INSTITUTE OF PLASMA PHYSICS
OF THE CZECH ACADEMY OF SCIENCES

CHEMISTRY ASSOCIATED WITH PLASMA-LIQUID INTERACTIONS: CHALLENGES AND OPPORTUNITIES

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IAEA Technical Meeting on Emerging Applications of Plasma Science and Technology, Vienna, Austria, Sep 19 – 22, 2023

PLASMA-LIQUID INTERACTIONS

TARGET APPLICATIONS USING PLASMA-LIQUID INTERACTIONS

a) Environmental (water treatment)

b) Biological (medicine)

c) Agriculture

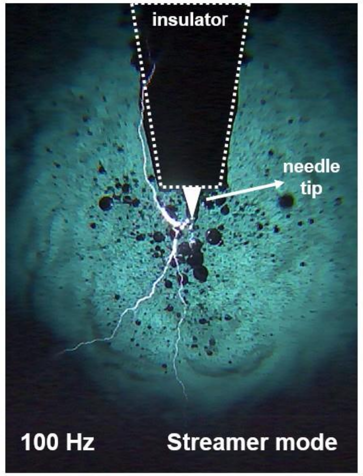
d) Materials processing

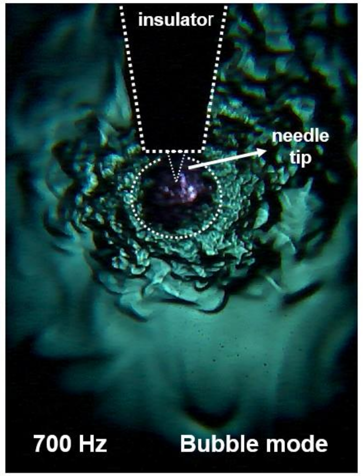
FUNDAMENTAL KNOWLEWDGE OF PHYSICAL, CHEMICAL, BIOLOGICAL PROCESSES/MECHANISMS INDUCED BY PLASMA: CHALLENGES & OPPORTUNITIES

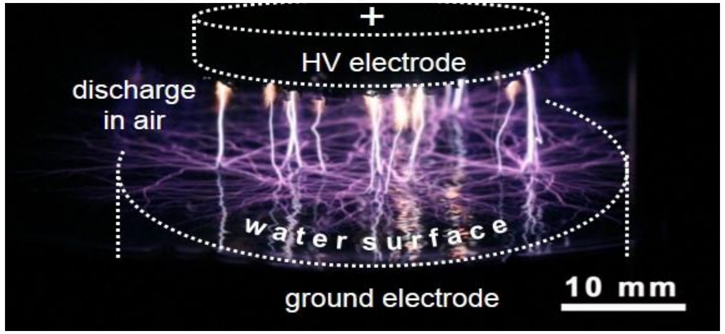
Effects dependent on the contact of plasma with liquid, power, electron density, physical properties and chemical composition of gas and liquid;

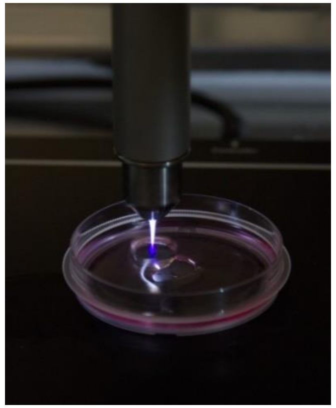
a) plasma formed directly in liquid - physical processes are more significant

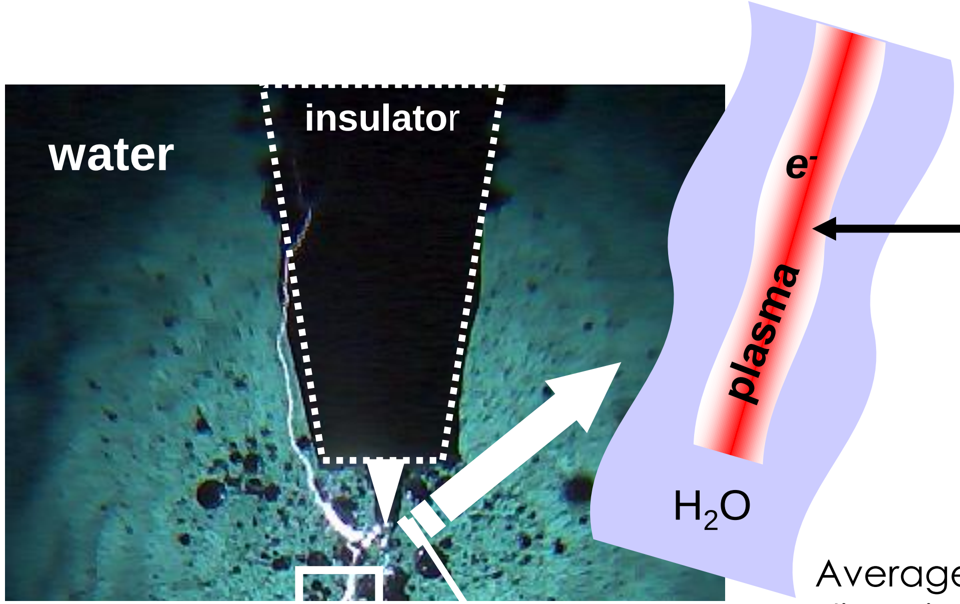
b) plasma formed in the gas phase in contact with liquid (in bubbles, droplets, aerosols, liquid spray, liquid surface) – chemical effects are dominant











Initiation reactions by discharge (plasma channel)

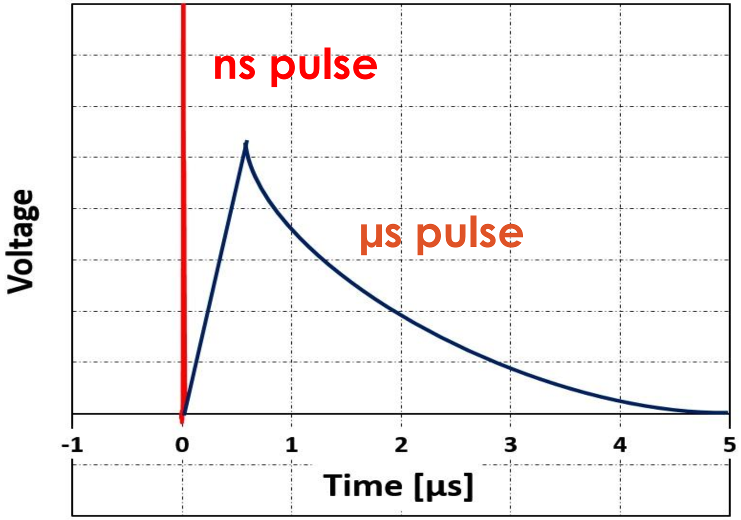
$H_2O + e^- \longrightarrow \bullet H + \bullet OH + e^-$

$H_2O + e^- \longrightarrow \bullet H + \bullet O + \bullet H + e^-$

$H_2O + e^- \longrightarrow H_2 + \bullet O + e^-$

$H_2O + e^- \longrightarrow H_2O^+ + 2\,e^-$

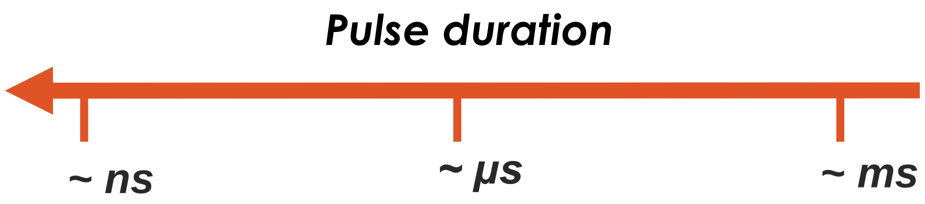
$H_2O + M \longrightarrow \bullet H + \bullet OH + M$



Average T_e in underwater plasma ~ 0.5 - 2 eV, which is insufficient for direct dissociation of water. More likely multistep process incl. charge exchange reactions of atomic ions with water molecules and subsequent dissociative recombination

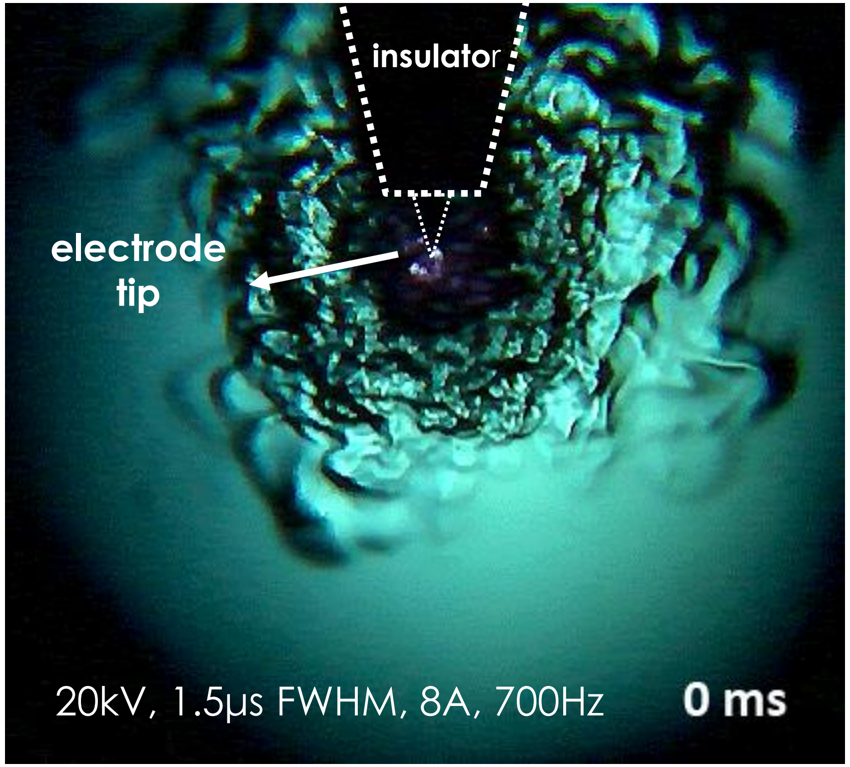
$e^- + H_2O^+ \rightarrow OH\bullet + H\bullet$; $e^- + H_3O^+ \rightarrow OH\bullet + H_2 + e^-$

What are time scales of these processes? Does pulse duration affect these processes?



THERMAL EFFECTS

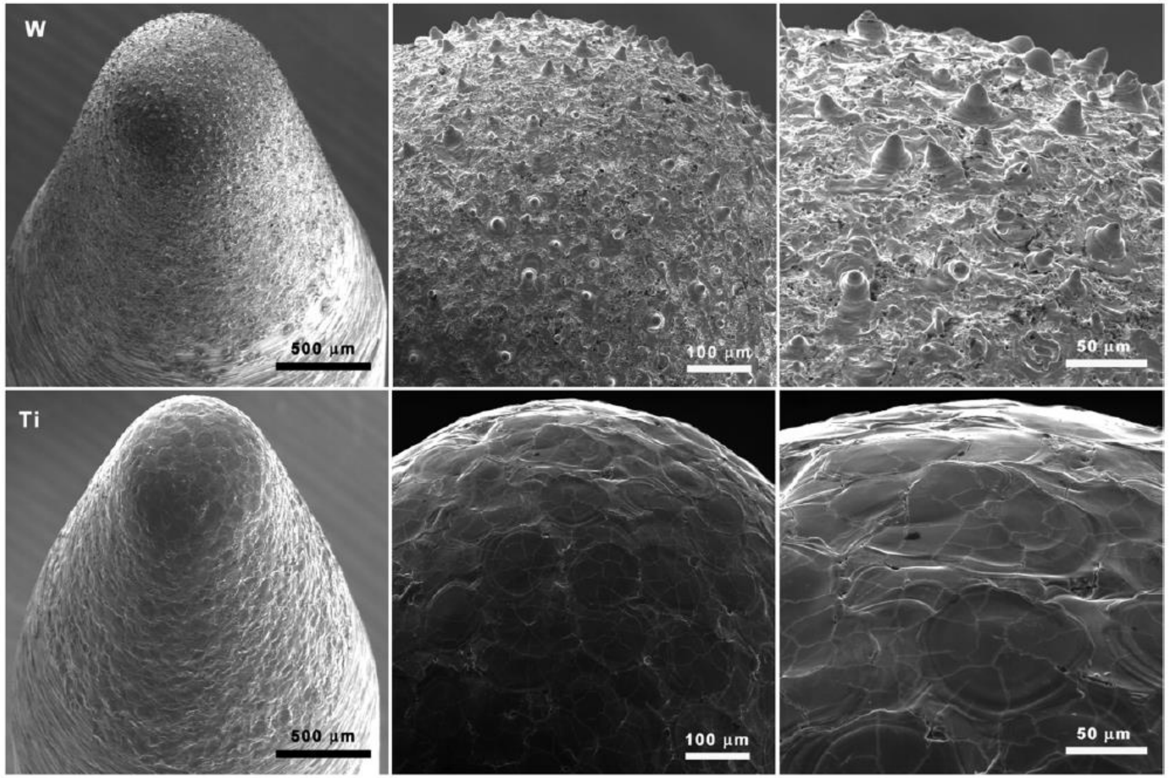
(applied power, liquid conductivity)



