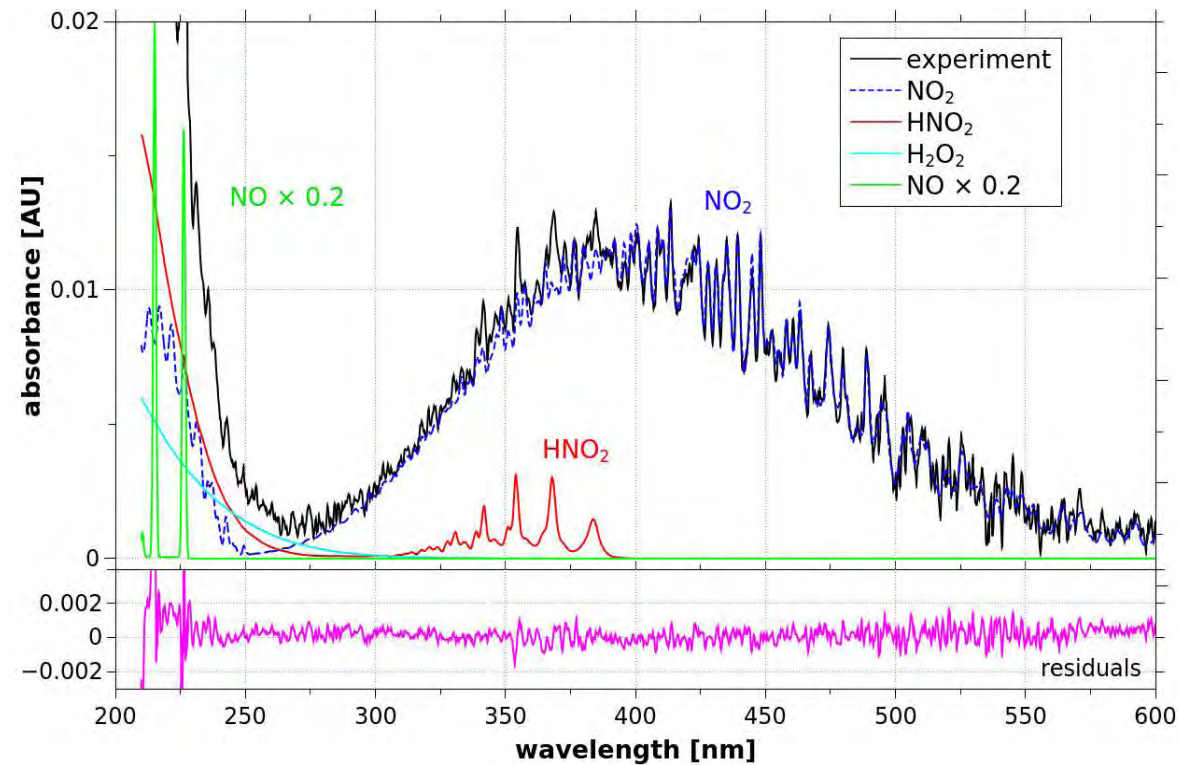


Emission spectra of TS, N_2 SPS bands and Specair fitting

Lower T_r with water ES

- Z. Machala et al., *J. Mol. Spectrosc.* 2007
- M. Janda et al., *Plasma Sources Sci. Technol.* 2014
- B. Tarabova et al., *Plasma Proces. Polym.* 2018

UV-vis/FTIR absorption of gaseous RONS

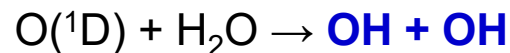
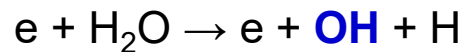
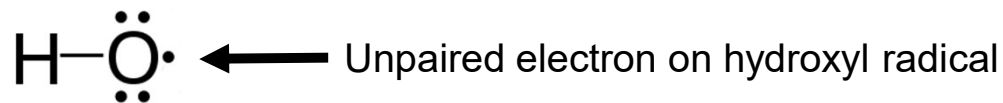


- UV-vis absorption – requires long-path cells (~ 0.75 m)
- FTIR – absorption depends on species concentration
- **Ozone** – good absorption in UV (256 nm) and IR (1060 cm^{-1})

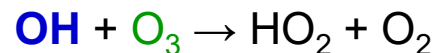
• M. Janda et al., *Appl. Sci.* (2021)



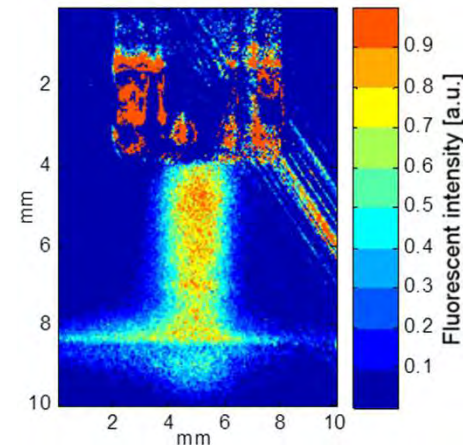
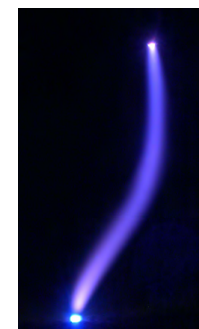
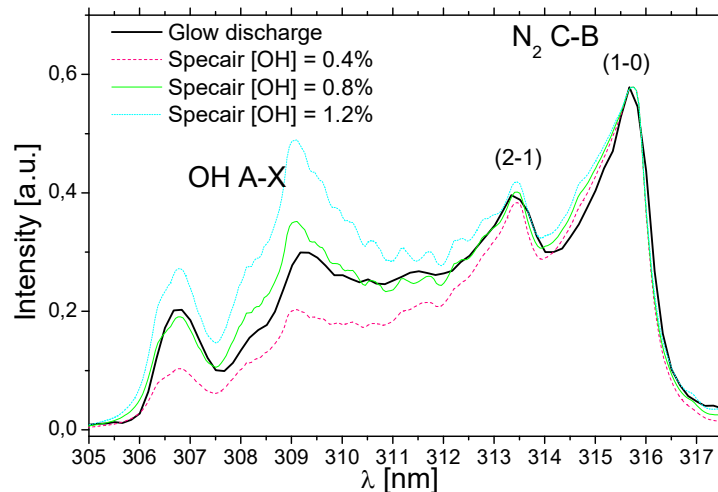
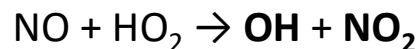
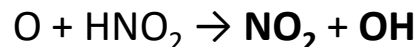
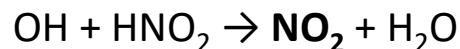
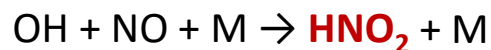
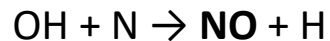
OH radicals → hydrogen peroxide



Evaporated water interacting
with electrons or O atoms



OH-RNS chemistry:



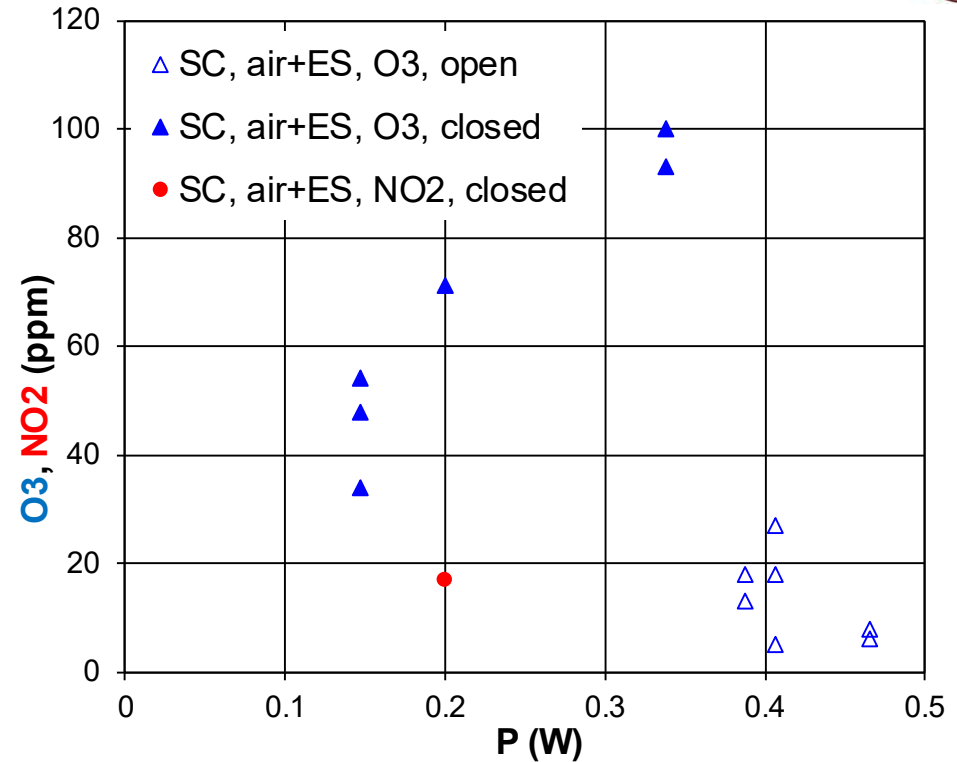
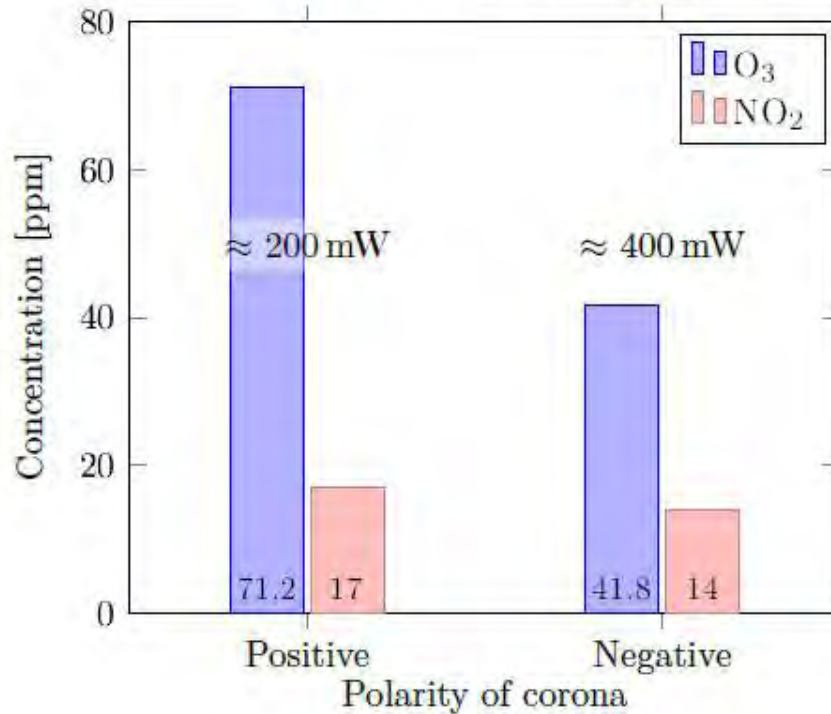
LIF OH measurement

- DC glow discharge with water cathode
- Fitting by SPECAIR spectral simulation software
- **Measurements of OH concentrations $\sim 10^{17} \text{ cm}^{-3}$** by accurate setting of initial OH concentration in Specair

- S. Reuter et al. *Plasma Sources Sci. Technol.* 2012
- Z. Machala et al., *J. Mol. Spectrosc.* (2007)
- Z. Kovalova, PhD. thesis, Univ. Paris-Saclay FR + Comenius Univ. Bratislava SK, 2016



Streamer corona generates O₃ and almost no NO



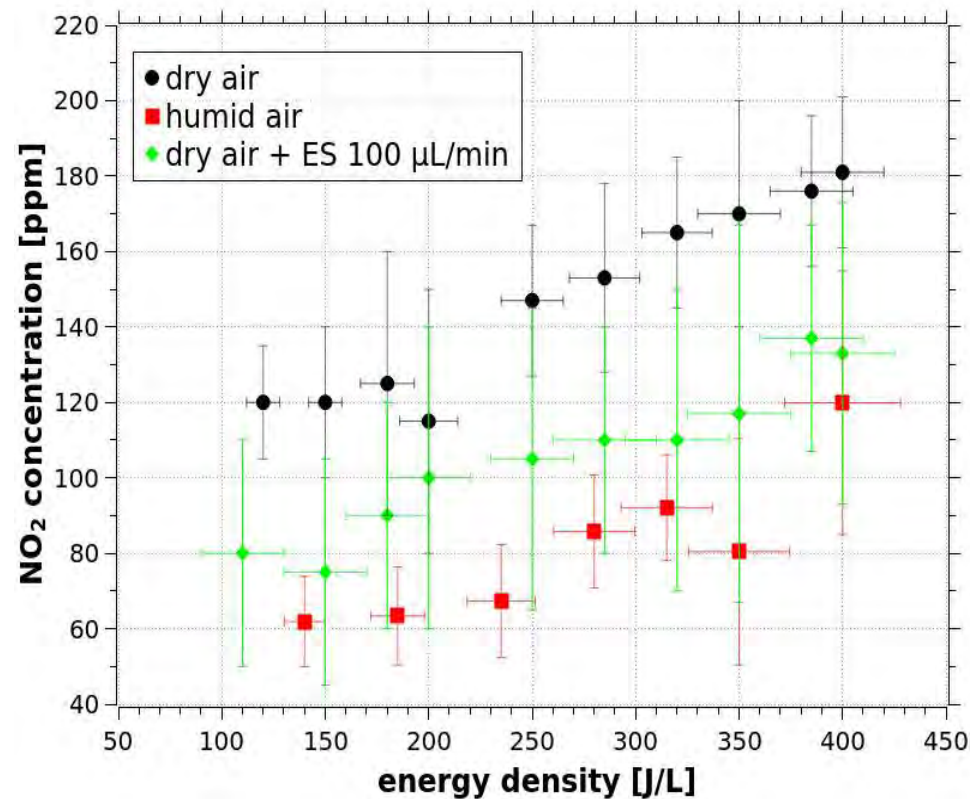
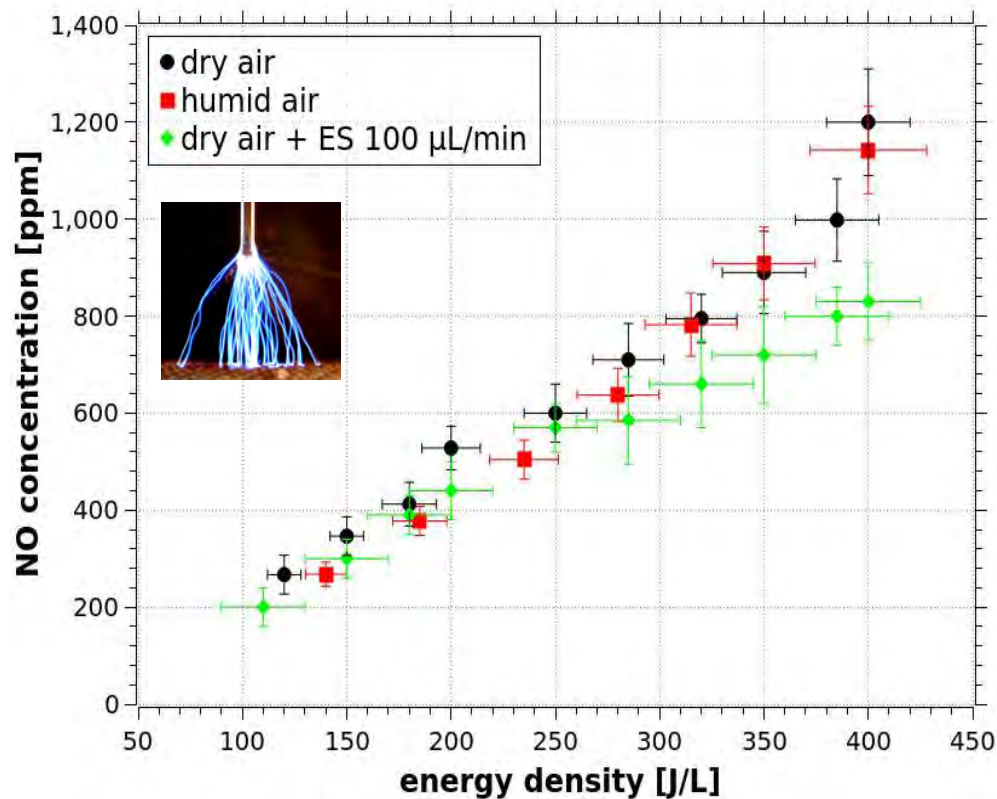
- O₃ and NO formation **compete**: $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- Open air system generates less O₃ than closed chamber

Gaseous O₃ and NO_x formation in SC
ambient air + water electro spray

- Z. Koval'ová et al., *Bioelectrochem.* 2016
- Z. Machala et al., *J. Phys. D: Appl. Phys.* 2019



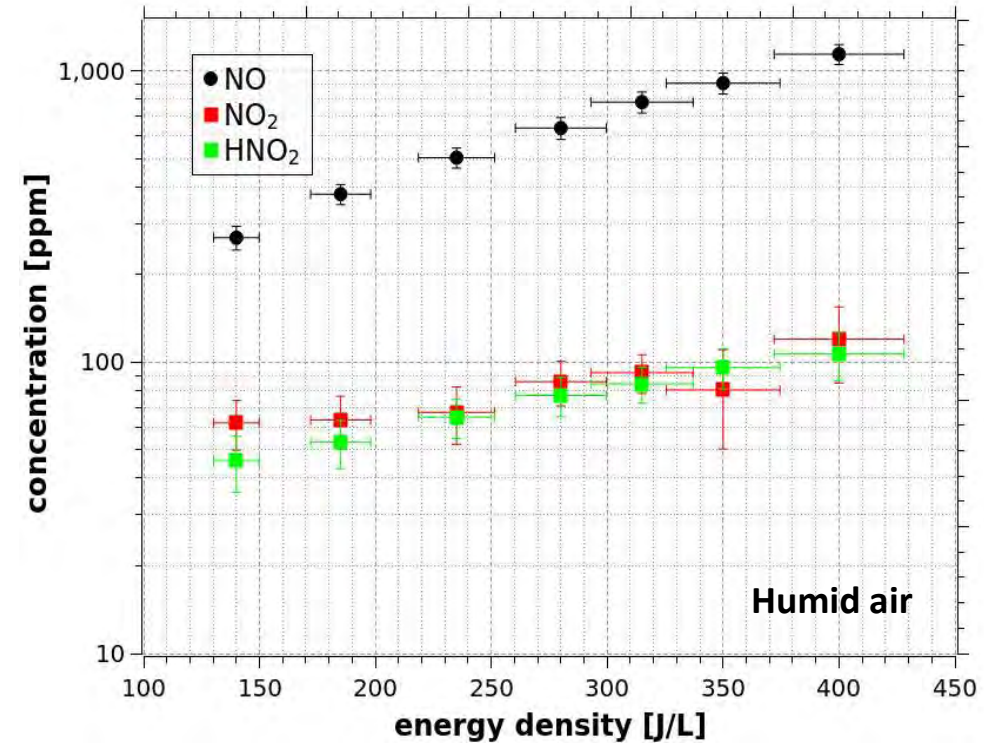
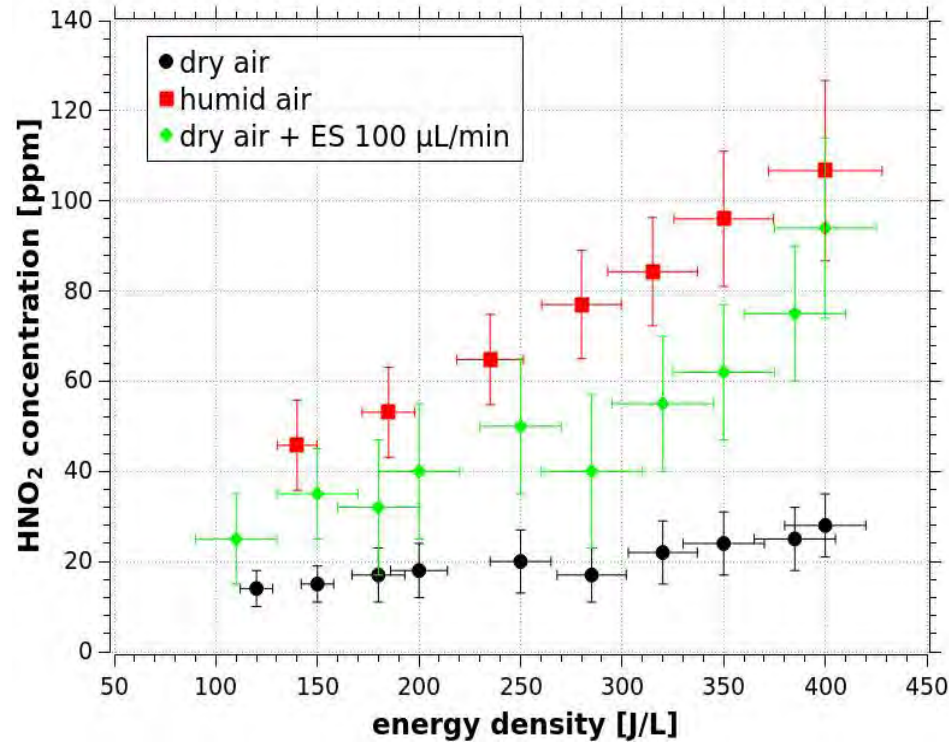
TS generates NO_x and no O₃



- NO_x formation increases with energy density
- **NO** – almost no effect vs. **NO₂** – strong effect of humidity or water microdroplets
- M. Janda et al., *Plasma Chem. Plasma Process.* (2016)
- M. Janda et al., *Appl. Sci.* (2021)



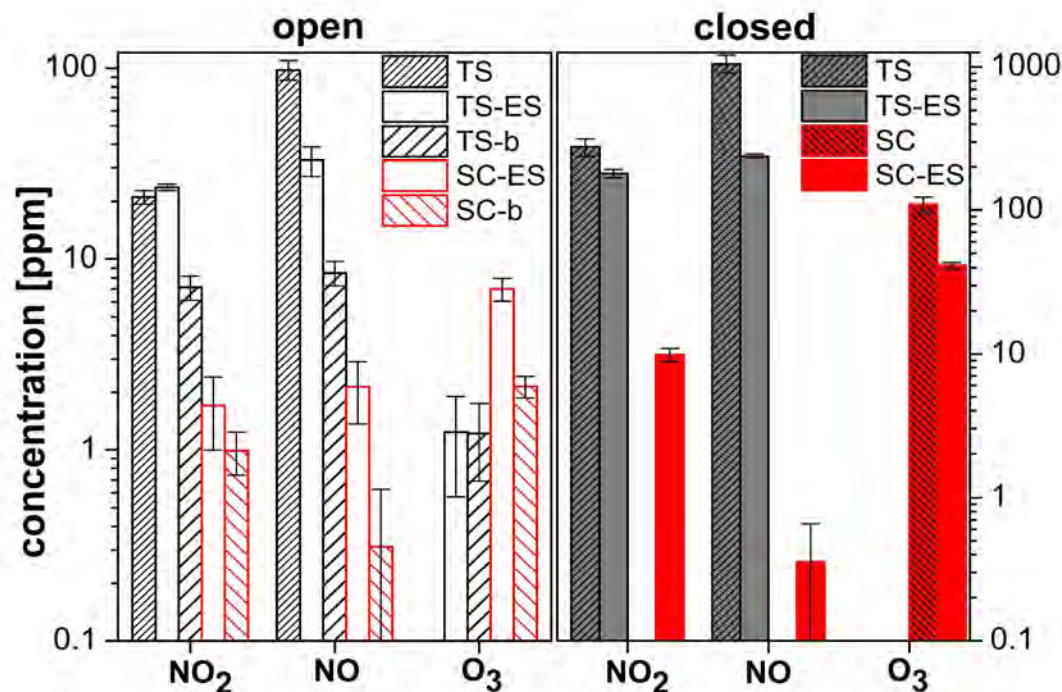
Gaseous HNO_2 formation in TS



- Discharge in humid air and dry air with water ES – formation of HNO_2
- Gaseous NO / NO_2 - weak solvation in water – low NO_2^-
- HNO_2 – strong solvation in water – high NO_2^-
- HNO_2 is the dominant source of NO_2^- in PAW



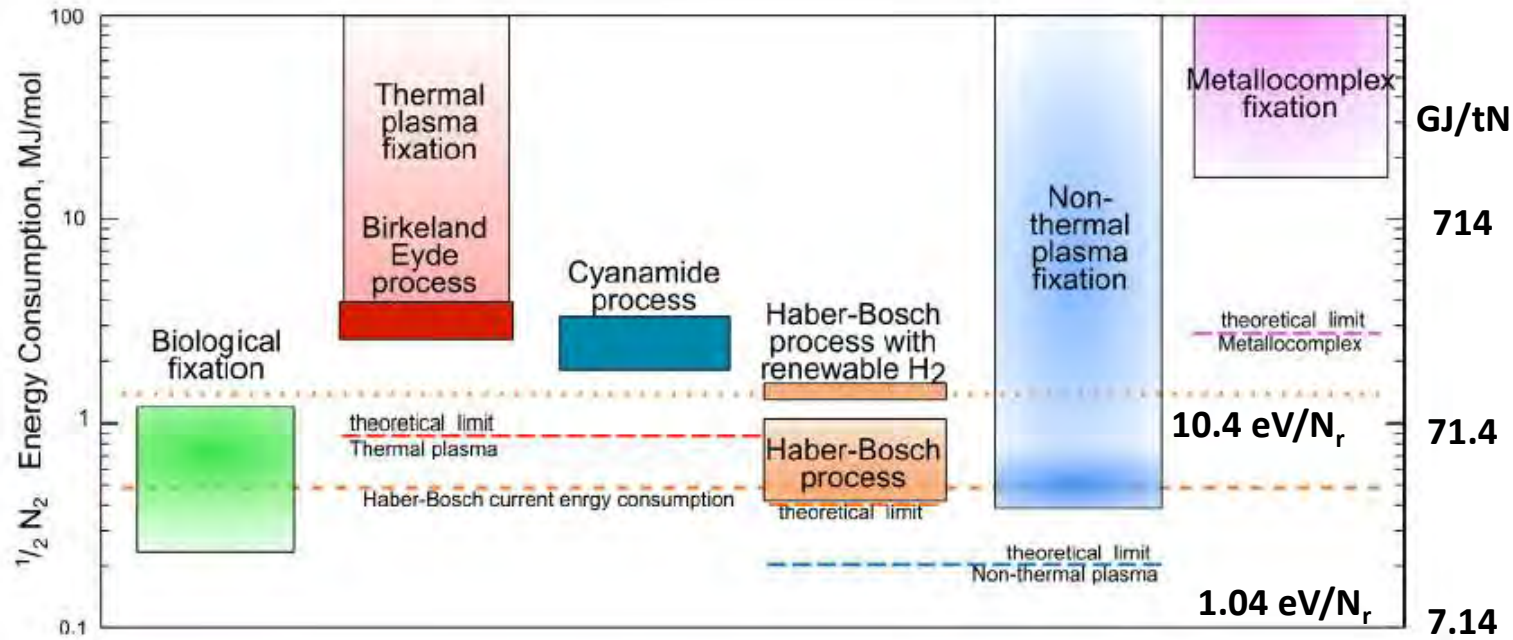
TS vs. SC: open vs. closed gaseous RONS formation



- **TS: NO_x-dominated** chemistry,
SC: O₃-dominated,
O₃ and NO formation compete: $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- Open air system generates about 10-100x less NO_x and O₃ than closed chamber

- Z. Machala et al., *J Phys. D* 2019
- M. Janda et al., *Appl. Sci.* (2021)

Existing and alternative methods for greener N-fixation



NH₃ currently manufactured via Haber-Bosch high pressure, high temperature catalytic process reacting H₂ and N₂:

- **1% world energy use**
- **3-5% world CH₄ use**

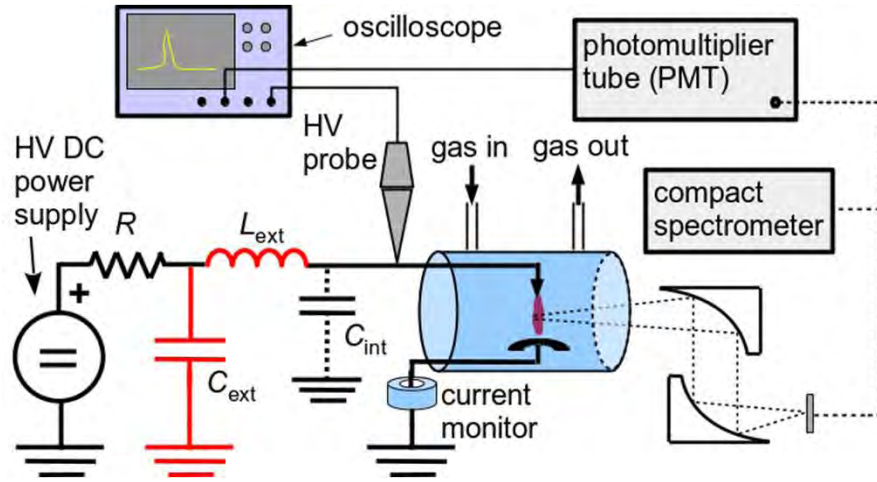
$$1 \text{ MJ/mol } N_r = 71.4 \text{ GJ/tN}_r = 10.4 \text{ eV/N}_r$$

$$1 \text{ MJ/mol } N_r = 6 \times 10^{17} \text{ N}_r/\text{J}$$

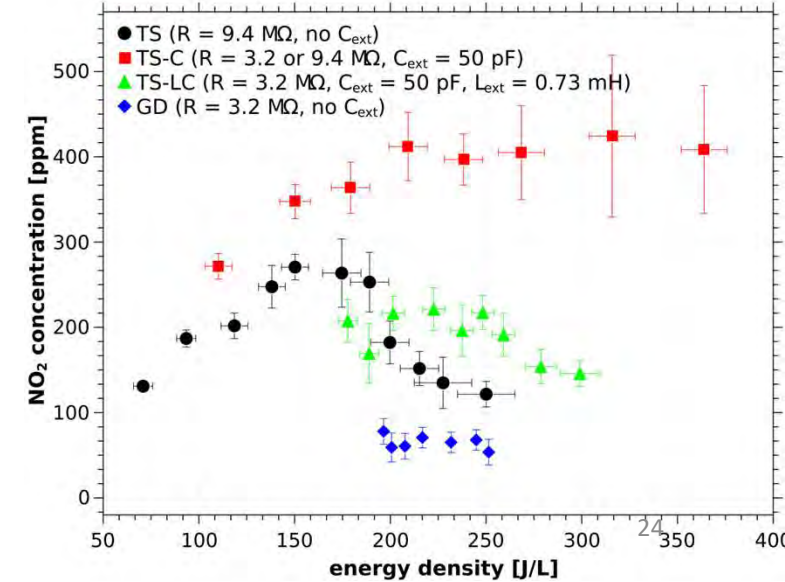
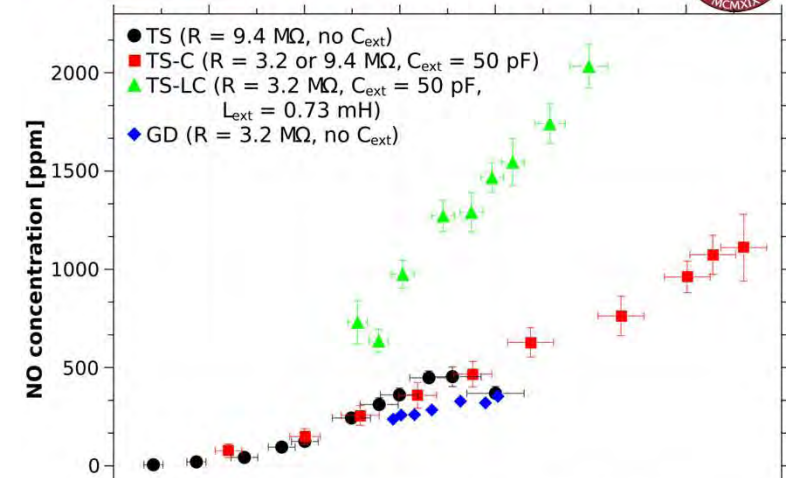
Non-thermal plasma - a promising route!