Ruma, Lukes (2013) *J. Phys. D: Appl. Phys.* 46: 125202

EROSION OF ELECTRODES

(sputtering, melting of metals by plasma)



Lukes et al (2006) *Czech. J. Phys.* 56: B916; Lukes et al (2011) *Plasma Sources Sci. Technol.* 20: 034011

PLASMA-LIQUID INTERACTIONS

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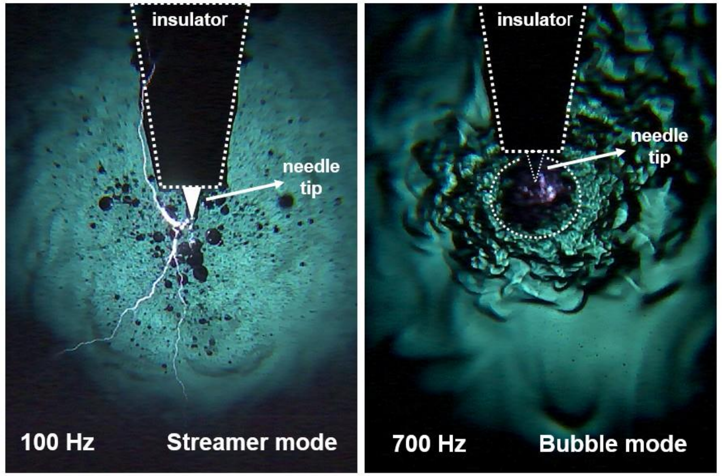
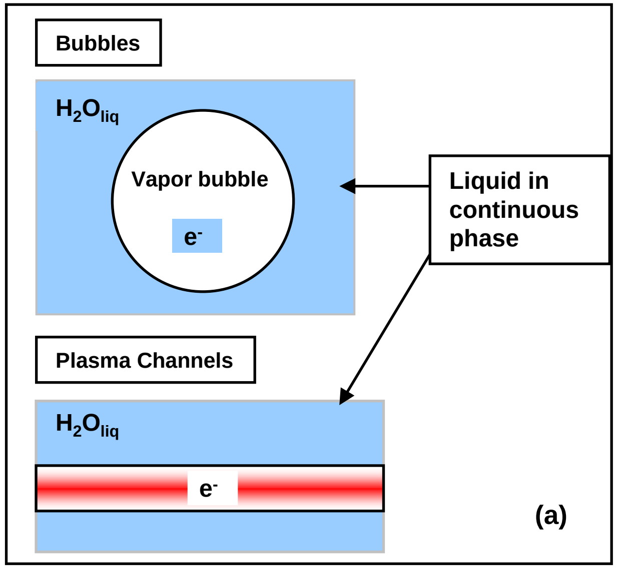
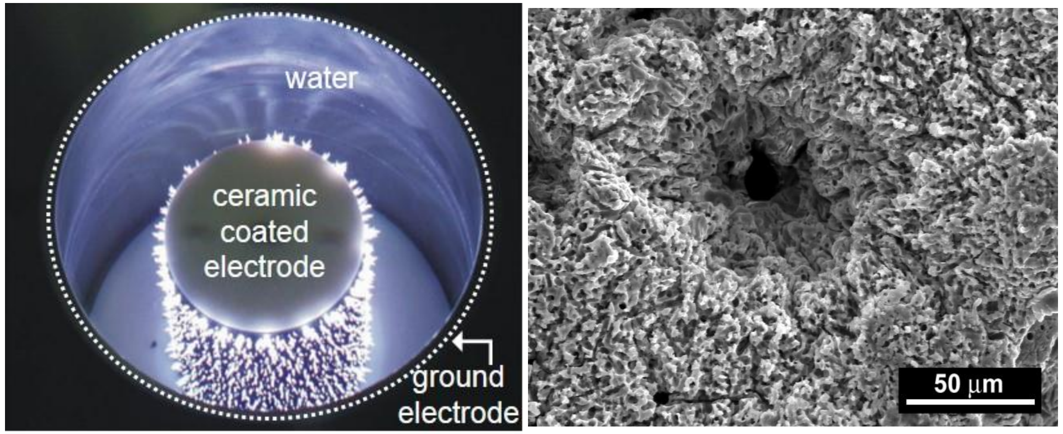
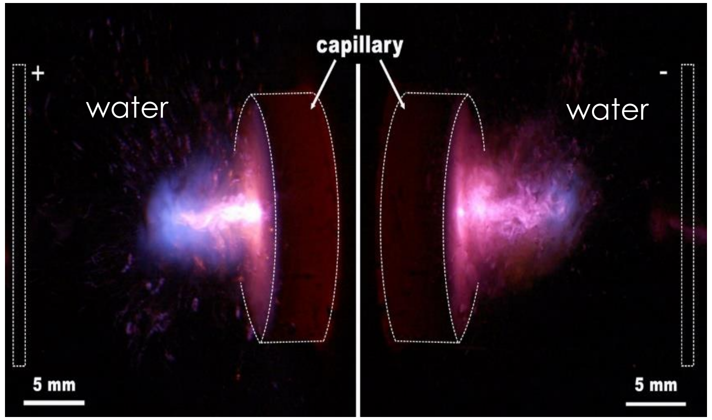
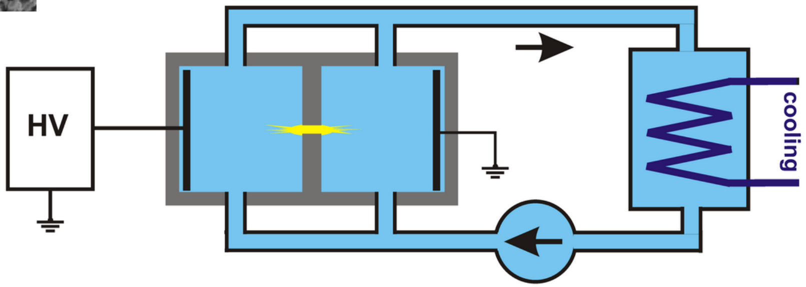






Lukes et al, *Plasma Process. Polym*. 6 (2009) 719





Locke and Shih: *Plasma Sources Sci. Technol*. 20 (2011) 034006
Locke, Lukes, Brisset: In *Plasma Chemistry and Catalysis in Gases and Liquids, Ch.6,* Wiley-VCH, 2012

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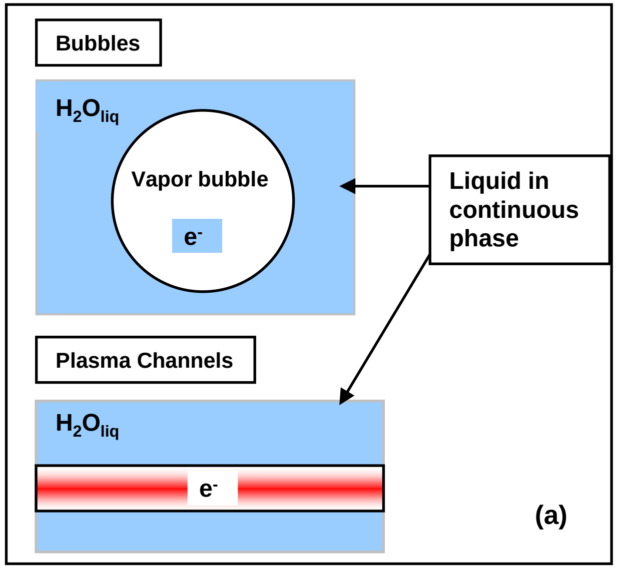