TS with additional C and L: stronger NO formation

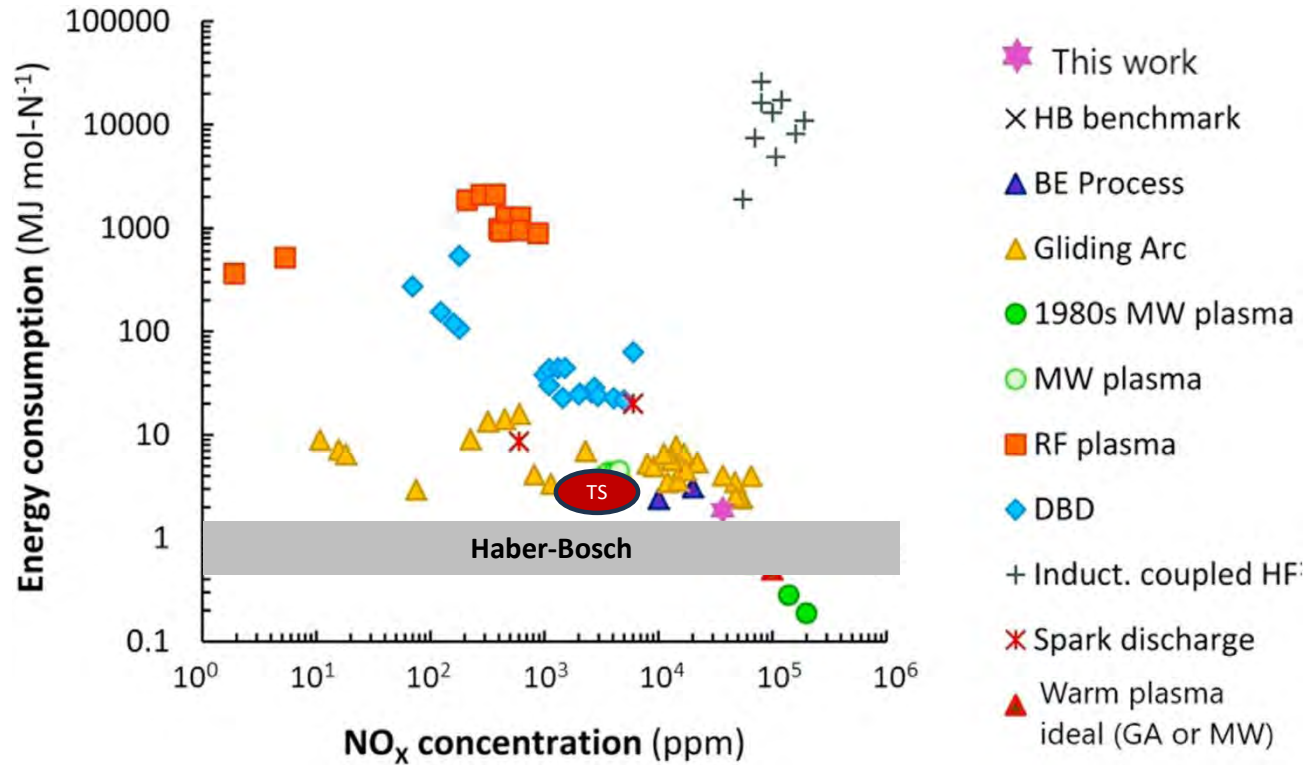


- **NO production is boosted** by the **addition of a capacitor and an inductor** to the TS electrical circuit.
- NO produced per joule per volume is doubled
- The yield of NO increased - the modified circuit enables higher discharge currents.
- This simple modification of the driving circuit may have potential for optimizing the plasma chemistry and for scaling up N-fixation from air.





Energy costs of N-fixation by TS-LC discharge

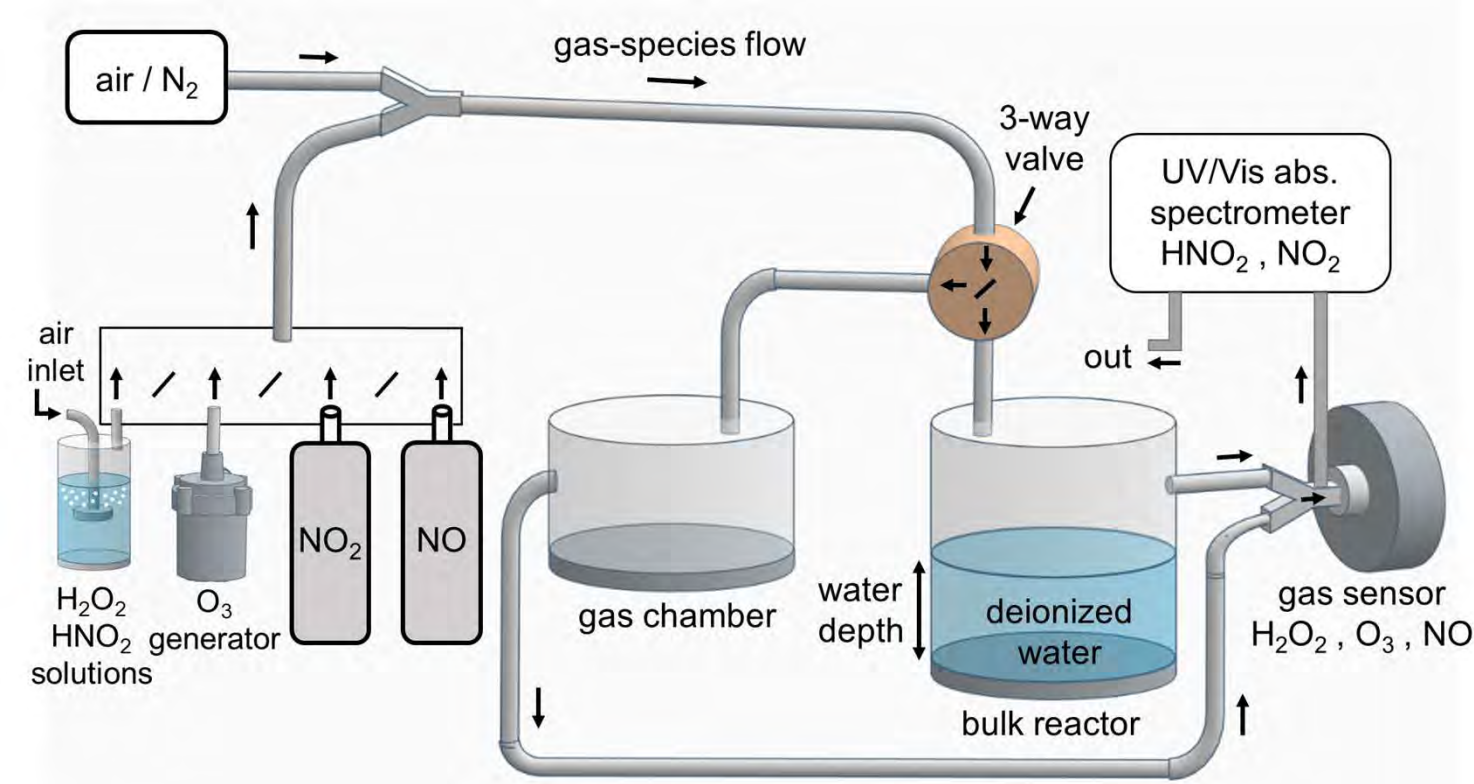


NO_x production in different types of discharges
+ added value of TS-LC

- S. Kelly & A. Bogaerts, Joule 2021
- M. Janda et al., J. Phys D. Appl. Phys. (2023)



RONs transport into bulk water



H₂O₂ : 9.8 M
HNO₂ : 20 mM

External sources of

ozone (450 ppm)

H₂O₂ (100 ppm)

HNO₂ (100 ppm)

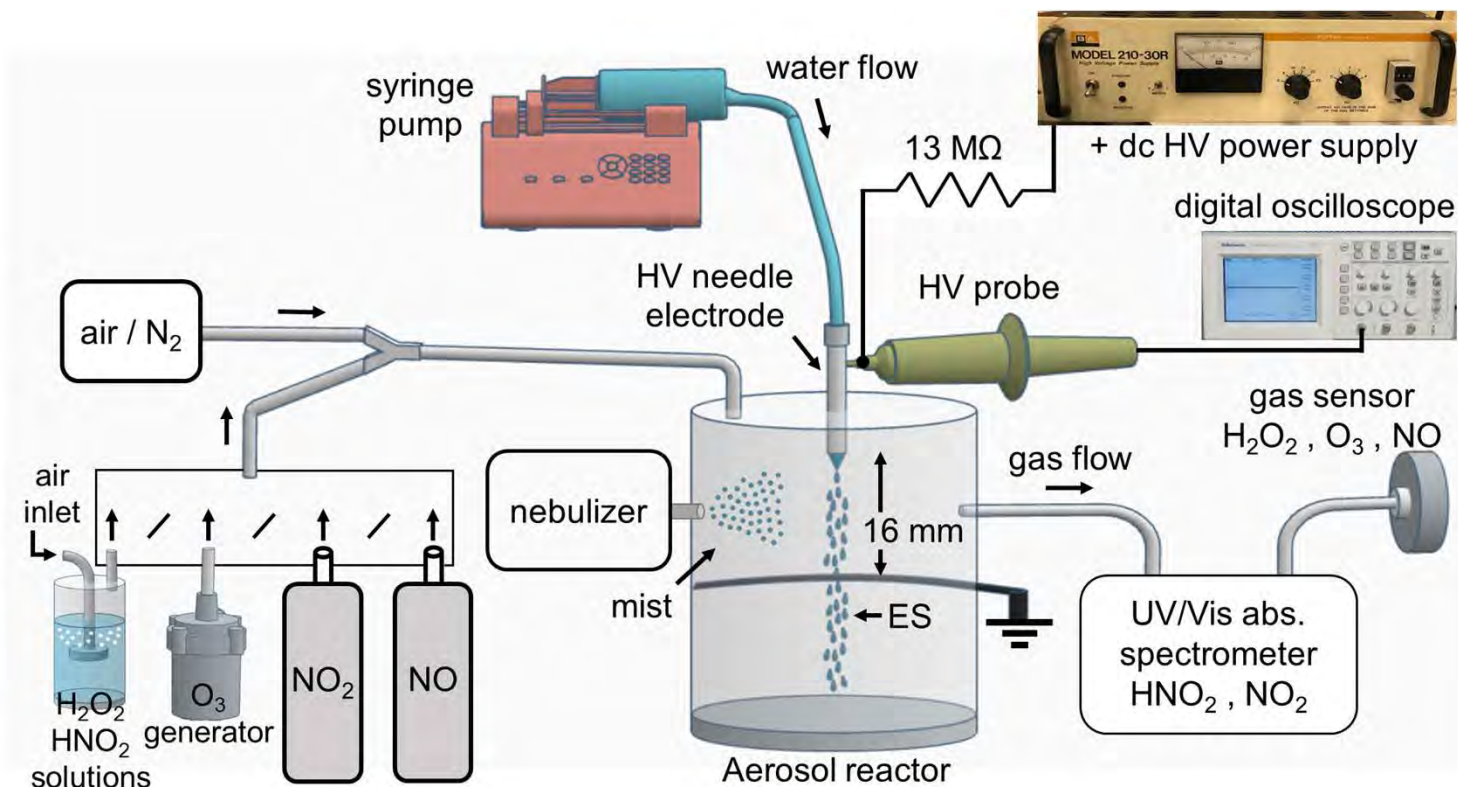
NO₂ (250 ppm)

NO (600 ppm)

- **Bulk** water
- Detection of gaseous O_3 , H_2O_2 , HNO_2 , NO , NO_2 :
electrochemical gas sensors, UV-vis absorption, FTIR
- Analysis of aqueous RONS
 O_3 : indigo blue reagent
 $(\lambda_{\text{abs}} = 600 \text{ nm})$
 H_2O_2 : TiOSO_4 ($\lambda = 407 \text{ nm}$)
 NO_2^- : Griess reagent
 $\lambda = 540 \text{ nm}$



RONS transport into microdroplets



H₂O₂ : 9.8 M
HNO₂ : 20 mM

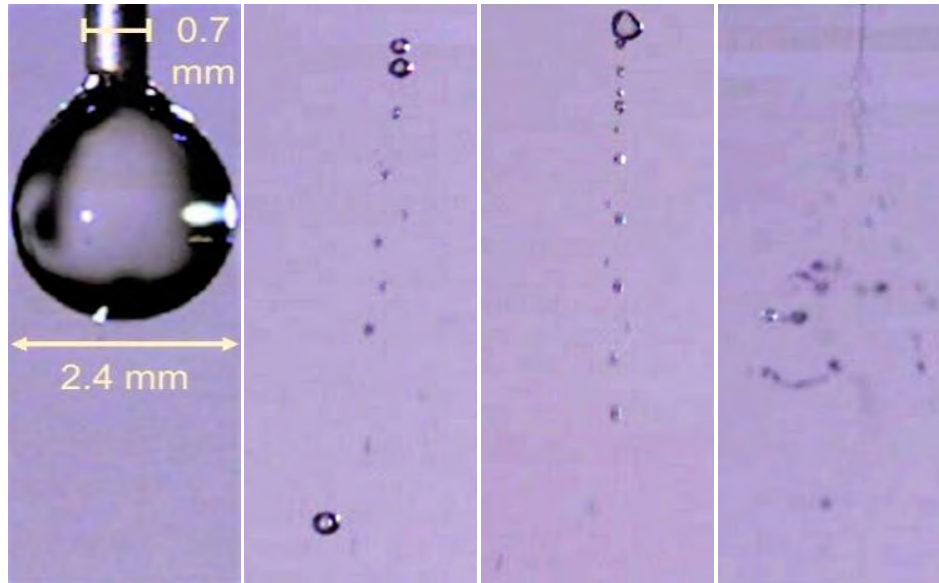
External sources of
ozone (450 ppm)
H₂O₂ (100 ppm)
HNO₂ (100 ppm)
NO₂ (250 ppm)
NO (600 ppm)

- Water **microdroplets:**
electrosprayed/nebulized
- Detection of gaseous **O₃**,
H₂O₂, **HNO₂**, **NO**, **NO₂**:
electrochemical gas sensors,
UV-vis absorption, FTIR
- Analysis of aqueous RONS
O₃: indigo blue reagent
($\lambda_{\text{abs}} = 600 \text{ nm}$)
H₂O₂: TiOSO₄ ($\lambda = 407 \text{ nm}$)
NO₂⁻: Griess reagent
 $\lambda = 540 \text{ nm}$

• M.E. Hassan et al., *Water* 2021



Electrospray



0 kV 9 kV 11 kV 13 kV

High speed camera imaging, 300 $\mu\text{L}/\text{min}$

Static Taylor cone criterion

$$E_{\text{onset}} = \sqrt{\left(\frac{2\gamma \cos \alpha}{\epsilon_0 r} \right)}$$

$E = 0$

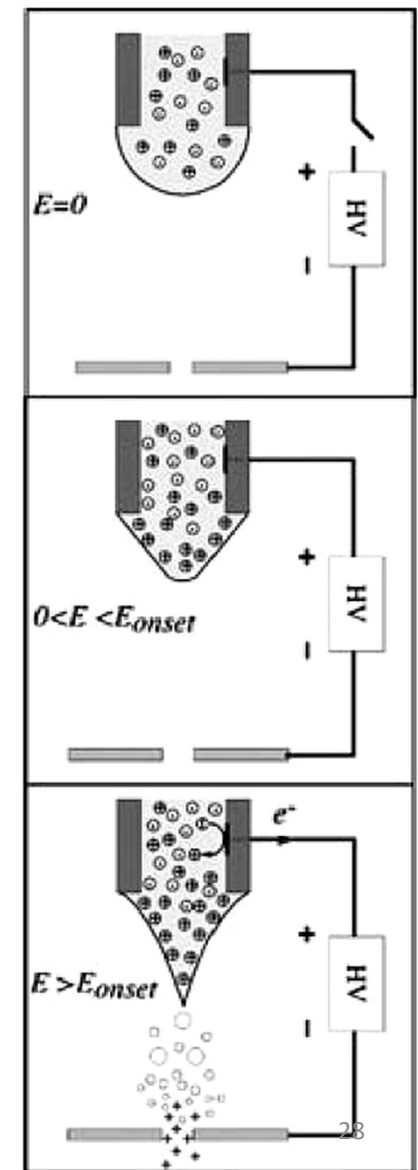
- Constant droplet shape and volume (given by surface tension)

$0 < E < E_{\text{onset}}$

- Volume of droplet decreases (electrostatic pressure against capillary pressure)
- Dripping rate increases

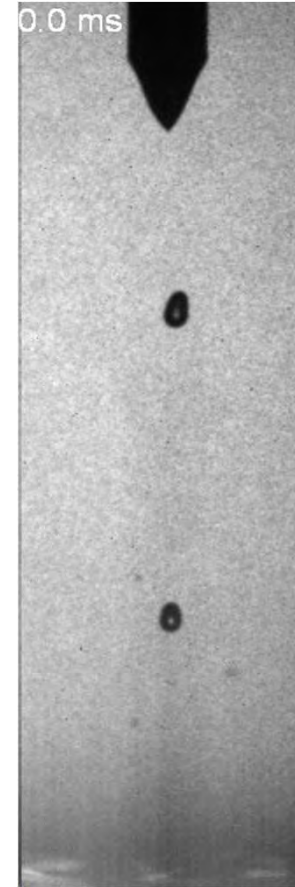
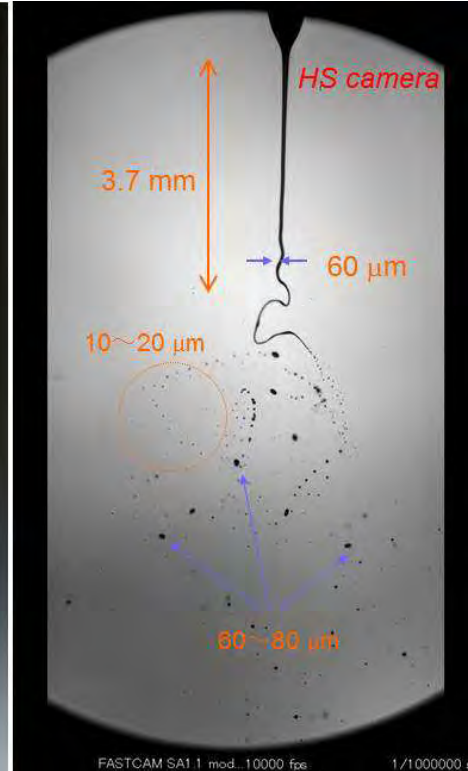
$E \geq E_{\text{onset}}$

- Taylor cone formation (force balance)





Electrospray



ICCD imaging

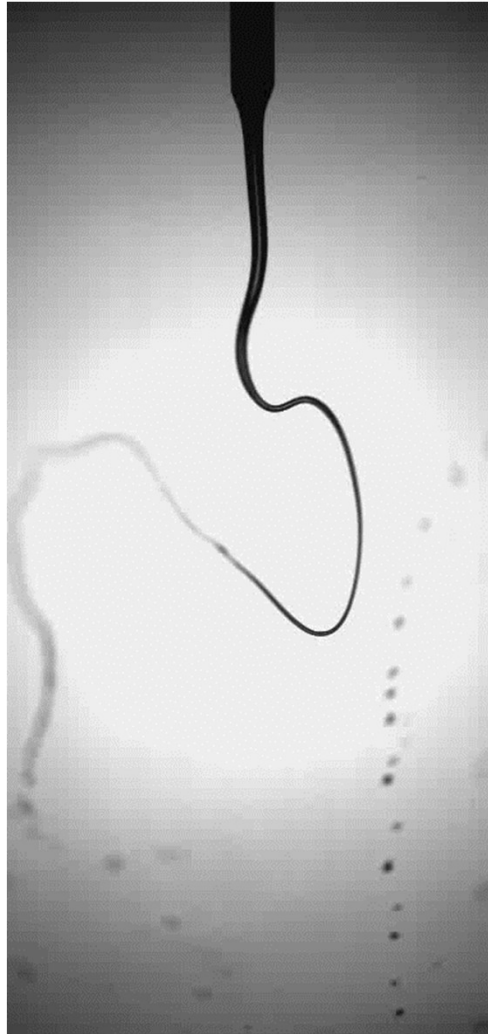
- B. Pongrac et al., *IEEE Trans. Plasma Sci.* 2011
- B. Pongrac et al., *J. Phys. D Appl. Phys.* 2014
- B. Pongrac et al., *J. Aerosol. Sci.* 2016
- A. Jaworek et al., *J. Phys. D Appl. Phys.* 2019



Electrospray : Influence of water conductivity



2 $\mu\text{S/cm}$,
4 ml/min,
14 kV

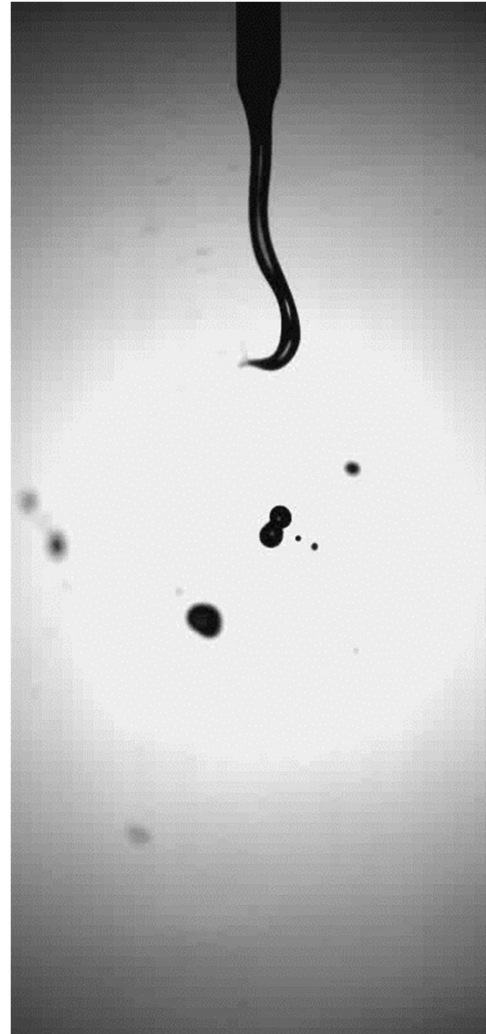


t_{exp} 1 μs

10 000 fps

1 s = 0.5 ms

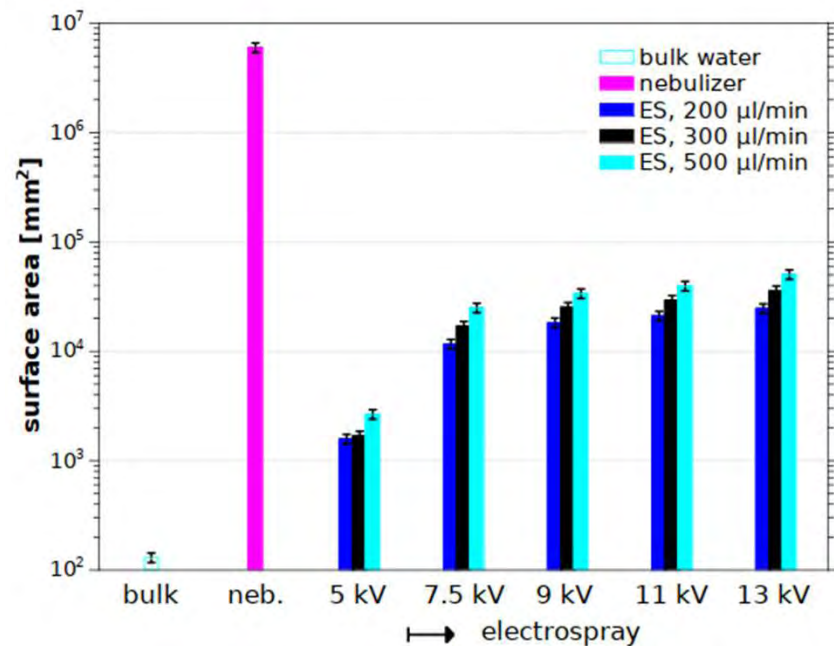
400 $\mu\text{S/cm}$,
4 ml/min,
14 kV



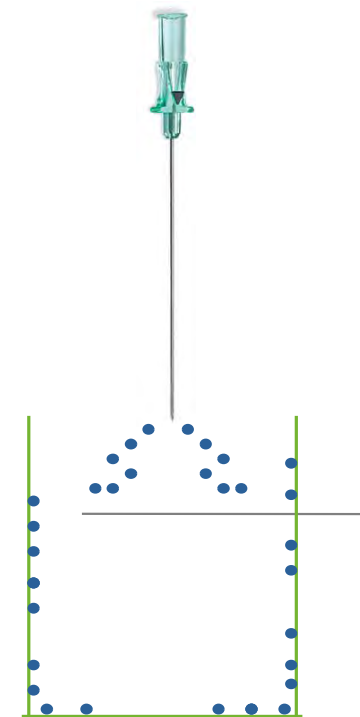
- B. Pongrácz et al., Eur. Phys. J. D
2014



Surface area of ES/nebulized microdroplets vs. bulk



Total surface area of water microdroplets formed by ES, nebulizer and bulk water, 1 min, different *water flow rates* and *applied voltage*



- Solvation (transport) of RONS is determined by the **surface area x treatment time**
- Total microdroplet treatment time: both **flying (ES) time** << **sitting on the bottom/walls time** contribute to the solvation

- Nebulizer 1-5 µm microdroplets << ES
- M.E. Hassan et al., *Water* 2021
- M.E. Hassan et al., *Plasma Chem. Plasma Proc.* 2024



Solvation of O_3 / H_2O_2 into water bulk vs. microdroplets



O_3

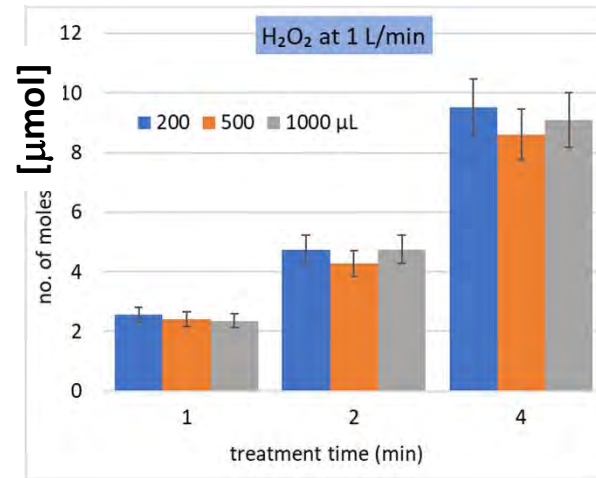
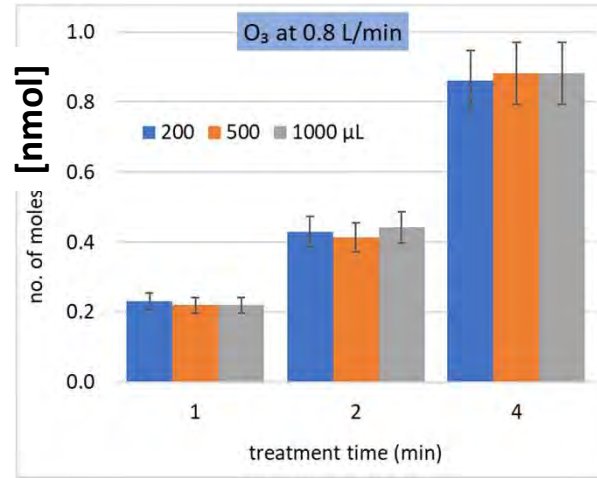
H_2O_2

H_2O_2 : $k_H \approx 9 \times 10^2 \text{ mol/m}^3 \text{ Pa}$

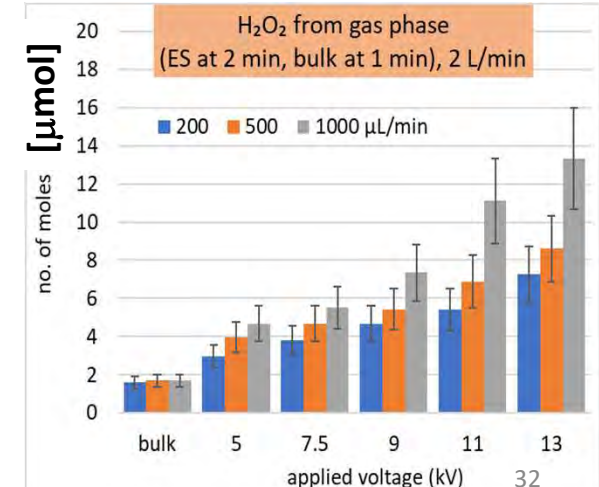
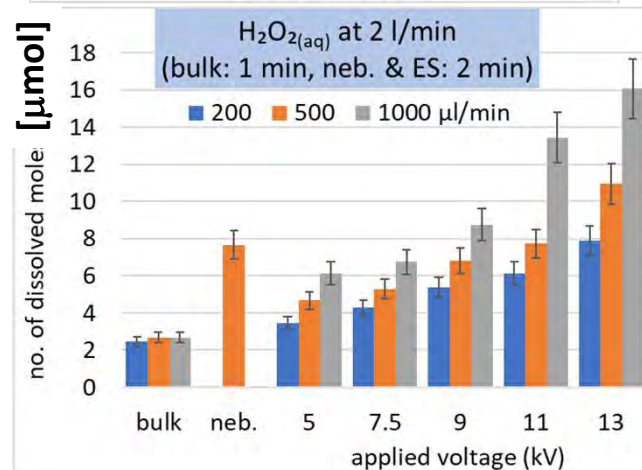
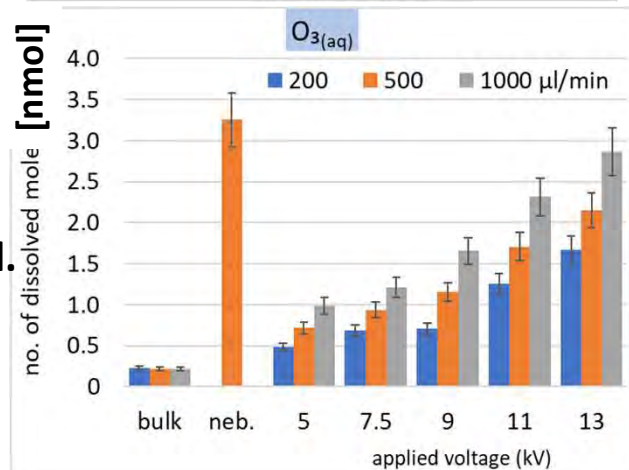
O_3 : $k_H \approx 10^{-4} \text{ mol/m}^3 \text{ Pa}$

- O_3 is gas–water interface area-dependent – low k_H and slow diffusion
- H_2O_2 is very soluble - **depletion from the gas** and slow diffusion into water

bulk

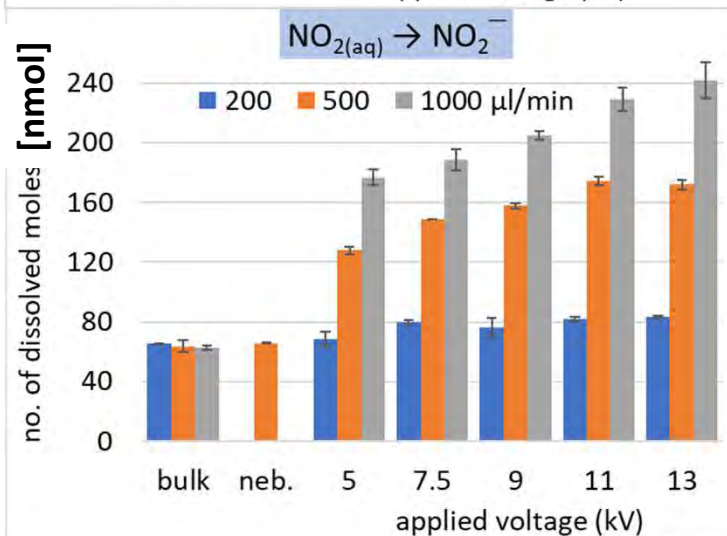
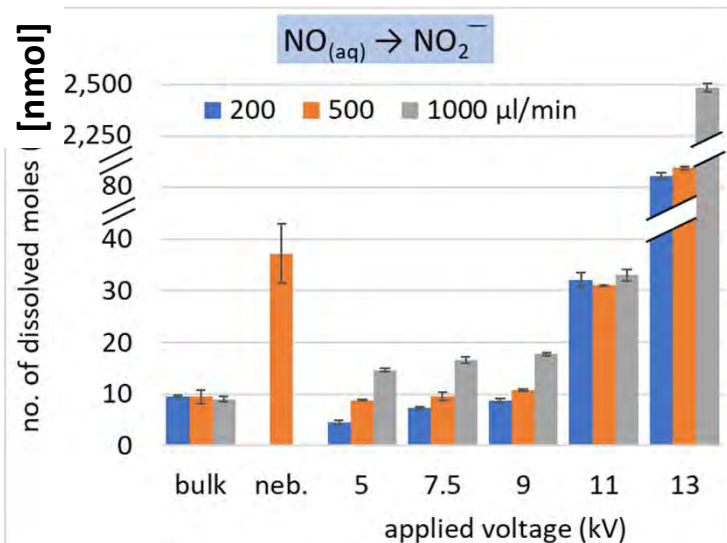


ES /
nebul.