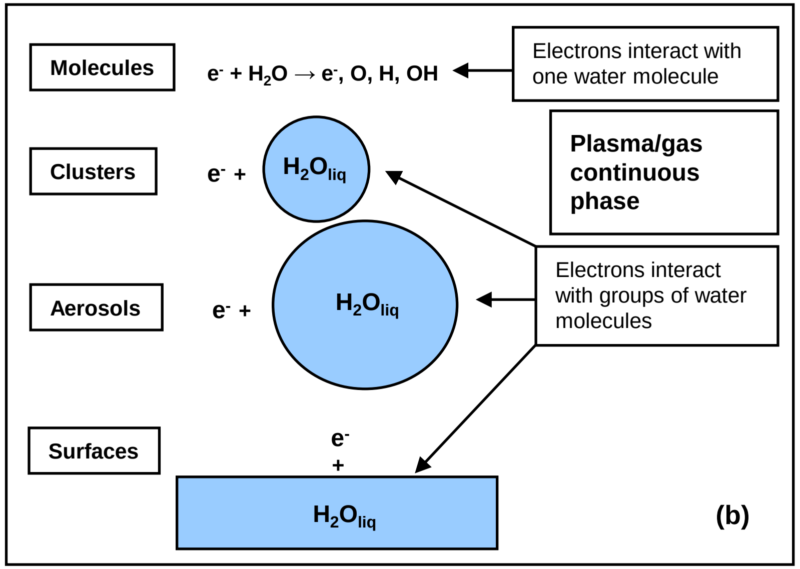

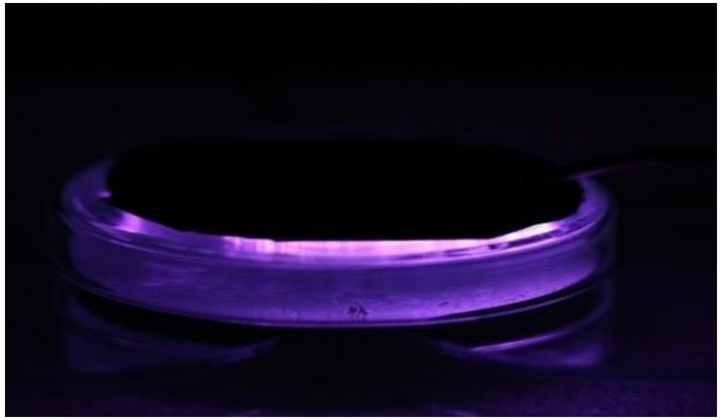

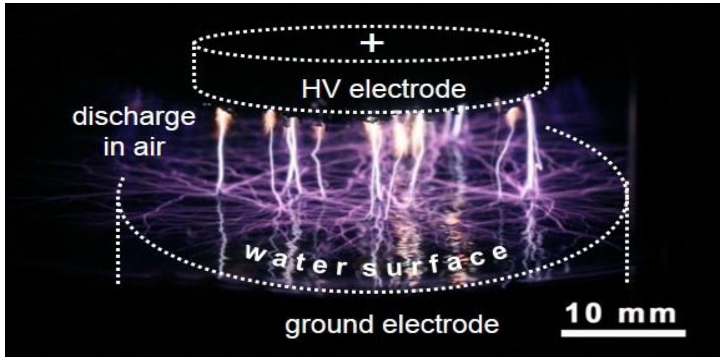

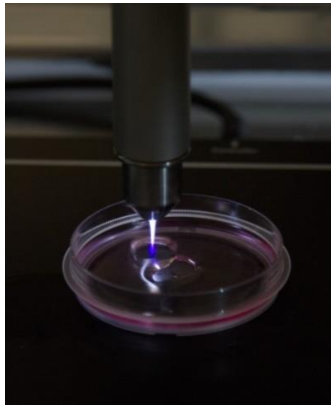

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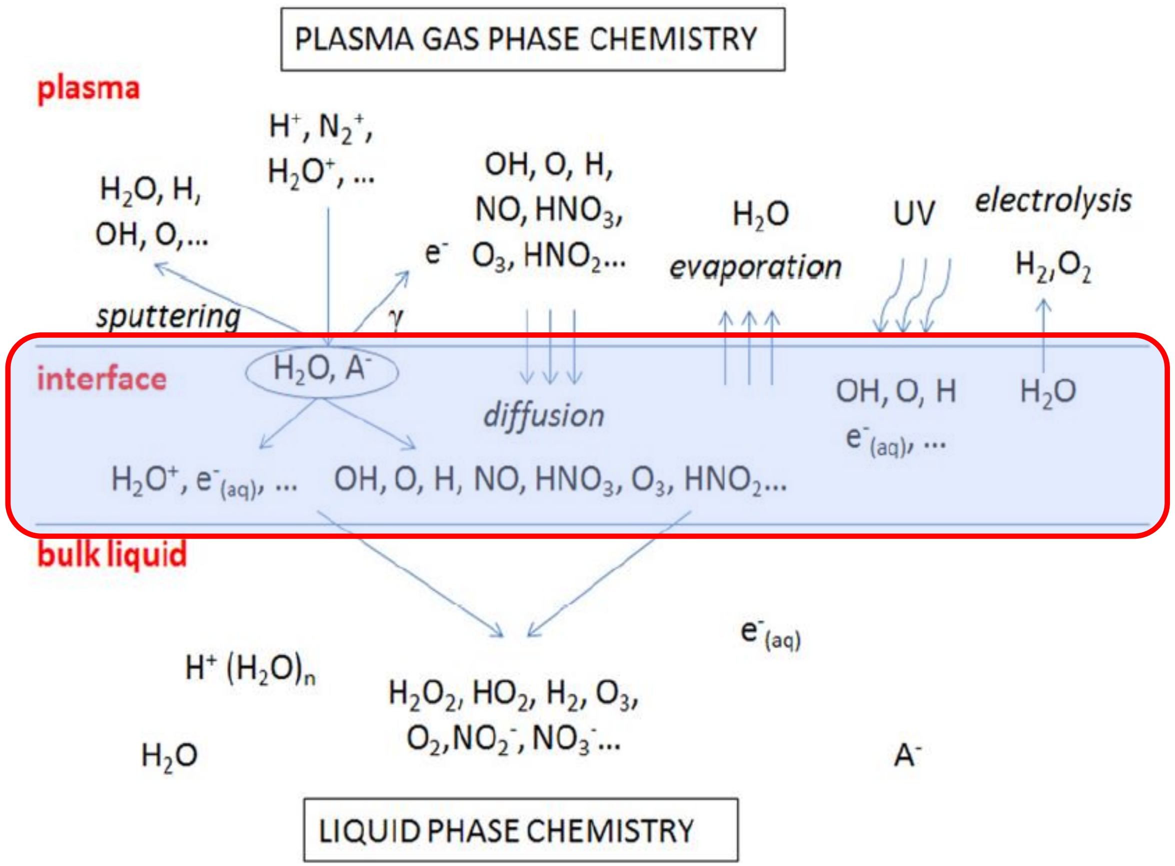
CHEMISTRY OF PLASMA-LIQUID INTERACTIONS

- reactions of primary and secondary species produced by plasma at **gas-liquid interface** (RONS)
- **transfer of chemistry from plasma** into the treated liquid
- **chemically reactive liquids** from plasma (extended lifetime of chemical reactivity, i.e. PAW, PCL, …)



Bruggeman *et al*, *Plasma Sources Sci. Technol.* 25 (2016) 053002

- Henry's law solubility coefficient $k_H \stackrel{\text{def}}{=} \frac{aqueous\ concen.}{partial\ pressure}$

species	k_H (mol/m³ Pa) ~	k_H normalized to O_3
H_2O_2	10^3	10^7
HNO_3	10^3	10^7
HNO_2	10^{-1}	10^3
NO_2	10^{-4}	1
NO	10^{-5}	10^{-1}
O_3	10^{-4}	1

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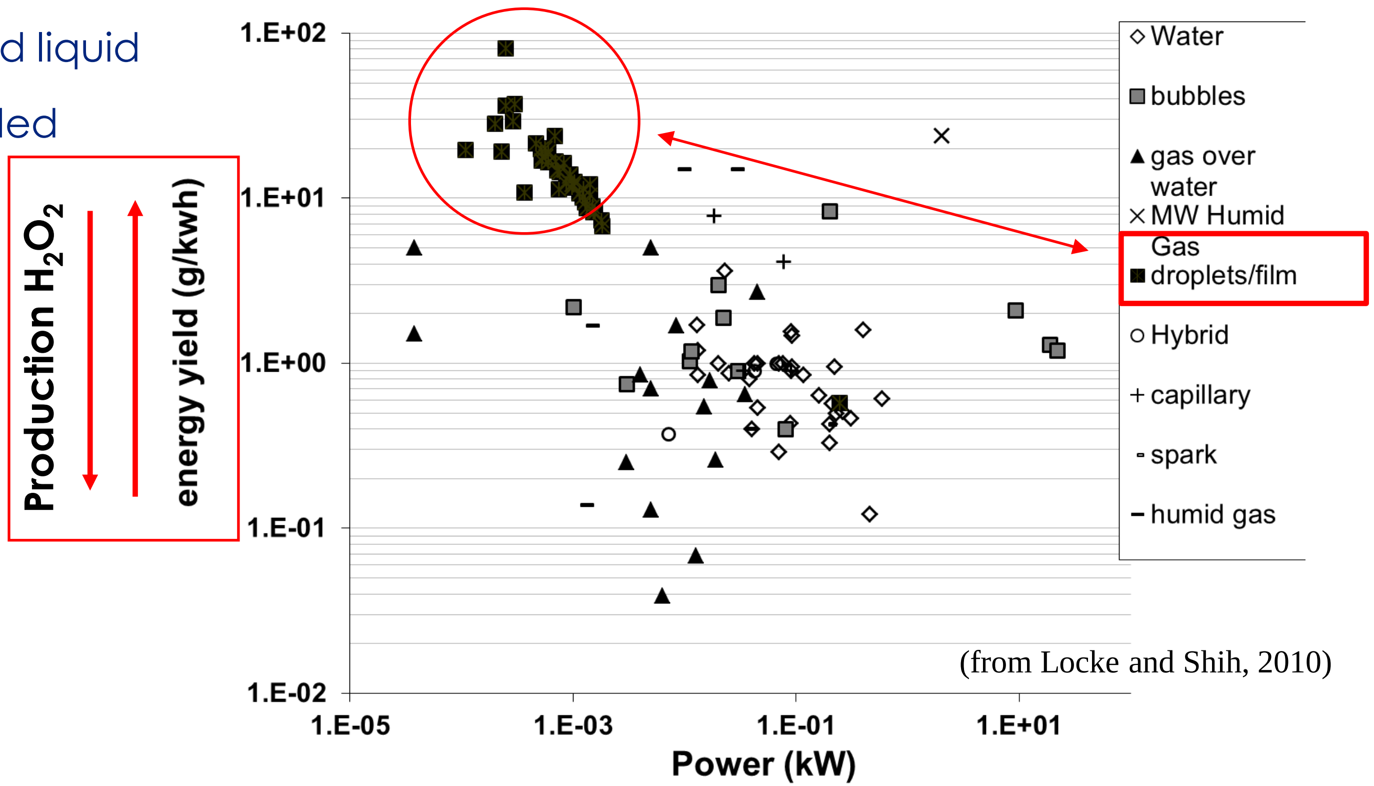
H_2O_2 yields by various plasma sources



- Best case: 50 to 80 g/kWh for gas/liquid phase plasma (water spray)
- Thermodynamic limit: 400 g/kWh ($H_2O_g \rightarrow H_2O_{2l}$); kinetic limit 180 g/kWh
- Current commercial costs (anthaquinone method): 10 to 100 g/kWh (equivalent)

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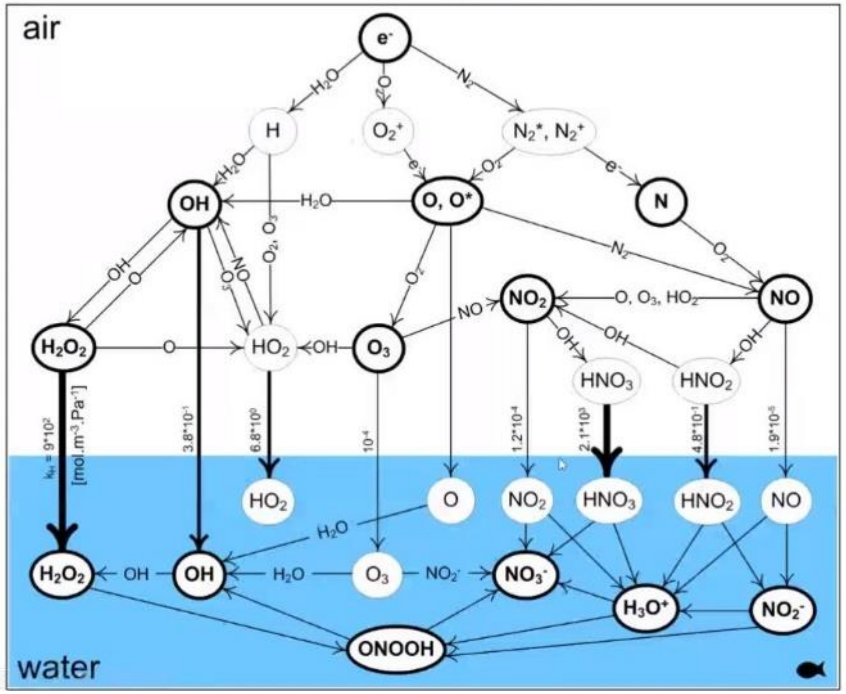
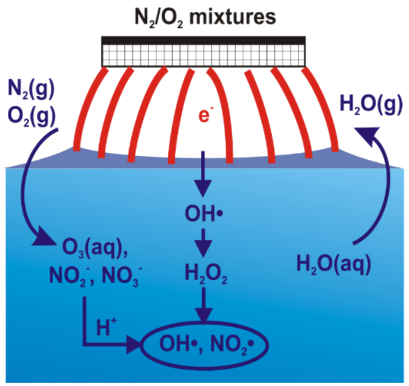
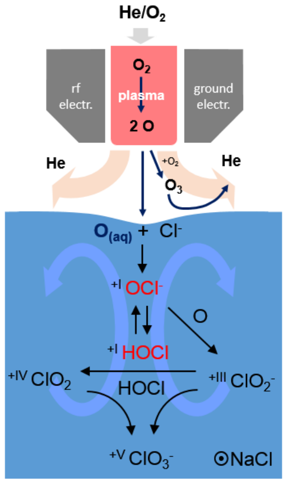


Machala *et al*, *J. Phys. D: Appl. Phys* 52 (2019) 034002





$$NO_2^- + H_2O_2 + H^+ \xrightarrow[-H_2O]{} O=NOOH$$

H_2O

$$OH\bullet + NO_2\bullet \qquad NO_3^- + H^+$$

$$Cl^- + O \rightarrow OCl^- \quad \& \quad H_2O_2,\ NO_2^-,\ H^+$$

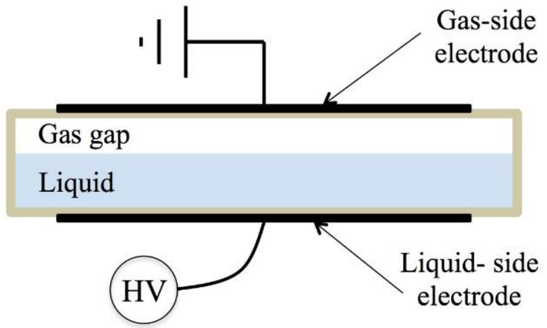
NaCl

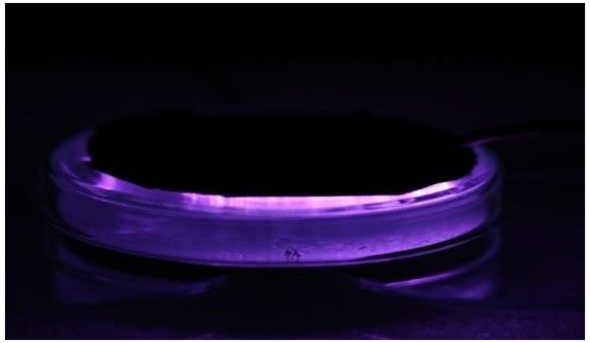
$$^1O_2,\ OCl\bullet,\ OH\bullet \qquad NO_2Cl,\ HOCl$$