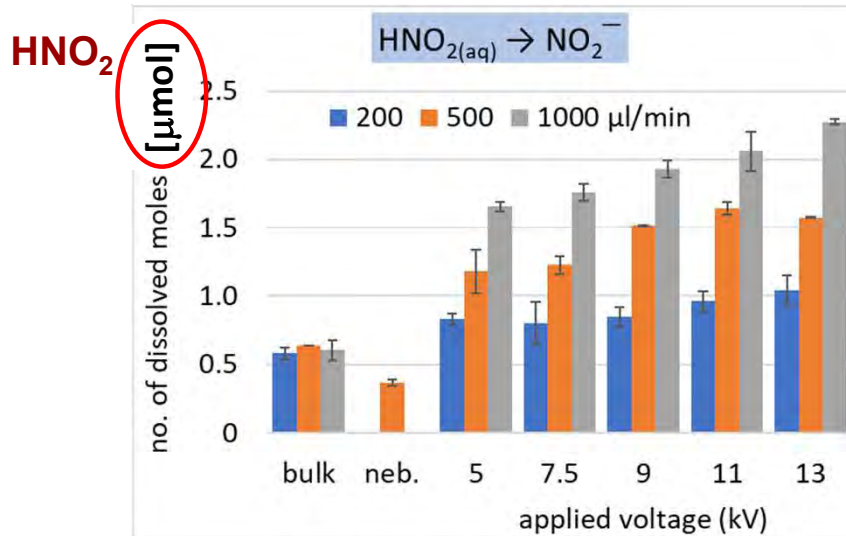


Solvation RNS into water bulk vs. microdroplets



Solvation of

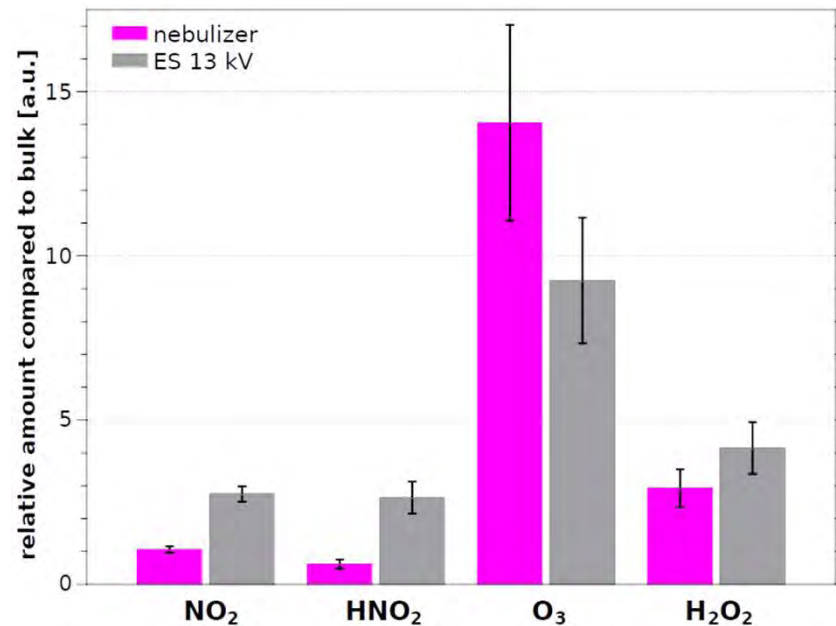
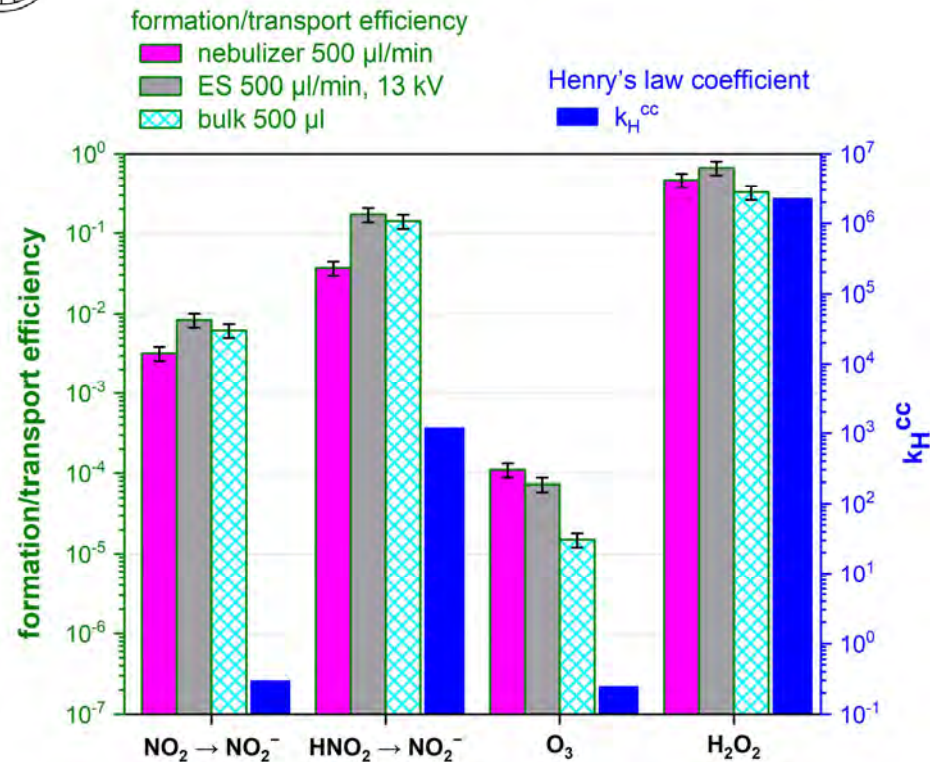
- (H)NO_x is higher than Henry's law – ionize into **NO₂⁻** and quickly diffuse in liquid water
- **NO** is gas – water interface area-dependent - low k_H
- **NO₂** solvation is **charge-dependent** – enhanced in ES, not in nebulizer
- **HNO₂** is a dominant source of **NO₂⁻** and is **charge-dependent**



- M. Janda et al., *Appl. Sci.* (2021)
- M. Hassan et al., *PCPP* (2024)



NO_2^- formation or $\text{H}_2\text{O}_2/\text{O}_3$ transport efficiencies vs. Henry's law

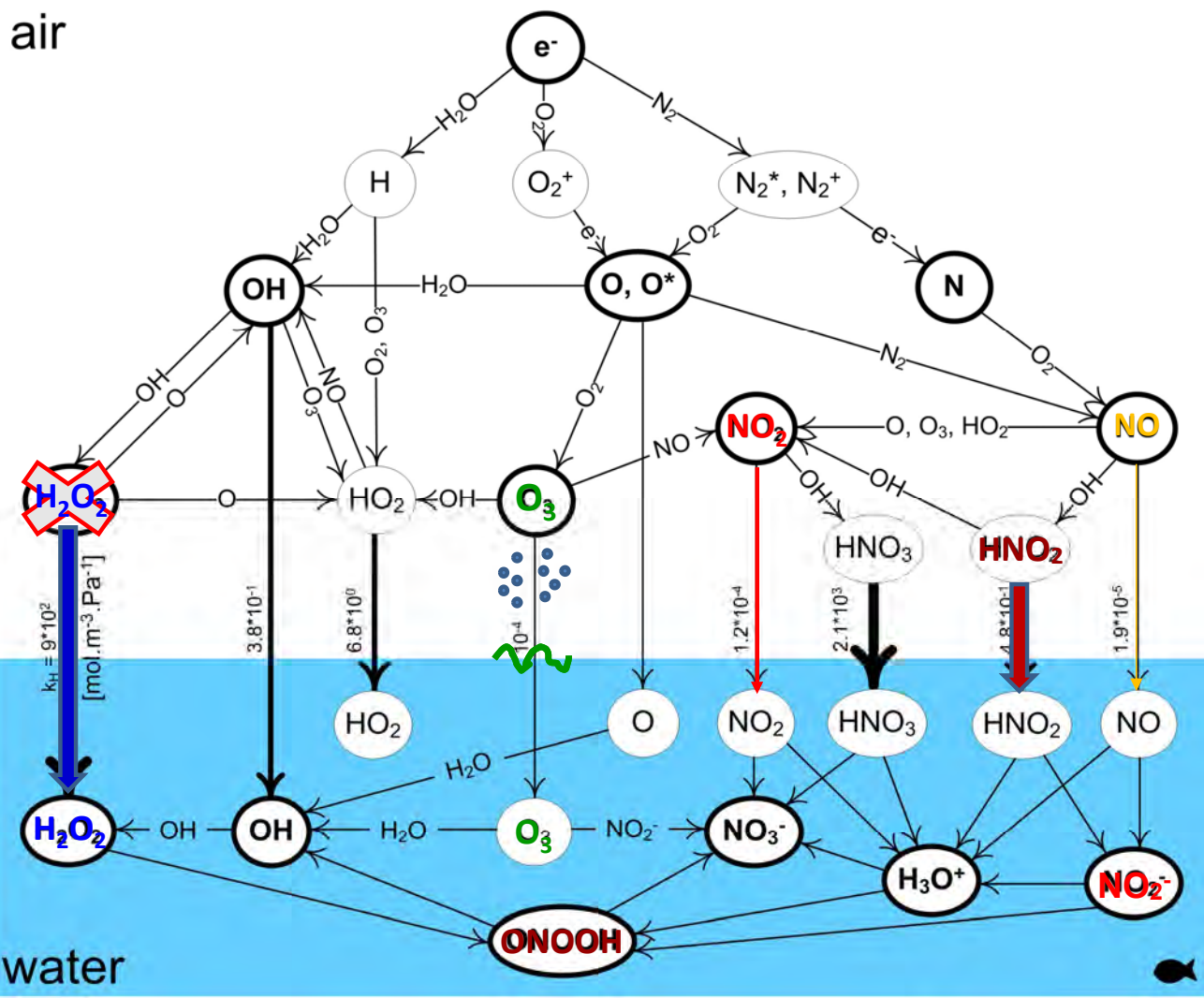


Formation efficiency of NO_2^- from NO_2 and from HNO_2 , and the transport efficiency of O_3 and H_2O_2 in the nebulized/ES microdroplets (13 kV, 2 minutes, 500 $\mu\text{l}/\text{min}$), and bulk water (1 minute, 500 μl) with the dimensionless Henry's law coefficients of NO_2 , HNO_2 , O_3 , and H_2O_2 .

Relative increase in the molar amount of NO_2^- ions formed from NO_2 or HNO_2 , and the solvated O_3 and H_2O_2 in **ES** (13 kV, 2 min, 500 $\mu\text{l}/\text{min}$) and **nebulized microdroplets** (in 2 min, 500 $\mu\text{l}/\text{min}$) **with respect to the bulk water** (1 min, 1000 μl).

Summary: transport of RONS

air



- Transport processes of RONS (H_2O_2 , O_3 and HNO_2 , NO_2 , NO) into bulk water vs. electrosprayed/nebulized microdroplets

– O_3 solvation depends on gas–water interface area - microdroplets

– H_2O_2 is very soluble – but **depletion from the gas**

– $(\text{H})\text{NO}_x$ solvation – transport is better than Henry's law – effects of charge, liquid $\text{NO}_2^-(\text{aq})$ ions

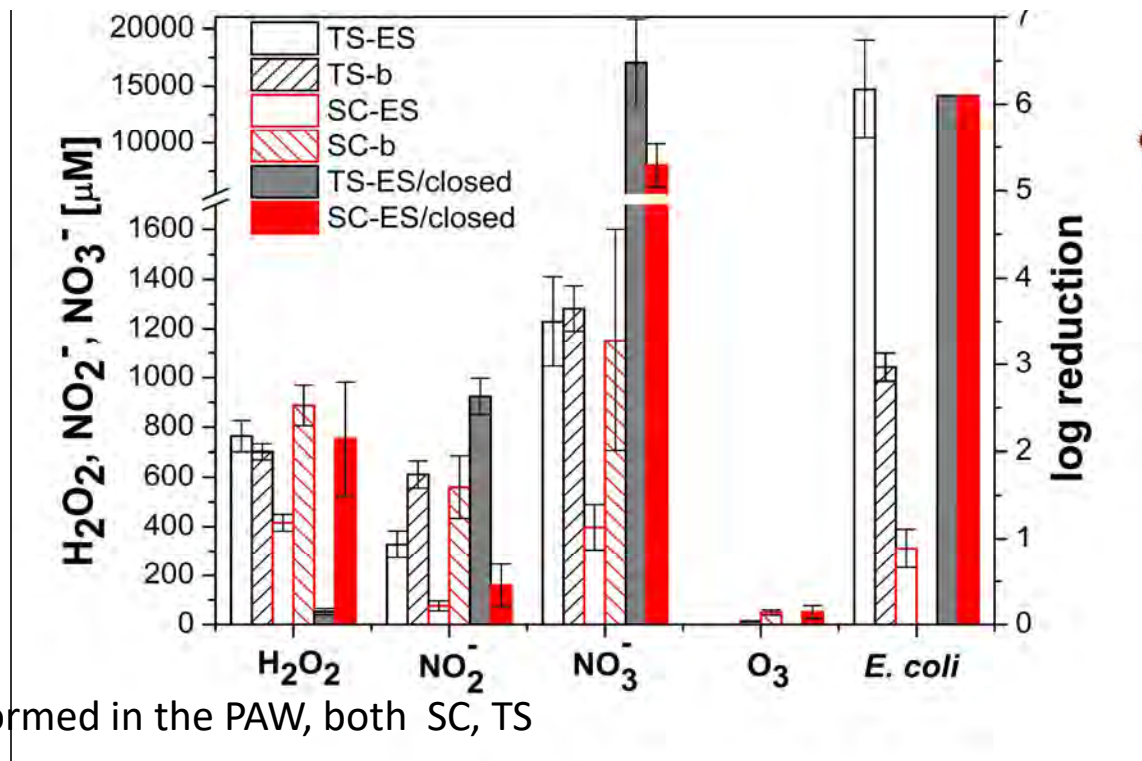
– HNO_2 is a dominant source of $\text{NO}_2^-(\text{aq})$

- Understanding plasma species chemistry and transport → **tuning PAW composition/properties** and specific applications

water



TS-SC: Aqueous RONS vs. antibacterial effect



- H₂O₂, NO₂⁻, NO₃⁻, O₃ formed in the PAW, both SC, TS
- PAW composition correlates with the antibacterial effect:
 - H₂O₂ + NO₂⁻ + H⁺ → **ONOOH** + H₂O → **·OH** + NO₂
– dominant mechanism in TS (open)
 - **Acidified nitrite**: NO₂⁻ and NO₃⁻ in acidic pH - dominates in TS (closed)
 - **Ozone + H₂O₂ rich PAW** - dominates in SC

B. Tarabova et al., *Plasma Proces. Polym.* 2018

• Z. Machala et al., *J Phys. D* 2019

• J. Pawlat et al., *Plas.Chem. Plas. Process.* 2019



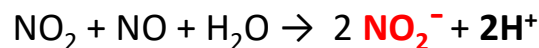
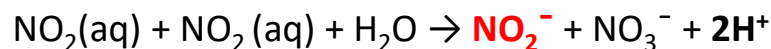
Aqueous chemistry in air discharges with water



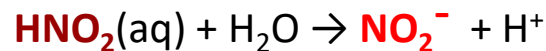
H_2O_2 formed from $\cdot\text{OH}$ radicals produced in air plasmas that readily dissolves in water



Solvation of NO_x into water $\rightarrow$ acidification



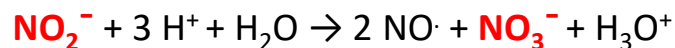
Gaseous HNO_2 - dominant source of NO_2^-



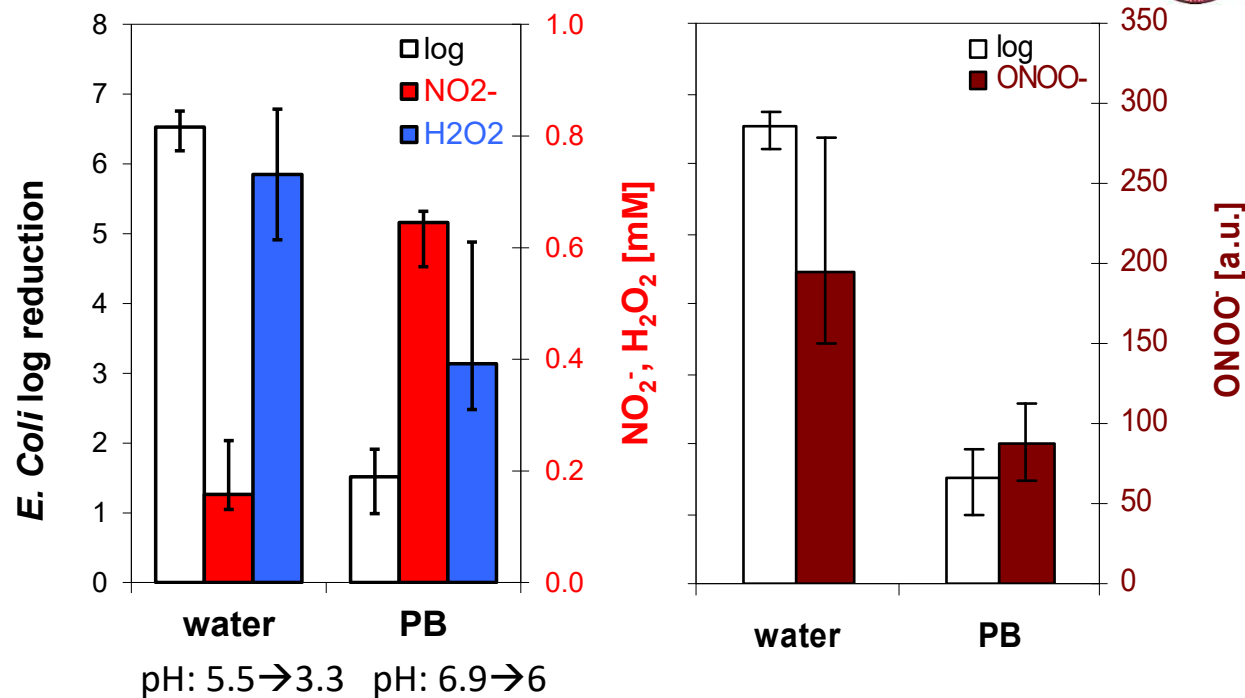
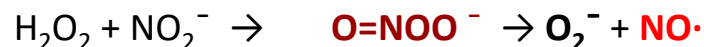
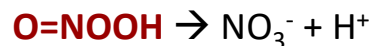
Nitrites NO_2^- decay in acidified water



acidic disproportionation



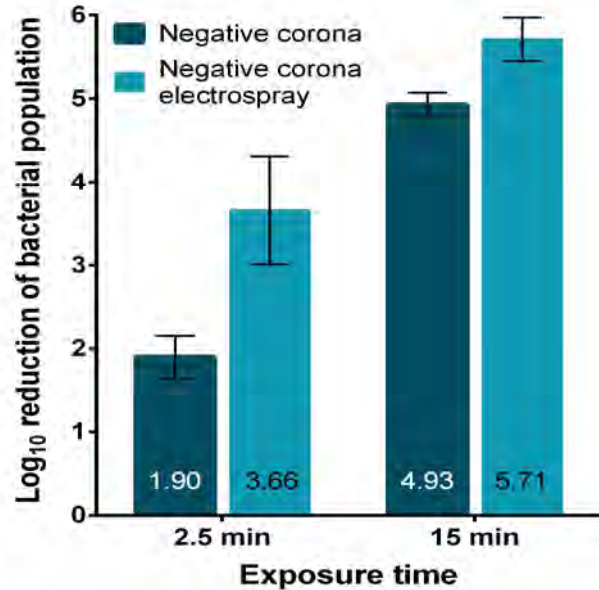
Both NO_2^- and H_2O_2 in acidified water $\rightarrow$ **peroxynitrites**



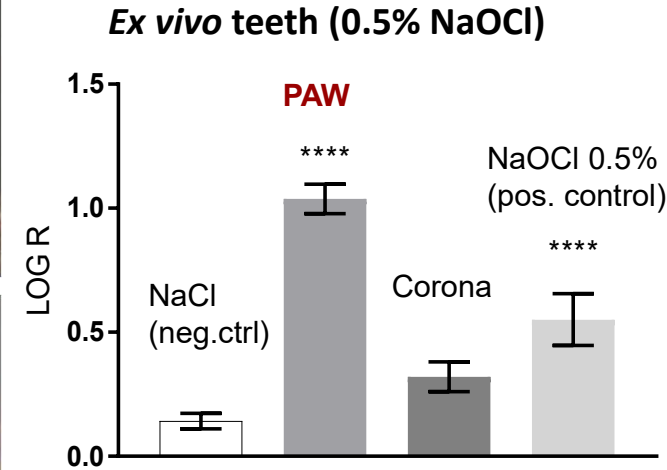
- Z. Machala et al. *Plasma Process. Polym.* 2013
- P. Lukes, *Plasma Sources Sci. Technol.* 2014
- Z. Machala et al., *J Phys. D* 2019
- M. Janda et al., *Appl. Sci.* 2021



Biofilm decontamination, endodontics



E. coli biofilm on glass



Endodontics

- *E. faecalis* biofilm in tooth root canal
- Saline solution control
- PAW or corona-direct treatment

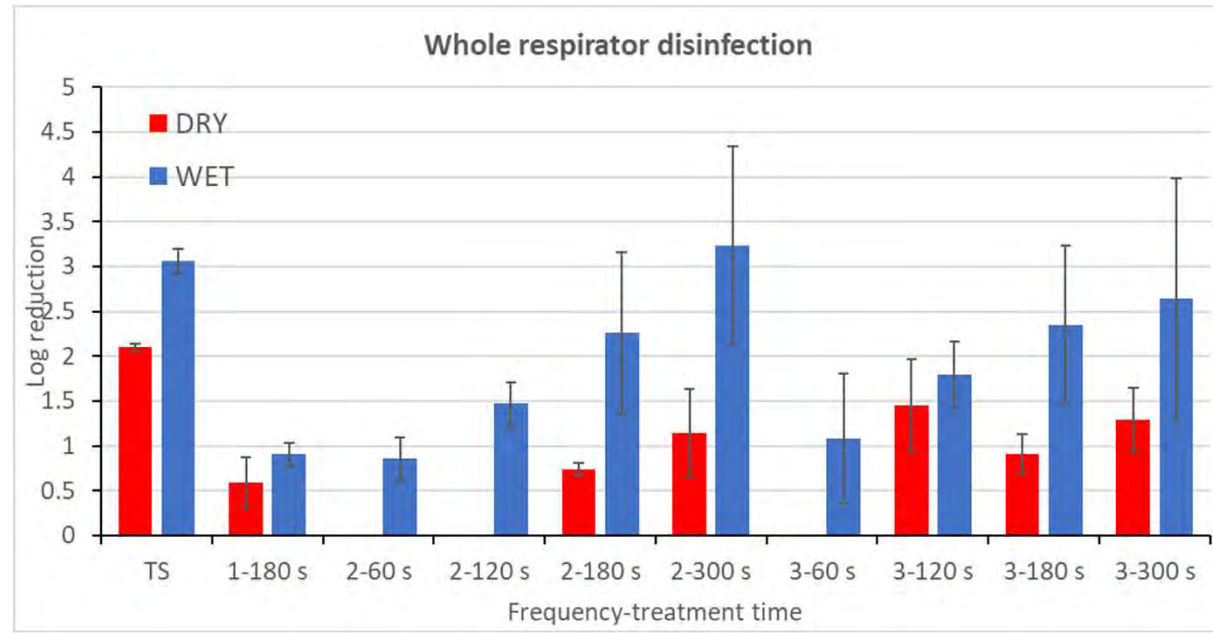
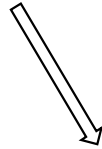
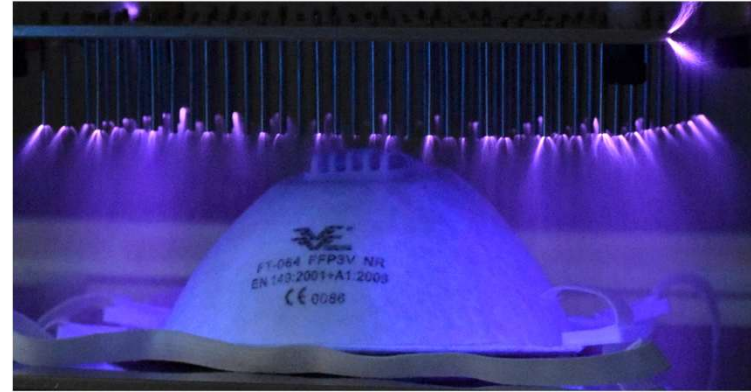
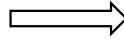
- Z. Šipoldová et al., *IEEE Trans. Plasma Sci.* 2011
- Z. Kovaľová et al., *Eur. Phys. J. Appl. Phys.* 2013
- Z. Kovaľová et al., *J. Phys. D. Appl. Phys.* 2014
- Z. Kovaľová et al., *Bioelectrochem.* 2016



Air plasma for respirator disinfection

Air plasma against COVID-19:

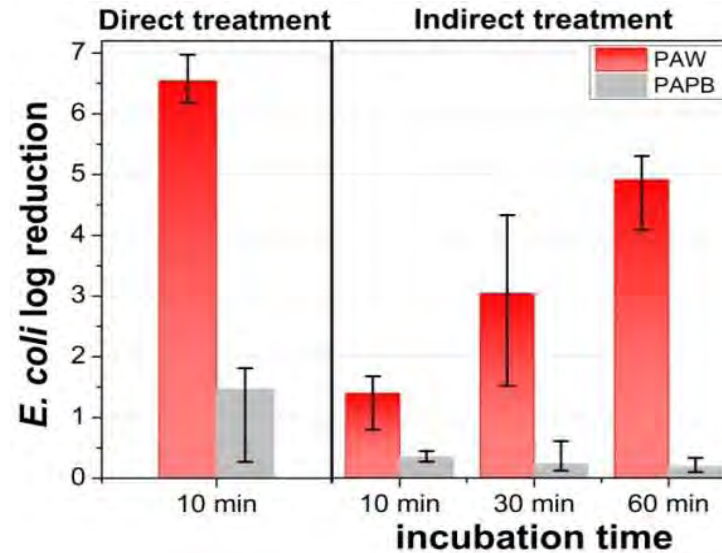
- air decontamination
- Respirator decontamination by indirect **TS** or **multipin pulsed streamer corona** (tested on sprayed *E. coli* as model pathogen)
- **Wet respirators** show stronger decontamination effect





Direct TS vs. PAW antibacterial effects

- Antibacterial effects strong in water, weak in buffered solutions
- **Direct TS stronger than PAW** only
- **Electrospray stronger** than batch treatment
- Effect of **short-lived RONS** or **electric field**?



Direct TS-ES vs. **PAW** or PA-phosphate buffer
TS-ES treated 10 min and incubated
with *E. coli* for 10, 30, 60 min at room T

- Antibacterial effect is enhanced by longer incubation in PAW
– **effect of long-lived RONS** or later-induced chemistry

- Z. Machala et al., *J. Phys. D Appl. Phys.* 2010
- Z. Machala et al., *Plasma Proc. Polym.* 2013

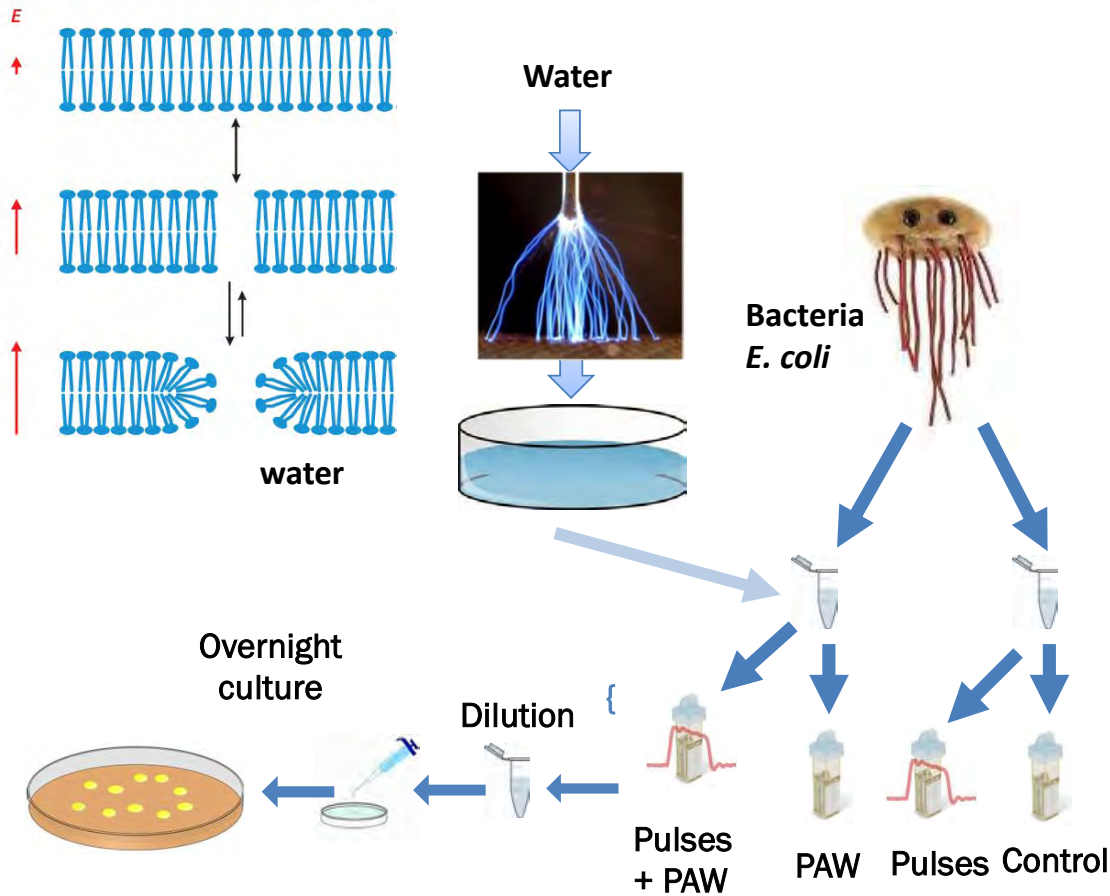


Combined effect of PAW and pulsed electric field

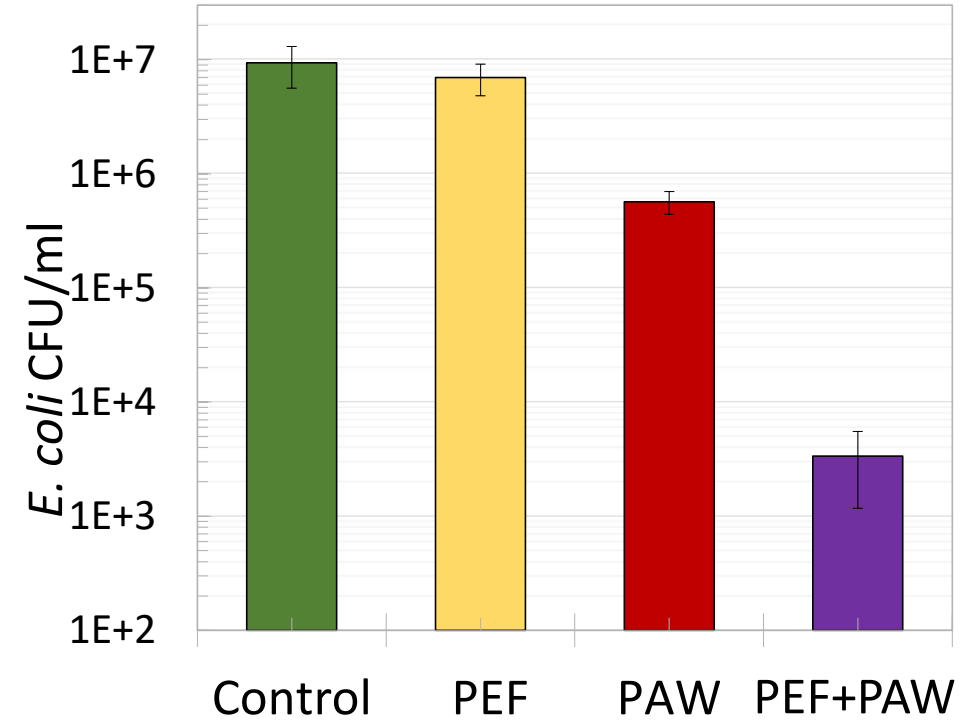


Effect of electric field

Electropermeabilization combined with RONS in PAW – enhanced



200ns Pulses 1kHz; 10s; 12.5kV/cm;
15min incubation

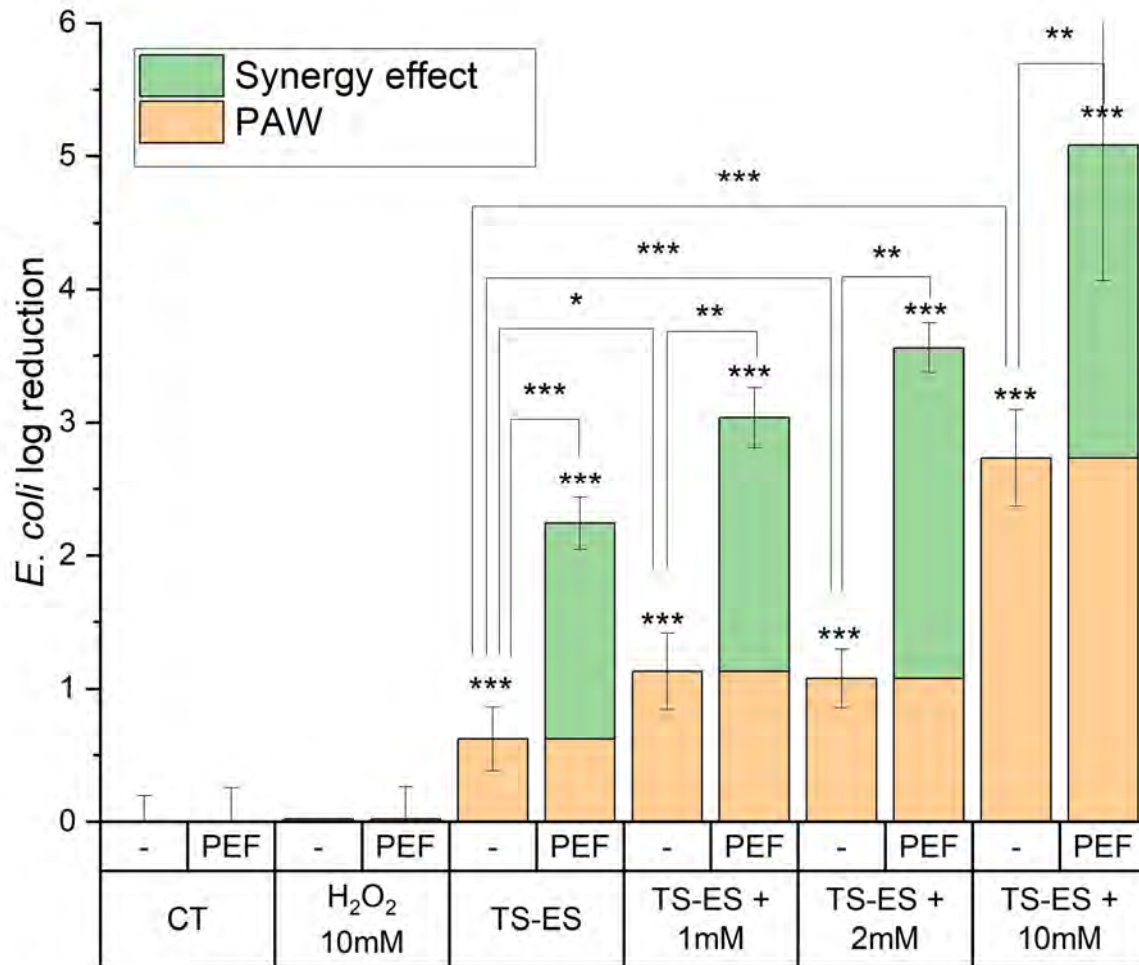




PAW+ pulsed electric field synergic antibacterial effect



- PEF treatment only: no antibacterial effect
- H_2O_2 only: no antibacterial effect
- **Open air TS-ES PAW + PEF: synergy effect** thanks to both H_2O_2 and NO_2^-
- $\text{H}_2\text{O}_2 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{O}=\text{NOOH} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{NO}_2\cdot + \text{H}_2\text{O}$
- Antibacterial effect and synergy increased with adding H_2O_2