PEROXYNITRITE CHEMISTRY IN AIR PLASMA TREATED LIQUIDS

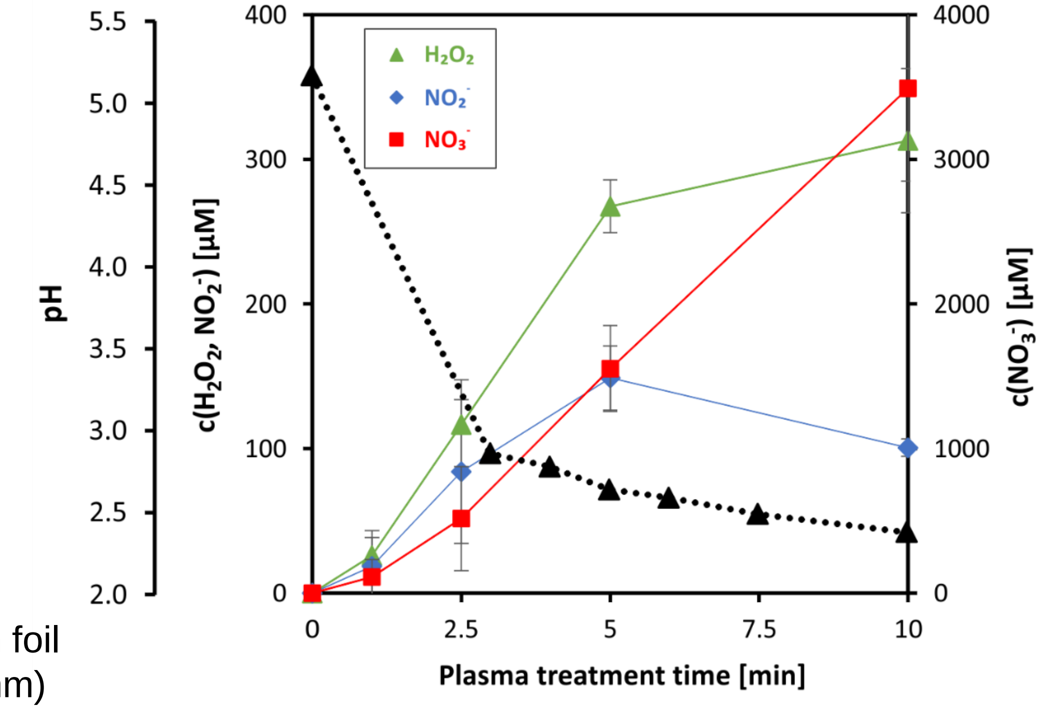
RONS produced in N_2/O_2 gas-liquid plasma systems

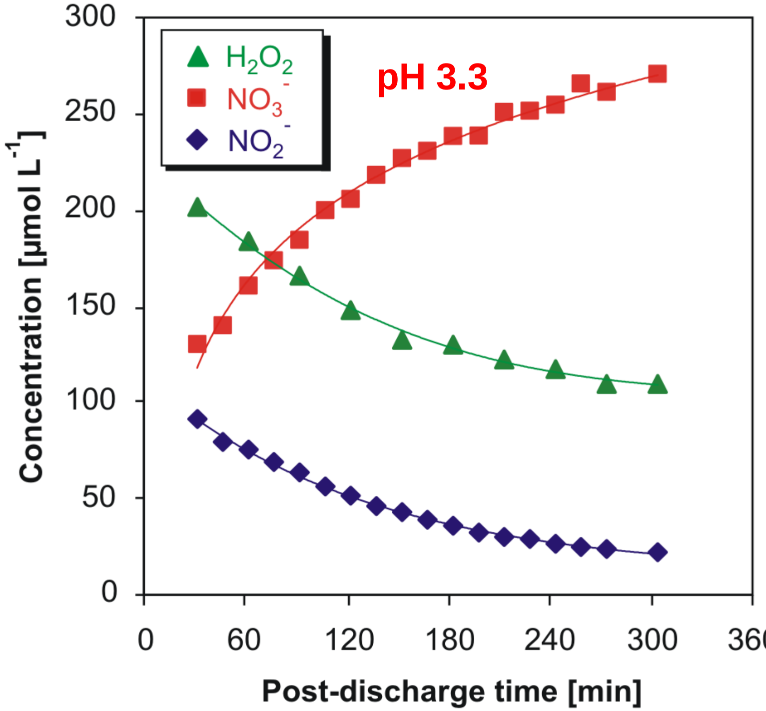
Formation of H_2O_2, NO_3^-, NO_2^- in water; concentrations variations with plasma treatment time dependent on pH of treated water. Increase of acidity of plasma treated water. Post-discharge changes in RONS concentrations.





glass Petri dish covered by aluminium foil as DBD electrodes: (d=100mm, l=2mm)

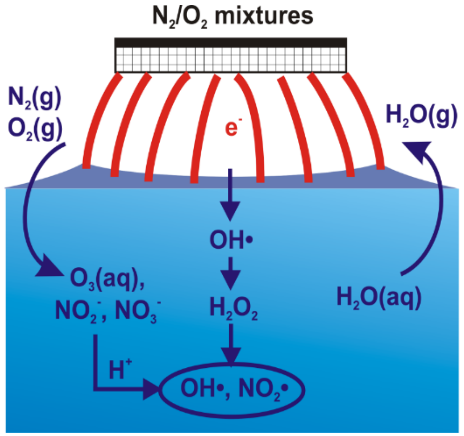




Laurita et al (2015) *Clin. Plasma Med*. **3** (2): 53-61

Post-discharge liquid phase reactions of RONS produced in N_2/O_2 gas-liquid plasma systems

Analytic evidence on ONOOH formation from the kinetics H_2O_2/HNO_2 decay in PAW – pH dependent, 3rd order rate reaction, detection of post-discharge formation of OH• and NO_2•



➢ Acidic decomposition of NO_2^-

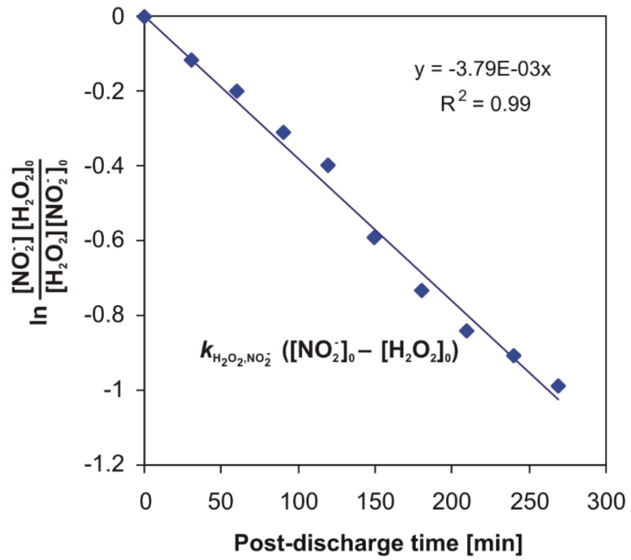
$$2\,NO_2^- + 2\,H^+ \leftrightarrow 2\,HNO_2 \xrightarrow{pH<3.5} NO\bullet + NO_2\bullet + H_2O$$

➢ Peroxynitrite formation via NO_2^-/H_2O_2

$$NO_2^- + H_2O_2 + H^+ \xrightarrow[-H_2O]{} O=NOOH \xrightarrow{pH<6.8} OH\bullet + NO_2\bullet$$

$$r_{ONOOH} = \frac{d[ONOOH]}{dt} = k\,[H^+][H_2O_2][NO_2^-]$$

$k = 4.2 \times 10^3\ M^{-2}\,s^{-1}$



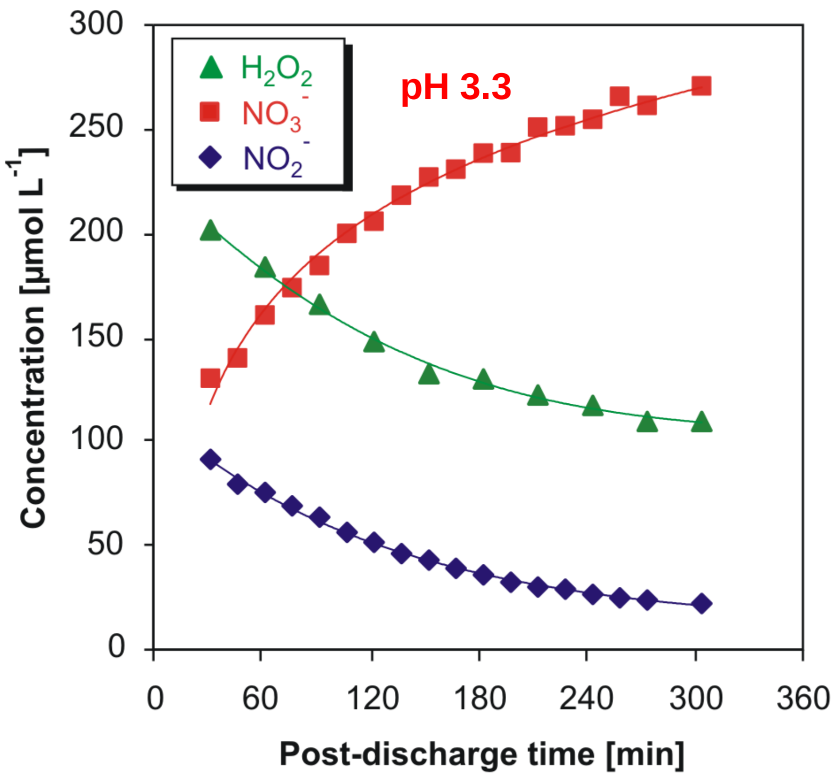
Lukes et al. *Plasma Sources Sci. Technol.* 23 (2014) 015019

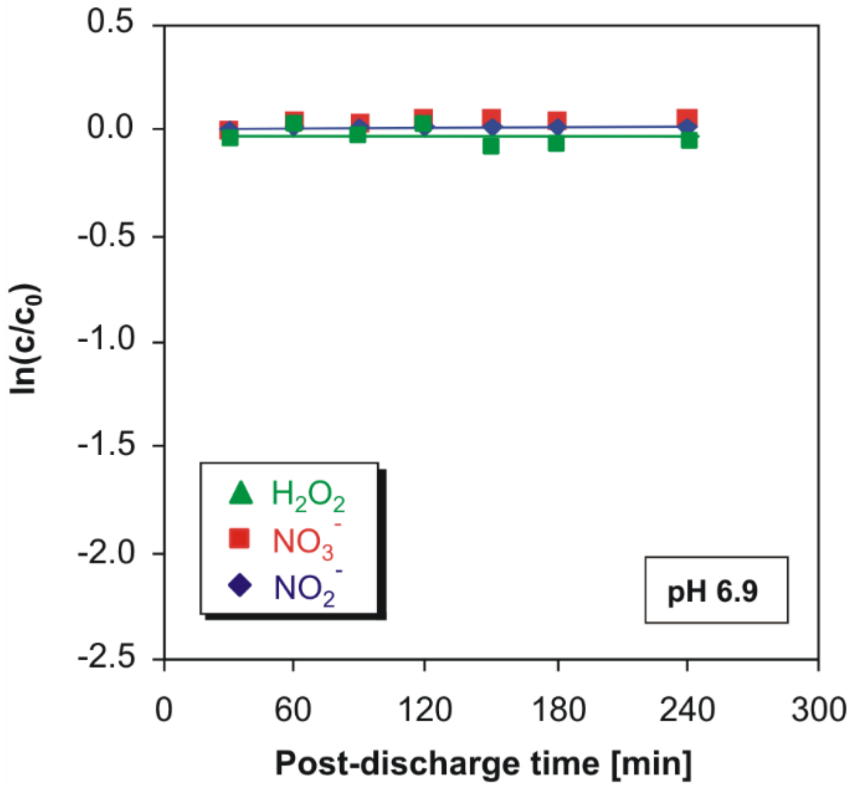
Lifetime/stability of PAW activity – effect of pH, H_2O_2/NO_2^-, temperature

$$NO_2^- + H_2O_2 + H^+ \xrightarrow[-H_2O]{} O=NOOH \xrightarrow{pH<6.8} OH\bullet + NO_2\bullet \quad \textbf{(A)}$$

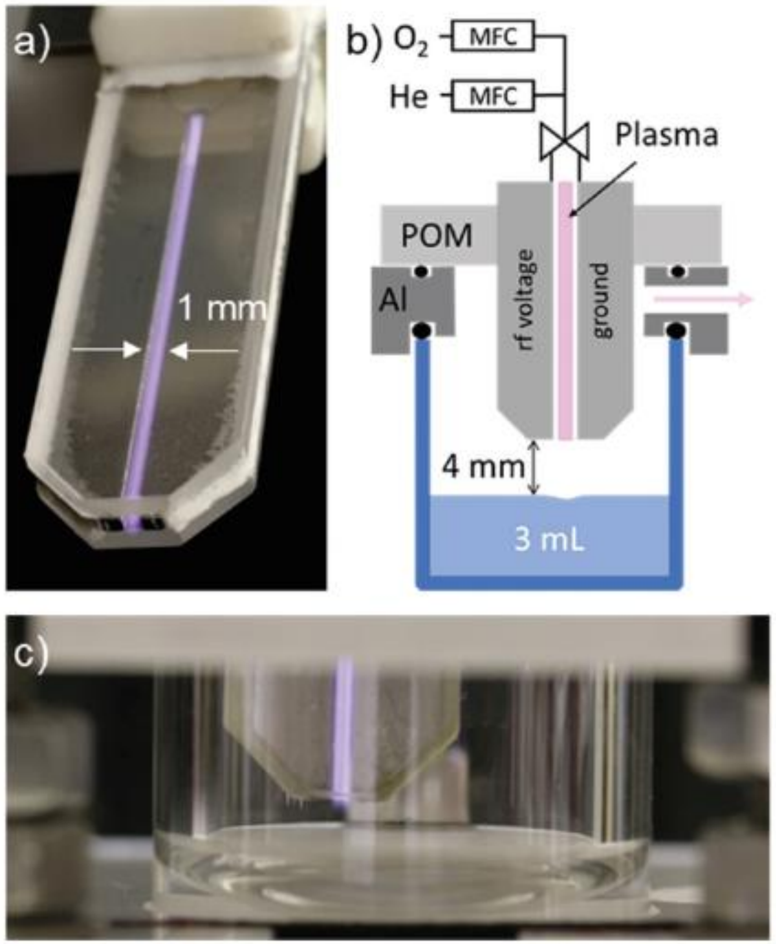
$$2\,NO_2^- + 2\,H^+ \leftrightarrow 2\,HNO_2 \xrightarrow{pH<3.5} NO\bullet + NO_2\bullet + H_2O \quad \textbf{(B)}$$

$$r_{ONOOH} = \frac{d[ONOOH]}{dt} = k(T)\,[H^+]\,[H_2O_2]\,[NO_2^-]$$



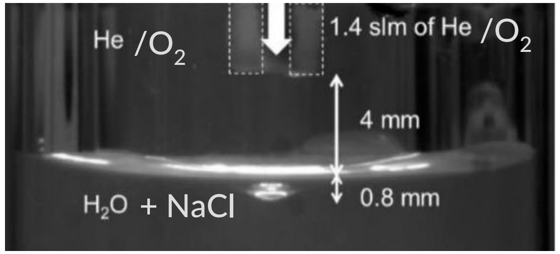


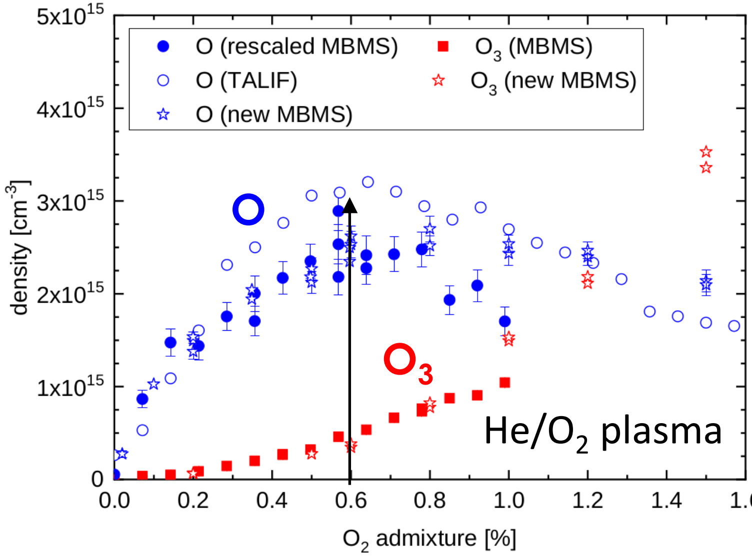
REFERENCE PLASMA SOURCE (EU COST PLASMA JET)



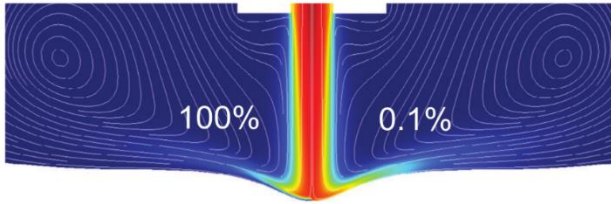
He + <1% of molecular gas (O_2, H_2O, N_2,…), RF driven 13.56 MHz at 230 Vrms

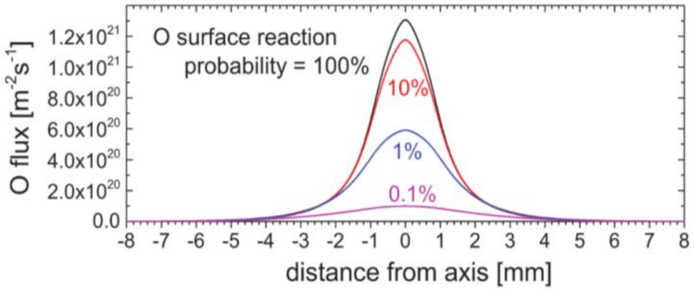
- well characterized source of reactive species (O, OH, N, NO, O_3…)
- radical "tunable" by gas mixture
- only effluent in contact with substrate





Flux of O atoms





Ellerweg *et al.* New Journal of Physics 12 (2010) 013021

REACTIONS OF O ATOMS AT GAS-LIQUID INTERFACE

O ATOMS FROM PLASMA CAN DIRECTLY INITIATE CHEMISTRY IN THE LIQUID

H_2O_2 formation + phenol as chemical probe

- direct oxidation by O atoms vs indirect reaction of O atoms via OH radicals? [1,2]

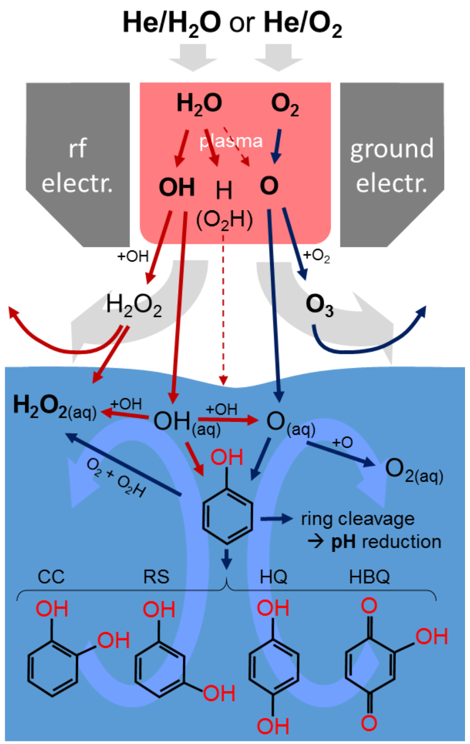
  $O_{(aq)} + H_2O_{(aq)} \rightarrow 2\ OH_{(aq)}$

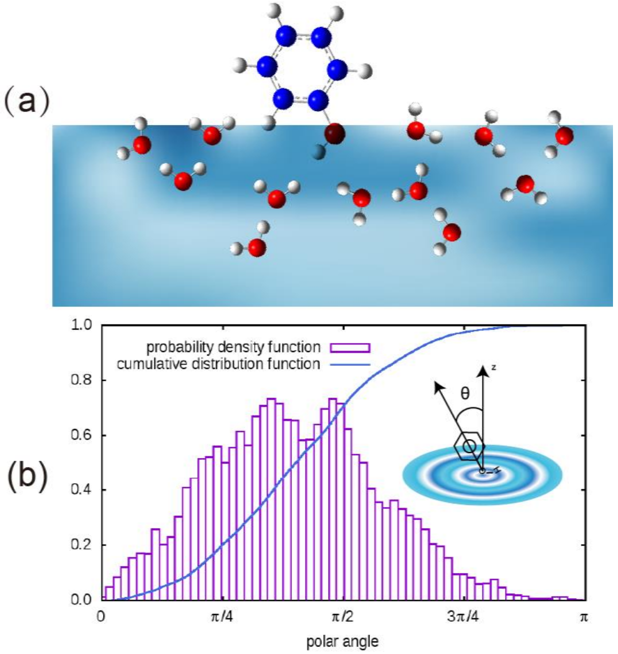
  $O_{(aq)} + H_2O_{(aq)} \rightarrow O\text{-}OH_{2(aq)} \rightarrow \rightarrow H_2O_{2(aq)}$

- study with labeled $^{18}O_2$ in He plasma jet [3]

  $^{18}O_2 \rightarrow {}^{18}O_{(aq)} + C_6H_5OH \rightarrow C_6H_4OH^{18}OH$

- reactions of phenol at gas-liquid interface via (MD) simulation studies [4,5]





[1] Hefny M.M. et al (2016) *J. Phys. D: Appl. Phys.* 49 (40): 404002; [2] Xu, Lukes (2020) *J. Phys.D: Appl. Phys* 53 (27): 275204, [3] Benedikt J. et al. (2018) *Phys. Chem. Chem. Phys.* 20 (17): 12037, [4] Sgonina K. et al (2021) *J. Appl. Phys.* 130: 043303, [5] Xu, Lukes (2021) *J. Mol. Liquids* 341: 117378

REACTIONS OF O ATOMS AT GAS-LIQUID INTERFACE

O ATOMS FROM PLASMA CAN DIRECTLY INITIATE CHEMISTRY IN THE LIQUID

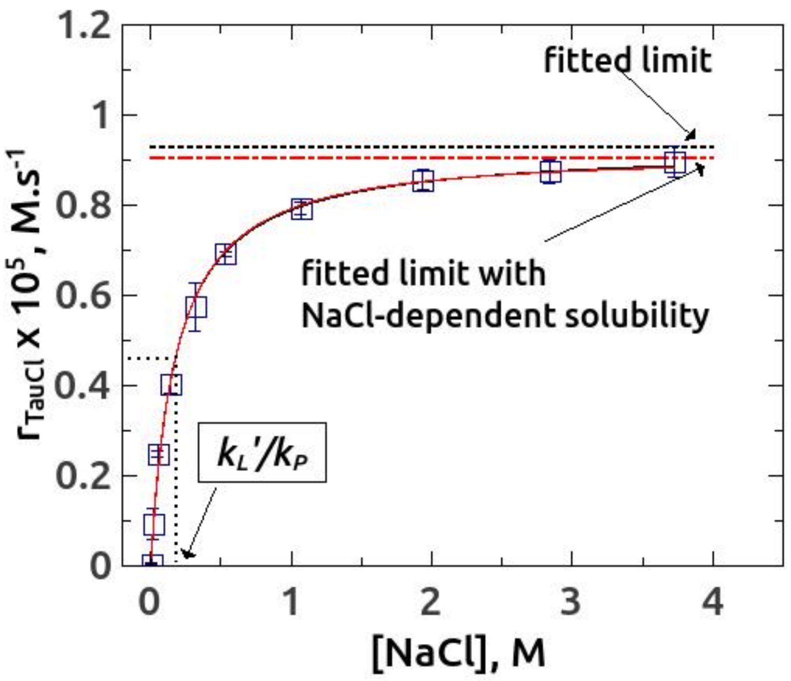
Oxychlorine chemistry in NaCl

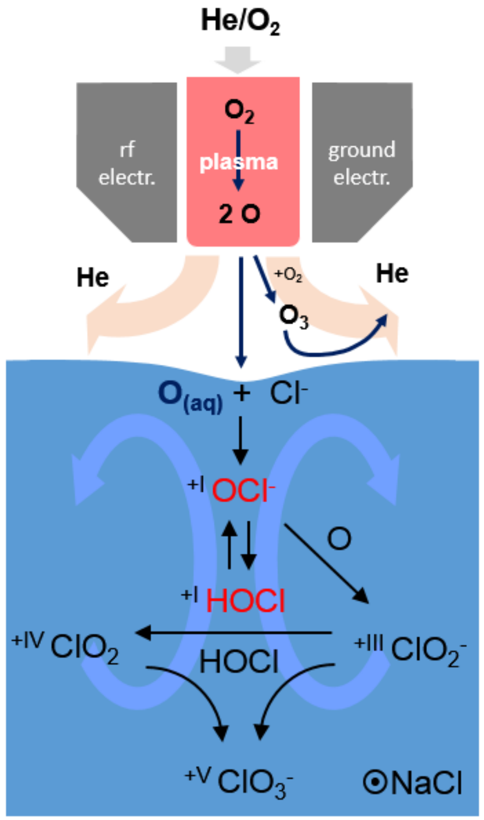
- formation of hypochlorite in plasma treated NaCl via reaction