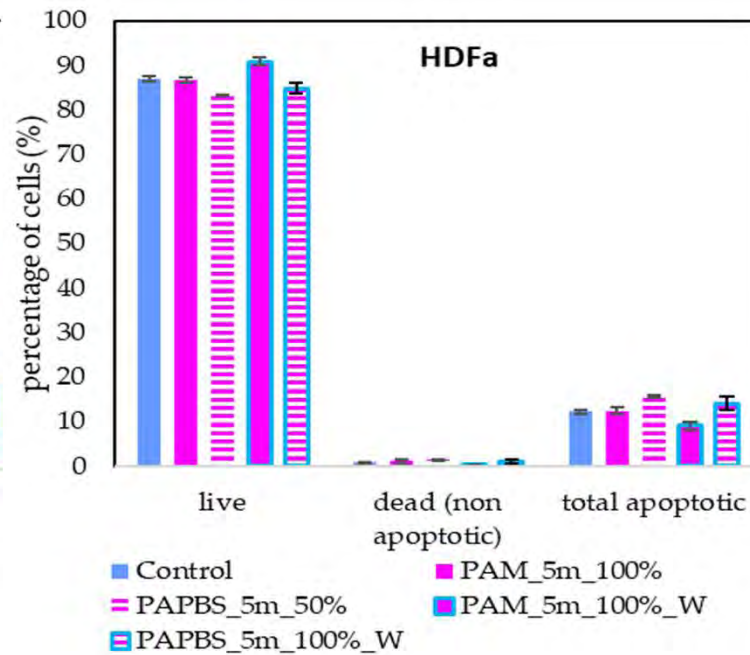
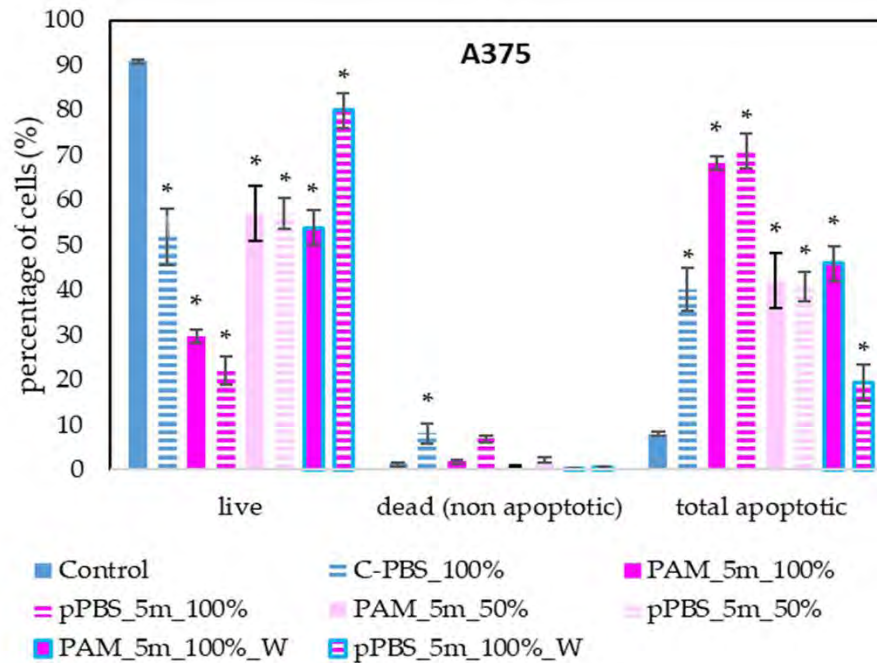




Cancer cell apoptosis induction by PAM/PAPBS

- **Human melanoma epithelial cancer cells A375**, normal human fibroblasts HDFa, Muse® Annexin V & Dead Cell Kit – flow cytometry
- Streamer corona treatment of cell culture medium or PBS, 5 min, 12.8 kV, 1 cm, 5 ml
- 50% diluted or 100% PAM/PAPBS, **W**-washed after 30 min of incubation in PAM/PAPBS

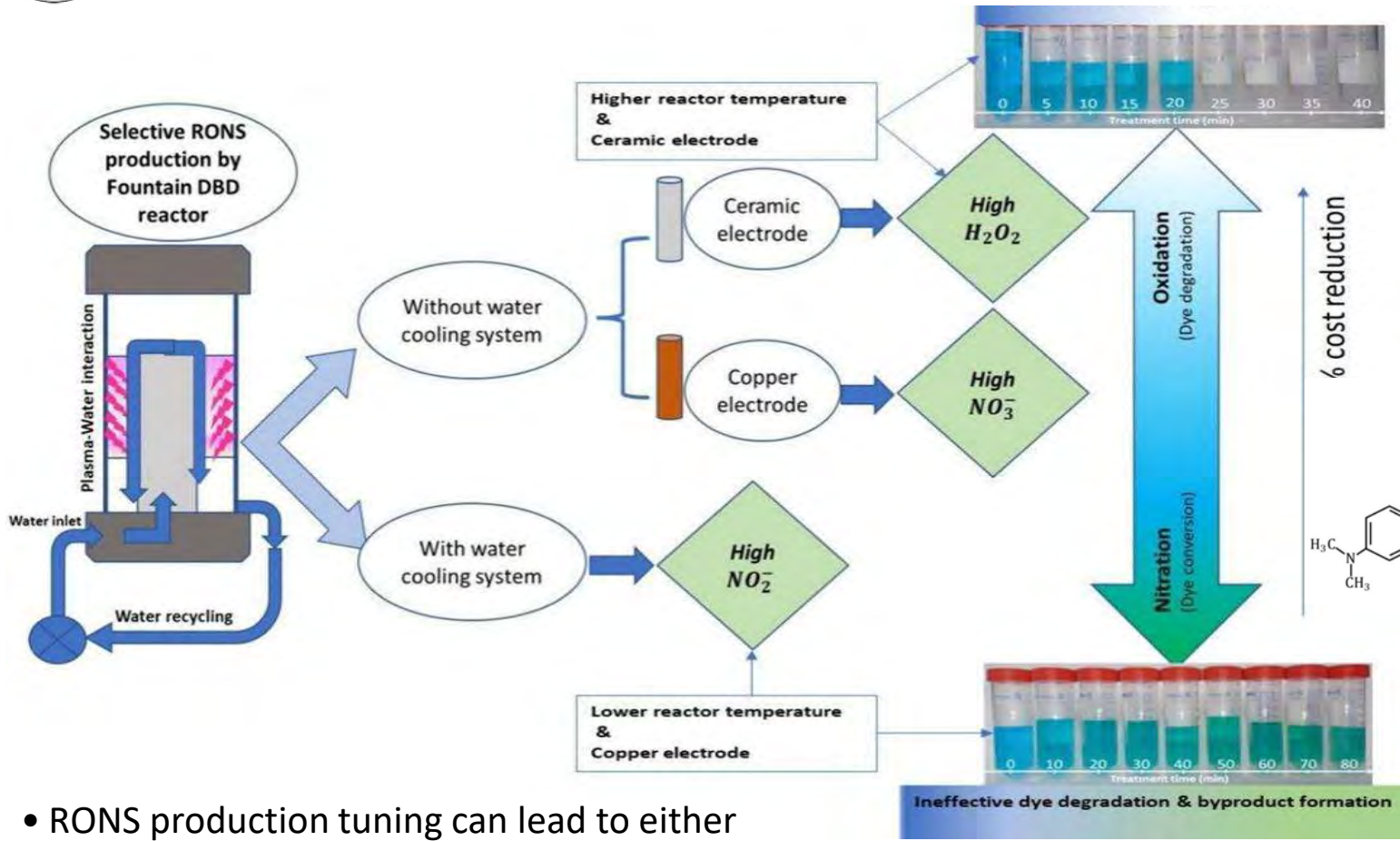
Collaboration with H. Gbelcová, V. Repiska
**Faculty of Medicine,
Comenius Univ.
Bratislava**



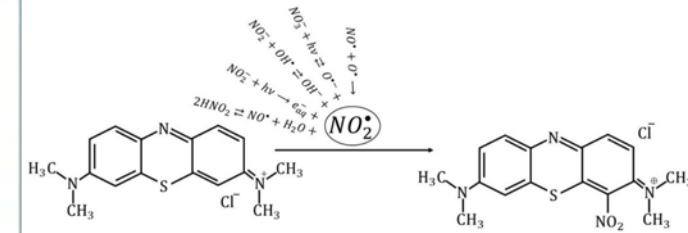
- **PAM and PAPBS** reduced cancer cell viability and caused **apoptosis**, even after washing – **no apoptosis in normal cells!**
 - D. Sersenova et al., *Molecules* 2021



Fountain DBD with liquid electrode: RONS tuning in PAW



oxidation



nitration

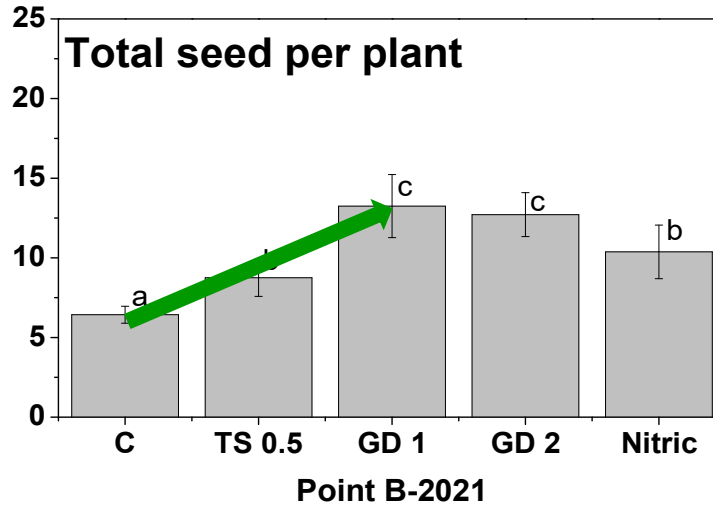
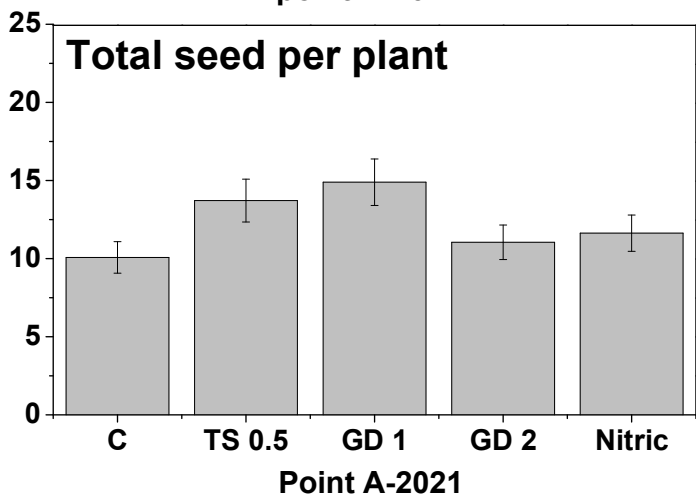
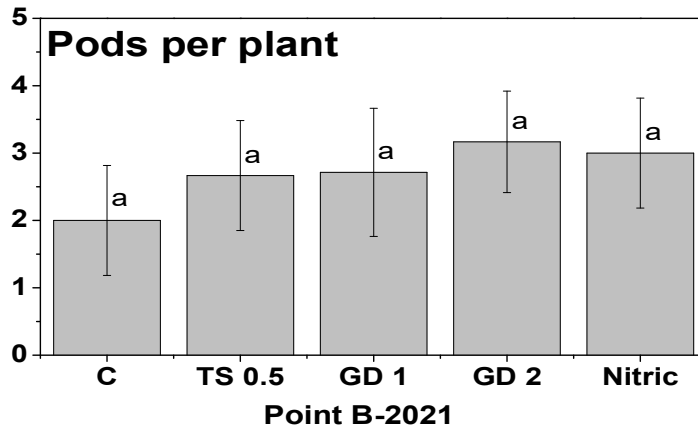
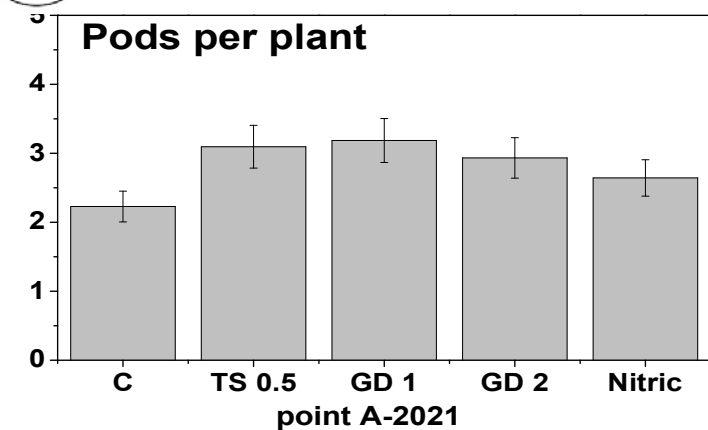
- S. Kooshki et al., *J. Water Proc. Eng.* 2024



Outdoor field planting: PAW-priming enhanced pea yield



Pea (*Pisum sativum* L. cv. Eso)



Pods and total seeds per plant, point A-2021 and point B-2021.

C – control, plasma: TS-0.5, GD 1, GD 2, and Nitric (pos. ctrl.)