  $O + Cl^- \rightarrow OCl^-$

- oxychlorine HOCl scales with treatment time and concentration of chlorides, saturation at very high [NaCl] > 2M, virtually all plasma-supplied O atoms can be captured by Cl- in highly concentrated NaCl
- => transport-limited rate for reaction of Cl- with ROS (O, OH)

$O + Cl^- \rightarrow OCl^-$ $k = 1.64 \times 10^5\ M^{-1}s^{-1}$





[1] Jirasek, Lukes (2019) *Plasma Sources. Sci. Technol*. 28 (3): 035015, [2] Jirasek, Lukes (2020) *J. Phys. D: Appl. Phys*. 53 (50): 505206

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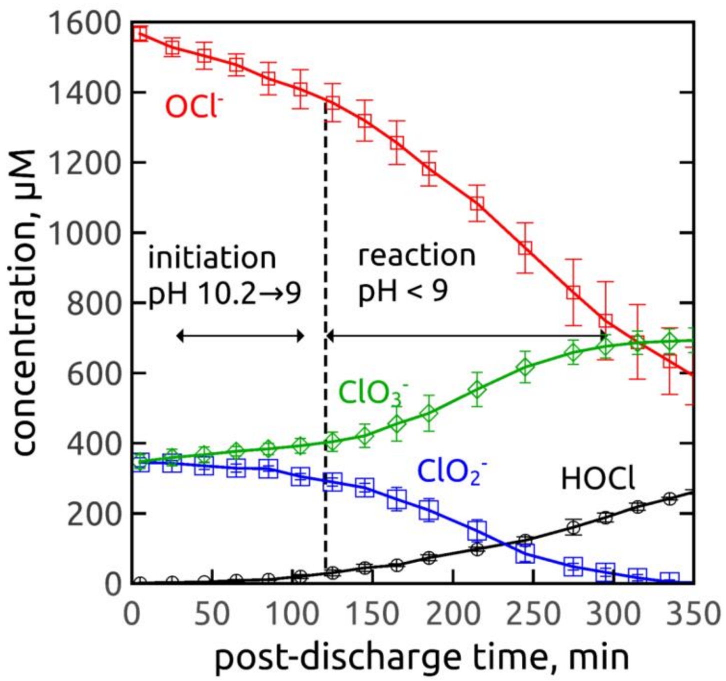
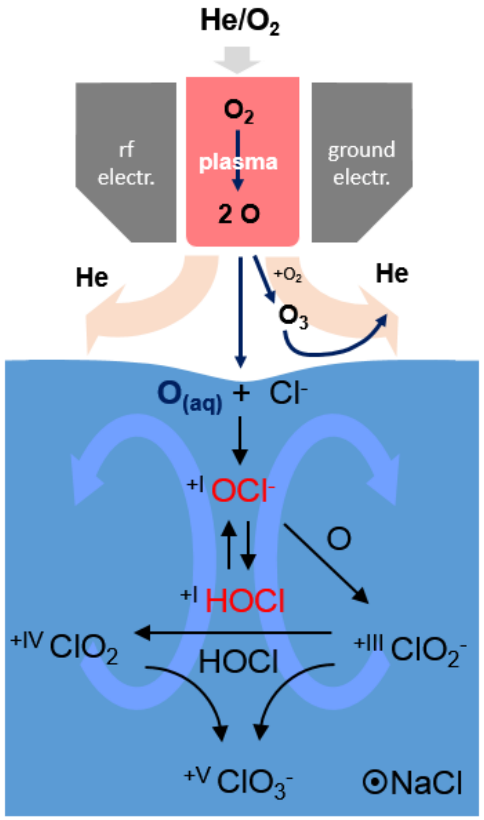
- oxychlorine chemistry by hypochlorite OCl^-, chlorite ClO_2^-, chlorine dioxide ClO_2, chlorate ClO_3^-
- post-discharge reactivity of plasma-treated saline solutions/PBS through oxychlorine products (oxidizing power remains for hours)

$3\ HOCl \rightarrow ClO_3^- + 2Cl^- + 3H^+$





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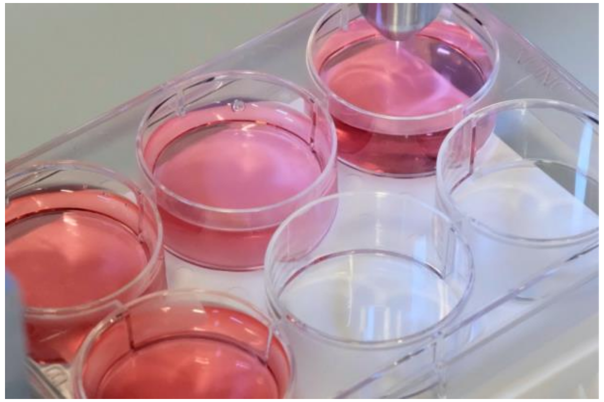
PROCESSES IN CULTURE MEDIA TREATED BY PLASMA

- **Culture media** - complex mixture of inorganic salts and organic compounds such as amino acids, vitamins, glucose, antibiotics, and other compounds - great effects on the properties and activity of the generated plasma-treated liquids.
- Diagnostics of reactive species and reaction pathways in these complex systems is challenging – selectivity, sensitivity, interferences – need of suitable analytical methods and correlation of chemical effects with their biochemical activity.
- Plasma treated media can have different biological effects – can affect gene expression, signal transduction, metabolic networks, induce apoptosis (cell death, important for cancer therapy) – coupling chemical effects with their biochemical activity.



Formulation for Dulbecco's Modified Eagle's Medium (DMEM) ATCC® 30-2002

Inorganic Salts (g/liter)	
$CaCl_2$ (anhydrous)	0.20000
$Fe(NO_3)_3 \cdot 9H_2O$	0.00010
$MgSO_4$ (anhydrous)	0.09770
KCl	0.40000
$NaHCO_3$	1.50000
NaCl	6.40000
$NaH_2PO_4 \cdot H_2O$	0.12500

Amino Acids (g/liter)	
L-Arginine·HCl	0.08400
L-Cystine·2HCl	0.06260
L-Glutamine	0.58400
Glycine	0.03000
L-Histidine·HCl·H_2O	0.04200
L-Isoleucine	0.10500
L-Leucine	0.10500
L-Lysine·HCl	0.14600
L-Methionine	0.03000
L-Phenylalanine	0.06600
L-Serine	0.04200
L-Threonine	0.09500
L-Tryptophan	0.01600
L-Tyrosine·2Na·2H_2O	0.10379
L-Valine	0.09400

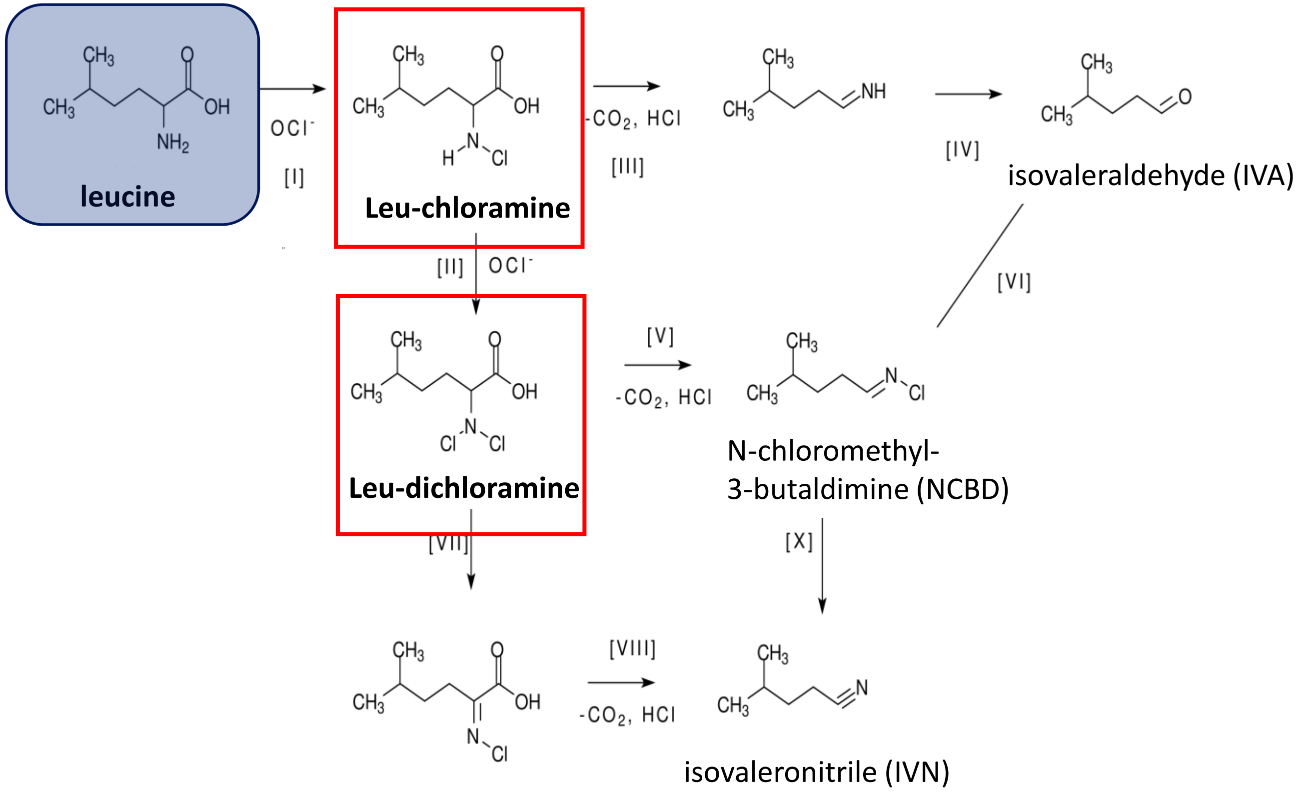
Vitamins (g/liter)	
Choline Chloride	0.00400
Folic Acid	0.00400
myo-Inositol	0.00720
Nicotinamide	0.00400
D-Pantothenic Acid (hemicalcium)	0.00400
Pyridoxine·HCl	0.00400
Riboflavin	0.00040
Thiamine·HCl	0.00400

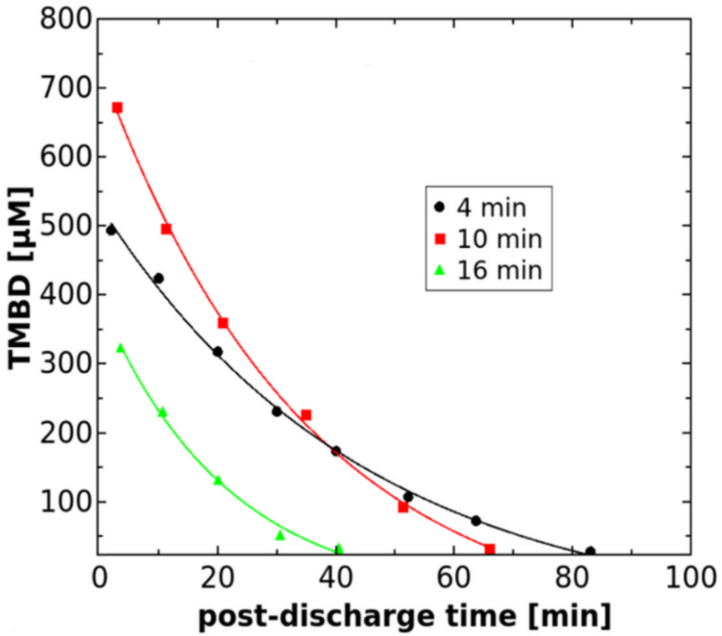
Other (g/liter)	
D-Glucose	4.50000
Phenol Red, Sodium Salt	0.01500
Sodium Pyruvate	0.11000

PLASMA TREATMENT OF AMINO ACIDS (Leucine, Phenylalanine, Tyrosine)

- Primary no oxidation of amino acids but formation of OCl^- followed by formation **chloramines of amino acids**
- Decay of chloramines of amino acids to tertiary products

$$O + Cl^- \rightarrow OCl^- \quad (1)$$
$$OCl^- + H_2O \leftrightarrow HOCl + OH^- \quad (2)$$
$$R - NH_2 + HOCl \rightarrow RNHCl + H_2O \quad (3)$$
$$R - COOH - NHCl \rightarrow R - COOH - NCl_2 \quad (4)$$



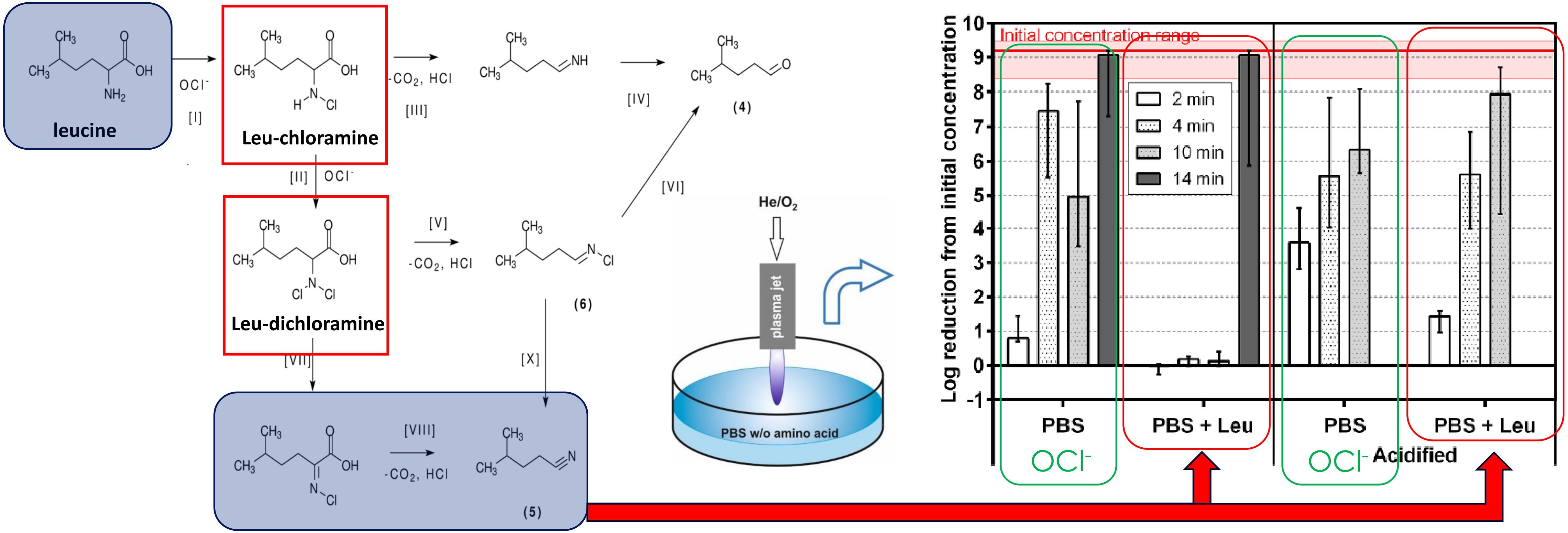


[1] Jirasek, Kovalova, Tarabova, Lukes (2021) *J. Phys. D: Appl. Phys*. 54 (50): 505206, [2] Jirasek, Tarabova, Lukes (2022) *Plasma Proc. Polym*. 19: 2200079

BACTERICIDAL EFFECTS OF AMINO ACIDS IN PLASMA TREATED PBS

PLASMA TREATMENT OF AMINO ACIDS (Leucine, Phenylalanine, Tyrosine)

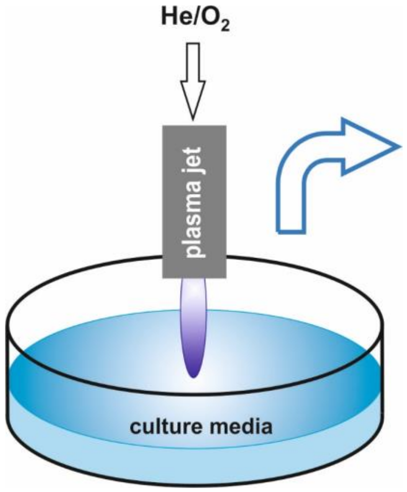
- Primary no oxidation of amino acids but formation of OCl^- followed by formation **chloramines of amino acids**
- bactericidal properties in PBS without AA due to OCl^-, with plasma treated amino acids due to chloramines

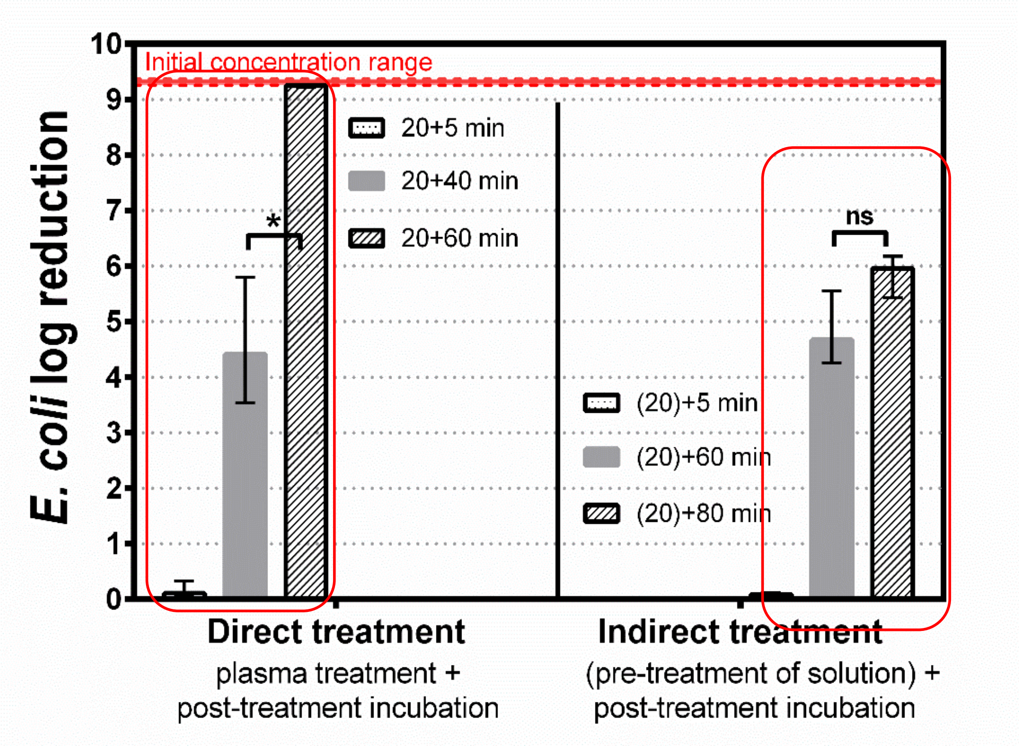


[1] Jirasek, Kovalova, Tarabova, Lukes (2021) *J. Phys. D: Appl. Phys*. 54 (50): 505206, [2] Jirasek, Tarabova, Lukes (2022) *Plasma Proc. Polym*. 19: 2200079

PLASMA TREATMENT OF DMEM/RPMI

- Time delay in bactericidal effect of PT-DMEM/RPMI on *E. coli*
- Major effects caused by post-discharge processes in plasma treated media





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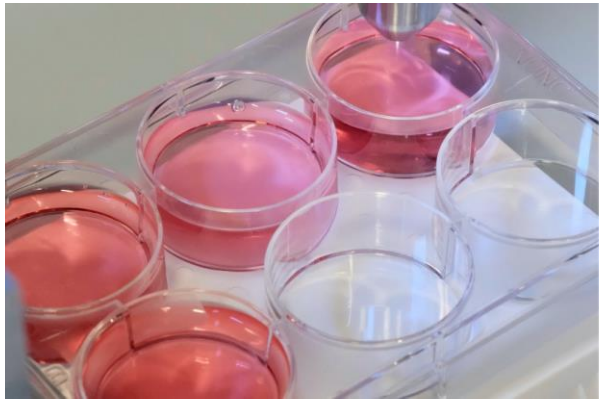


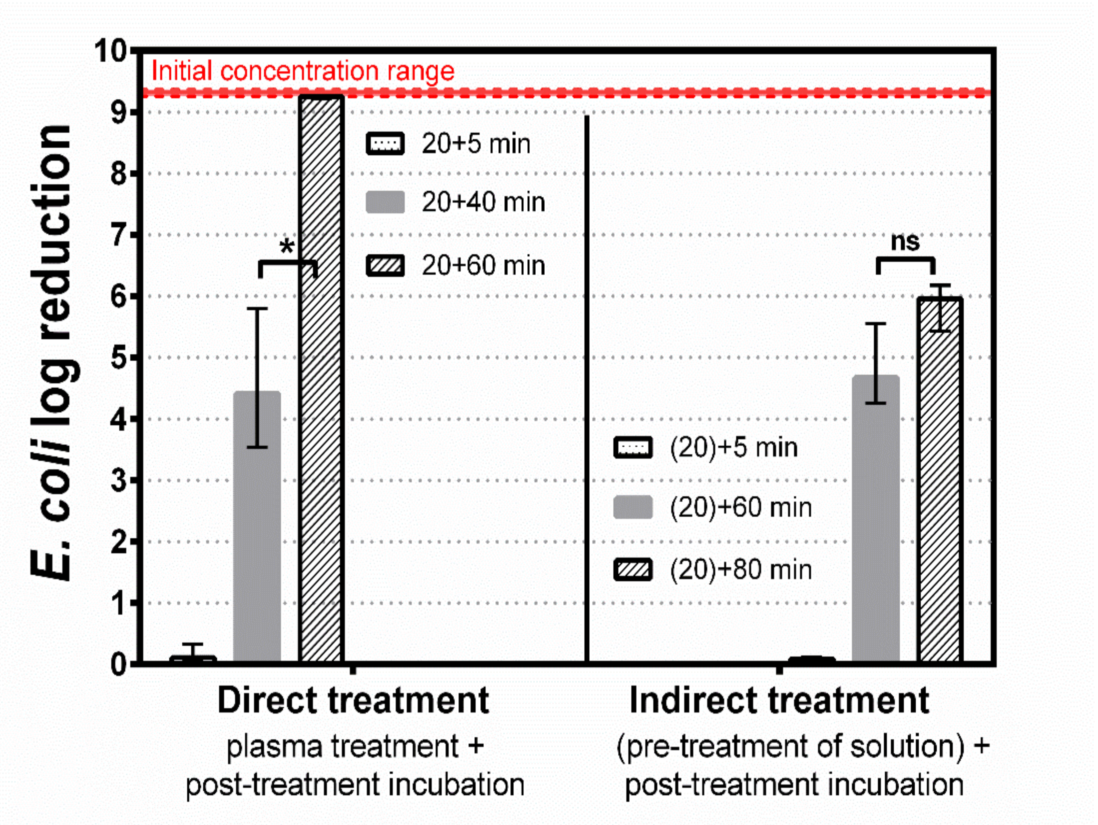
Formulation for Dulbecco's Modified Eagle's Medium (DMEM) ATCC® 30-2002