Collaboration with R. Švubová,
D. Kostoláni, S. Kyzek
Faculty of Natural Sciences,
Comenius Univ. Bratislava



Hydroponic cultivation in PAW - lettuce



Treatment groups:

- **C- control** (1/2 Hoagland nutrient solution, pH 6.2)
- **CP – control + seed priming in PAW** 1.5h, cultivation in 1/2 Hoagland solution)
- **P - cultivation in TS multineedle PAW** mixed with 1/2 Hoagland
- **PP – PAW + seed priming**

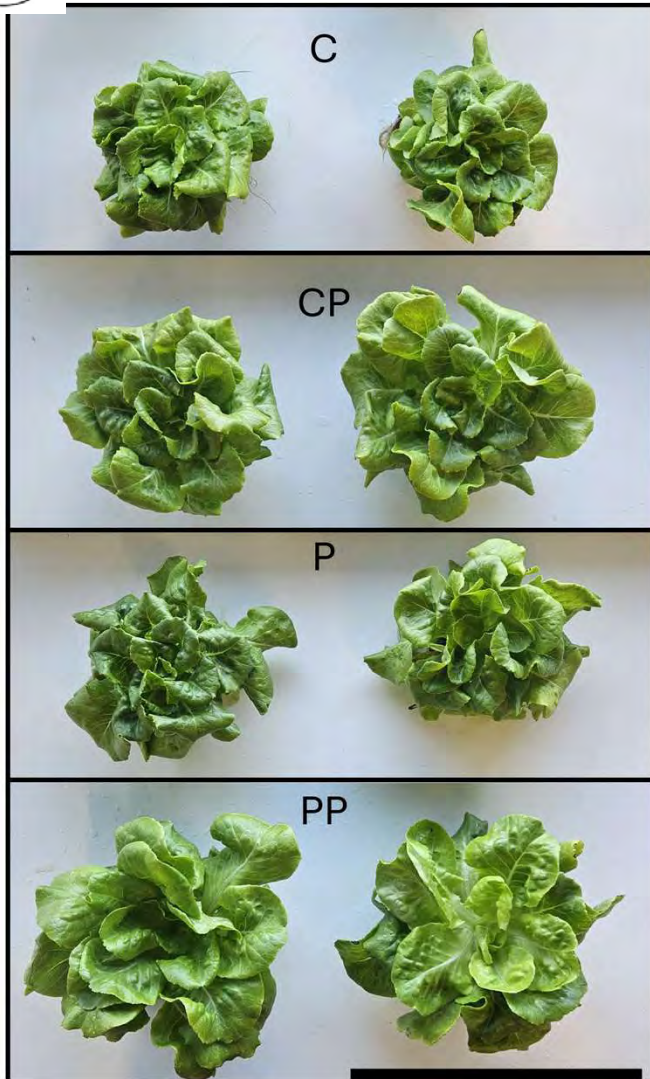
Hydroponic cultivation: 10 weeks

- **Lettuce** *Lactuca sativa* (hybrid Cassini)
- Vertical columns, horizontal systems
- Hoagland and PAW+Hoagland exchanged every week
– based on the progressive decay of H_2O_2 , NO_2^- and NO_3^- were stable
- Solutions were aerated during cultivation
- During the 1st 4 weeks – red/blue light
- Then 16h /8 h white light/dark period
- Light intensity PAR : $250 \mu\text{mol.m}^{-2}.\text{s}^{-1}$
- $T=23^\circ\text{C}$

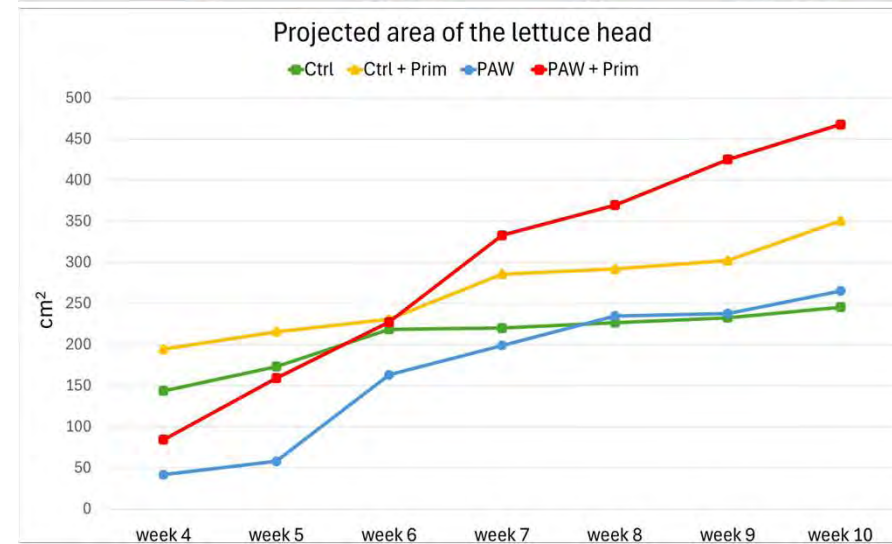
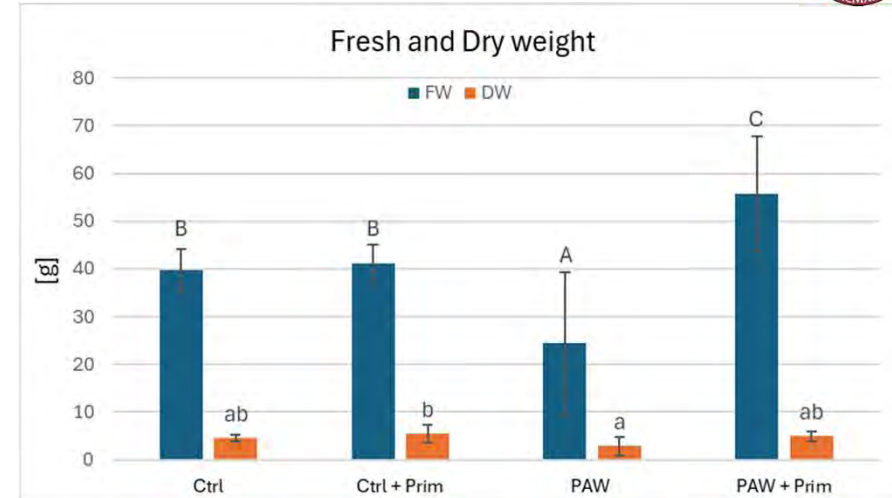




Hydroponic cultivation – PAW enhanced lettuce



- **PAW+ Priming** - the largest fresh leaf area by weight
- PAW - the smallest fresh leaf area
- **PAW+priming** leaves contained more water – juicier – which corresponds to the sensoric test.



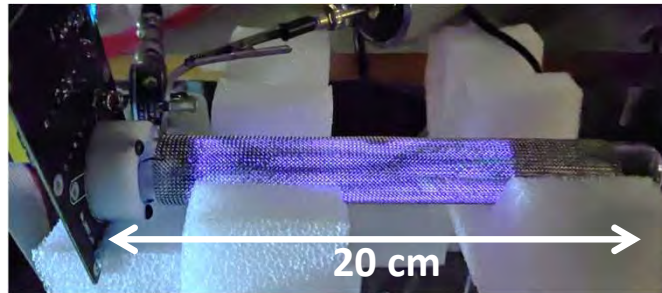
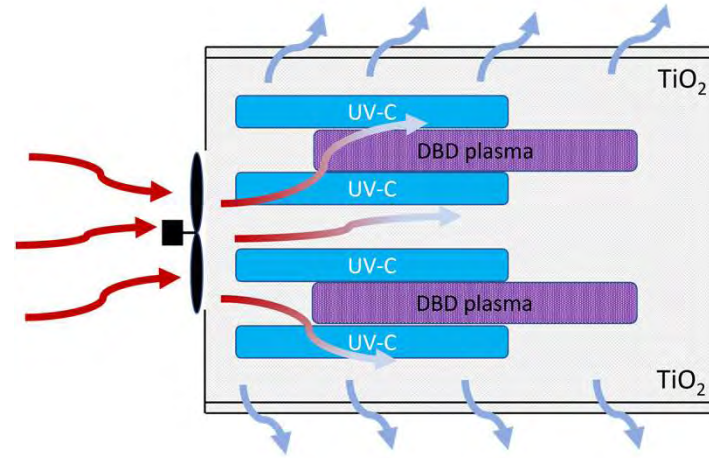


Indoor air decontamination by DBD combined with TiO_2 photocatalysis - system 1

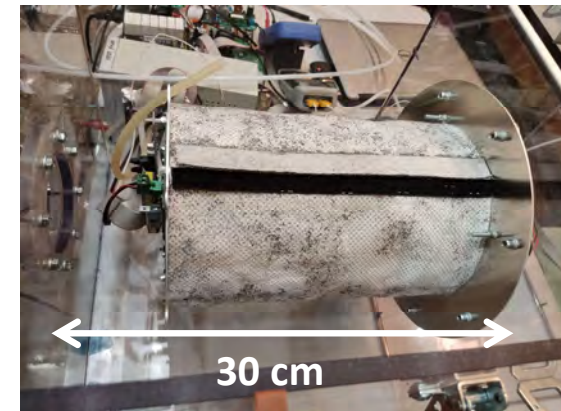


System 1:

- 2 DBD tubes
- 4 UV-C lamps (Hg, 254 nm)
- Low plasma power ~ 30 W (AC ~ 25 kHz)
- Gas flow rate = 100-650 L/min
- Specific Input Energy (SIE) of DBD = 3 J/L



DBD tube



System 1 with TiO_2 layer

- T. Vazquez et al., J. Electrostat. 2025 (under rev.)



Indoor air decontamination by DBD combined with TiO_2 photocatalysis - system 2

System 2:

- DBD module (direct treatment)
- 16 UV-A LEDs (370 nm)
- Higher plasma power $\sim 20\text{-}130\text{ W}$ (AC power supply 40-61 kHz)
- Gas flow rate = 100-650 L/min
- SIE = 2 - 12 J/L

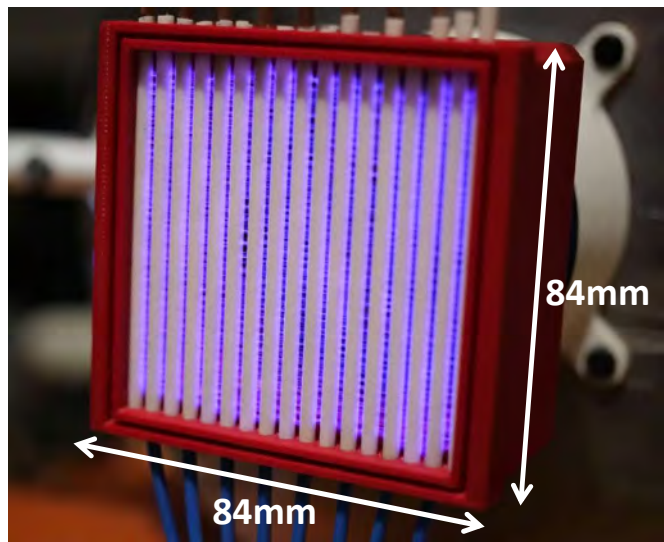
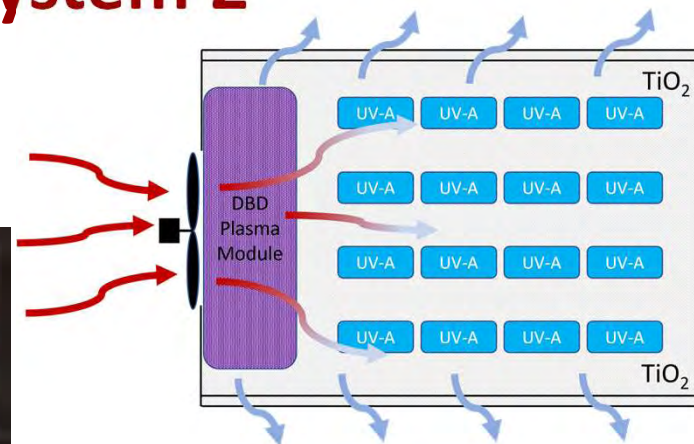


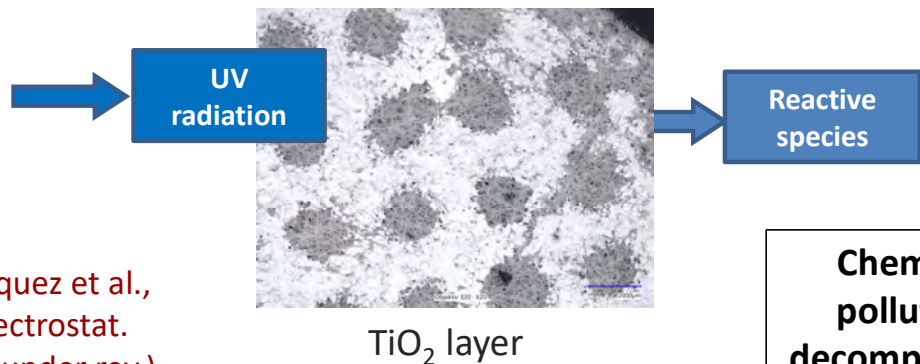
Photo of the DBD module



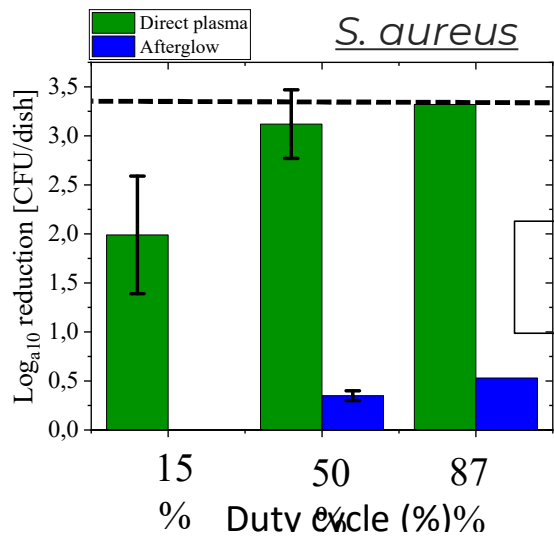
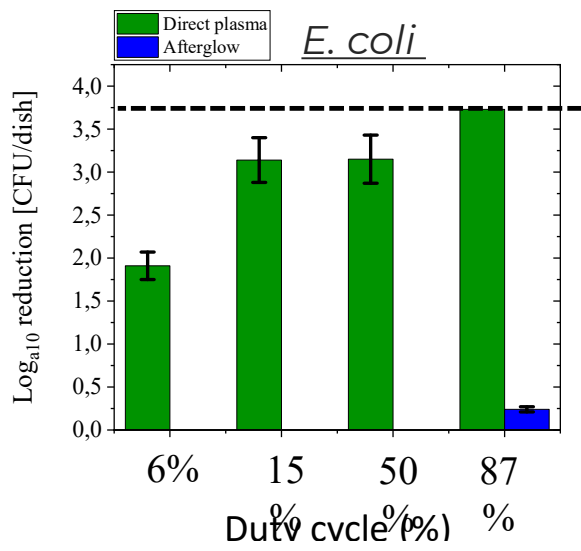
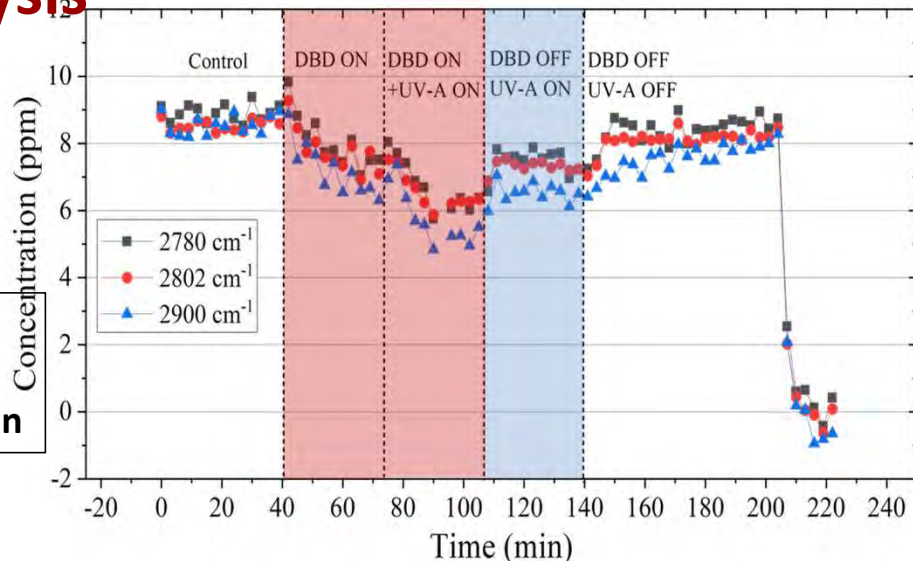
- T. Vazquez et al., J. Electrostat. 2025 (under rev.)



Indoor air decontamination by DBD combined with TiO_2 photocatalysis

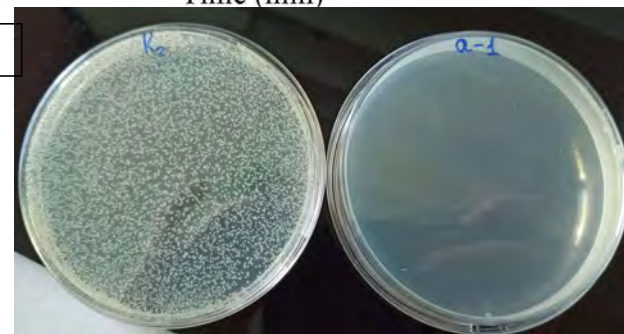


- T. Vazquez et al.,
J. Electrostat.
2025 (under rev.)



100%
inactivation

Bacteria
inactivation



Bio-aerosols containing *E. coli* collected during 60s. Left: control, Right: plasma treated, 87%



Summary

- Air plasma discharges: O_3 vs. NO_x mode – modulated by power, flow rate, reactor geometry
- Air transient spark with added L,C – efficient **N-fixation**
- **Transport processes of RONS** (H_2O_2 , O_3 and HNO_2 , NO_2 , NO) - bulk water vs. electrosprayed/nebulized microdroplets
- **Plasma gas-liquid chemistry and antibacterial effects** in air discharges with water
- Understanding plasma species chemistry and transport into water → **tuning PAW properties** for applications
- (Antimicrobial) PAW effects depend on **PAW chemistry** and synergize with the electric field

Examples of our bio/agro/eviro applications:

- **Dentistry, Wound healing, cancer treatment** – portable corona pen, respirator and indoor air disinfection
- Effects on **plant growth enhancement** depend on PAW composition
- Indoor air decontamination by DBD plasma + TiO_2 photocatalysis