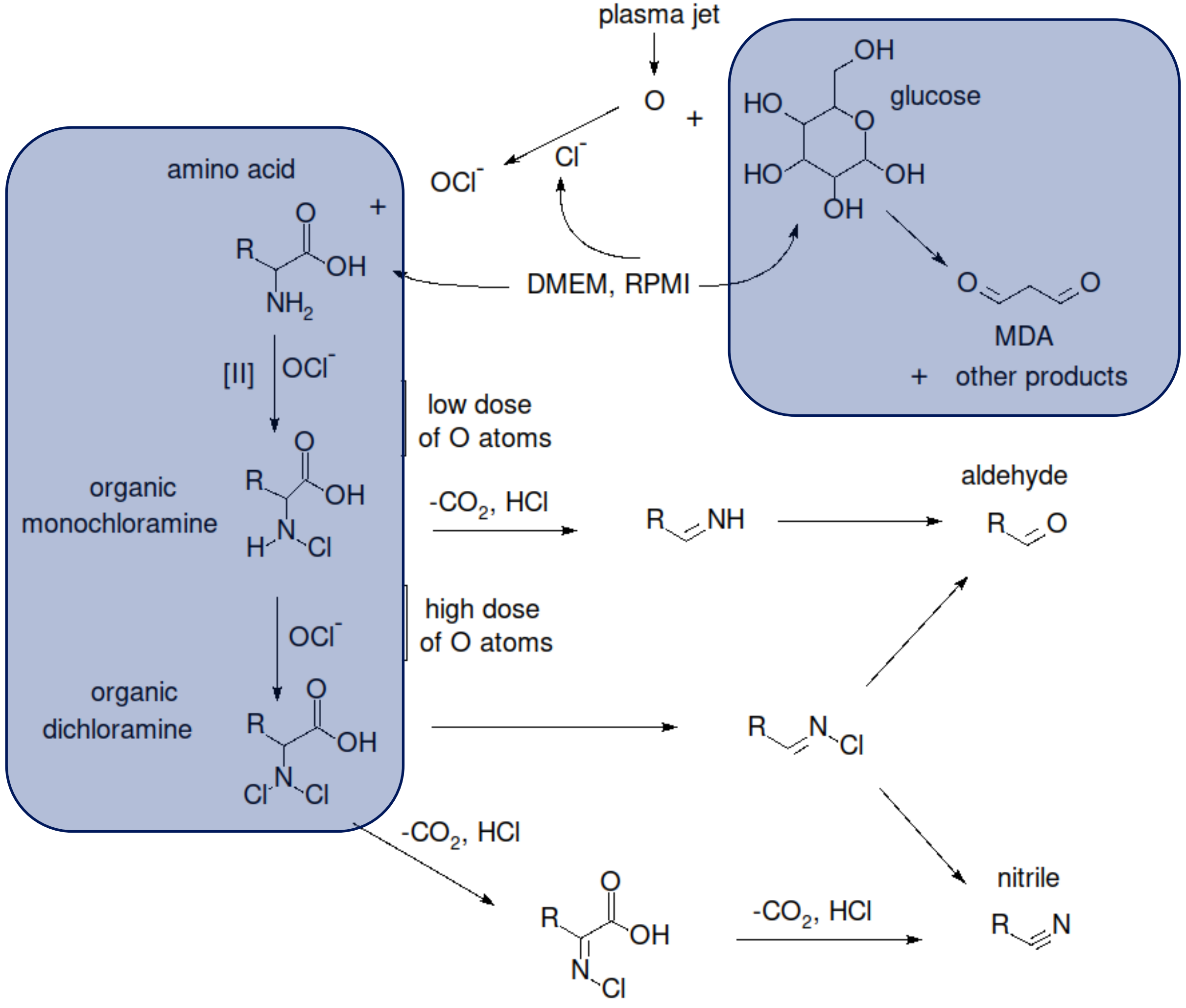
Inorganic Salts (g/liter)	
$CaCl_2$ (anhydrous)	0.20000
$Fe(NO_3)_3 \cdot 9H_2O$	0.00010
$MgSO_4$ (anhydrous)	0.09770
KCl	0.40000
$NaHCO_3$	1.50000
NaCl	6.40000
$NaH_2PO_4 \cdot H_2O$	0.12500
Amino Acids (g/liter)	
L-Arginine·HCl	0.08400
L-Cystine·2HCl	0.06260
L-Glutamine	0.58400
Glycine	0.03000
L-Histidine·HCl·H_2O	0.04200
L-Isoleucine	0.10500
L-Leucine	0.10500
L-Lysine·HCl	0.14600
L-Methionine	0.03000
L-Phenylalanine	0.06600
L-Serine	0.04200
L-Threonine	0.09500
L-Tryptophan	0.01600
L-Tyrosine·2Na·$2H_2O$	0.10379
L-Valine	0.09400

Vitamins (g/liter)	
Choline Chloride	0.00400
Folic Acid	0.00400
myo-Inositol	0.00720
Nicotinamide	0.00400
D-Pantothenic Acid (hemicalcium)	0.00400
Pyridoxine·HCl	0.00400
Riboflavin	0.00040
Thiamine·HCl	0.00400
Other (g/liter)	
D-Glucose	4.50000
Phenol Red, Sodium Salt	0.01500
Sodium Pyruvate	0.11000

PLASMA TREATMENT OF DMEM/RPMI

- Chlorination of amino acids – **AA-chloramines**
- Oxidation of glucose - **malondialdehyde**





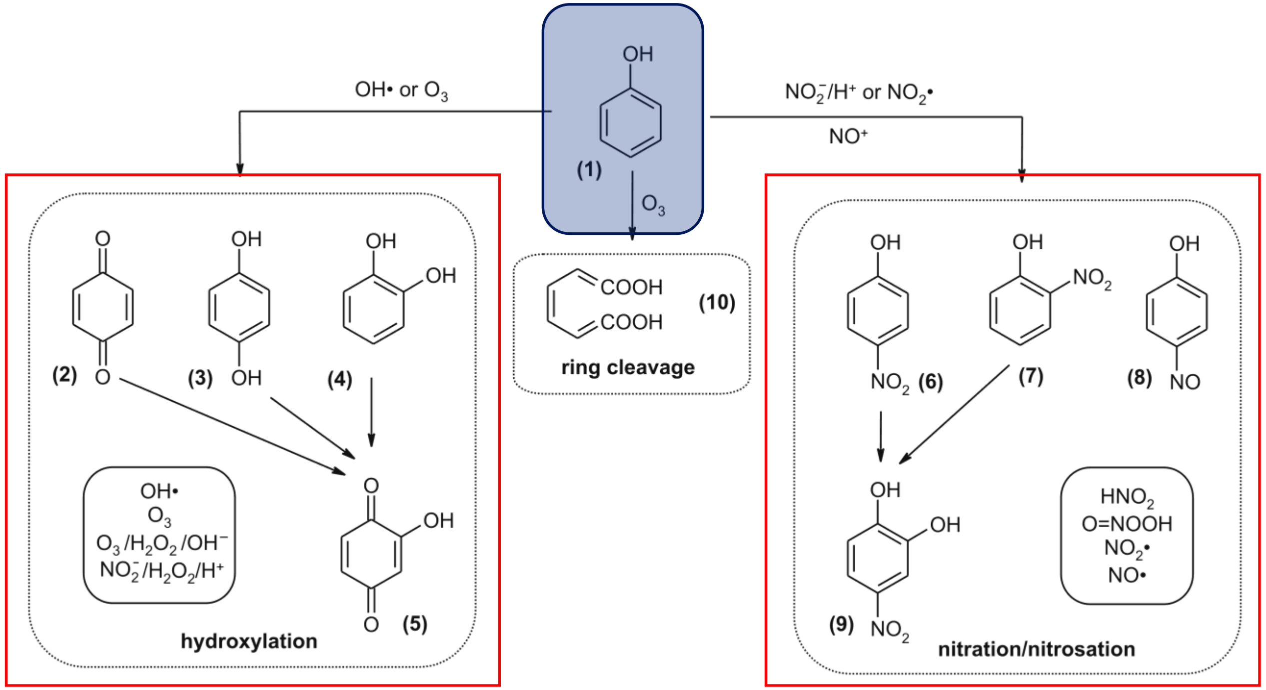
Jirasek, Tarabova, Lukes (2023) *Plasma Proc. Polym.* 20: e2300052

OXIDATION VS NITRATION VS CHLORINATION REACTIONS IN LIQUIDS

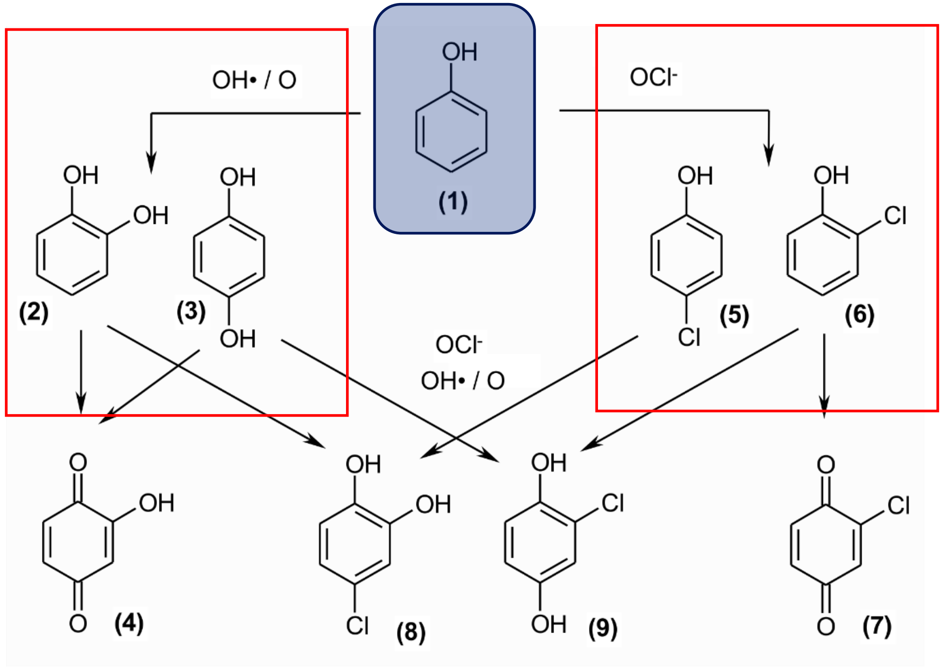
- phenol as chemical probe – oxidation (O, OH, O_3) nitration (NO_2•, NO•, NO+), chlorination (HOCl)

OH (O) + Phe → Phe(ox) k = ~ 1 x 10^9 $M^{-1}s^{-1}$

O + Cl^- → OCl^- k = 1.64 x 10^5 $M^{-1}s^{-1}$



Lukes et al. (2014) *Plasma Sources Sci. Technol*. 23: 015019



Jirasek, Lukes (2019) *Plasma Sources. Sci. Technol.* 28 (3): 035015

CHEMISTRY IN PLASMA TREATED LIQUIDS

Great variability due to used plasma source, composition of the gas and liquid. Complexity of the chemistry and diagnostics challenges increases with the chemical content.

	water	NaCl / PBS	Culture media
pH	acidic	acidic/neutral/alkaline	neutral
Measured /proposed active species	H_2O_2/O_2^-• HNO_2/NO_2^-, ONOOH, O_2NOOH (OH•, NO_2•)	H_2O_2/O_2^-• HNO_2/NO_2^-, ONOOH (OH•, NO_2•) OCl^-, NH_2Cl	H_2O_2 (R-O-O-R') plasma modified aminoacids/other comp. OCl^-, NH_2Cl, $ONOO^-$
Observed lifetime/stability	minutes to hours (dependent on pH, temperature, H_2O_2/HNO_2 conc.)	minutes to hours (dependent on pH, temperature, H_2O_2/HNO_2 conc.)	hours to months (dependent on temperature, chemical content)

CHEMICAL PROCESSES/MECHANISMS INDUCED DUE PLASMA-LIQUID INTERACTIONS: CHALLENGES & OPPORTUNITIES

- **Tailoring plasma for specific effects**: Effects dependent on the contact of plasma with liquid, power, electron density, physical properties and chemical composition of gas and liquid
- Chemistry in **plasma-treated liquids** – direct vs indirect processes
- **Diagnostics** of reactive species and reaction pathways with increasing complexity systems – **selectivity, sensitivity, interferences** – suitable analytical methods and correlation of chemical effects with their biochemical activity coupled with modeling.
- **N-related chemistry**: peroxynitrite formation H_2O_2+NO_2^- under acidic conditions, decay into NO_2• and OH• radicals, nitrogen fixation in liquid
- **O atom-related chemistry**: chlorination vs oxidation of organics in saline solutions, cytotoxicity of Cl-compounds (e.g., decay products of dichloramines of amino acids)
- **Cl-related chemistry** in saline solutions: formation of OCl^- by O atoms, competition reactions OCl^- with higher oxychlorine products, $O + Cl^- \rightarrow OCl^-$ ($k = 1.64 \times 10^5\ M^{-1}s^{-1}$)