Project 1

- **Title:** Plasma chemistry of water and other liquids
- **PI:** Greg Fridman, Drexel
- **Need and Relevance:** medical, food processing, and AG industries require high volume of plasma treatment of liquids at low energy cost.
  Goals: to develop water treatment and droplet cluster formation system for surface treatment, disinfection, and drying
- **Approach:** tune plasma parameters and system temperature to optimize existing systems, analyze water chemistry and cluster/droplet formation dynamics
- **Outcomes/Deliverables:** high volume flowing liquid treatment system with high yield of disinfectant
- **Project Duration, Budget:** 2 years / $40,000/year

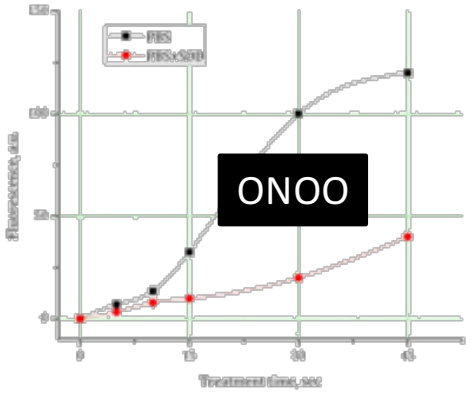
Need and Relevance

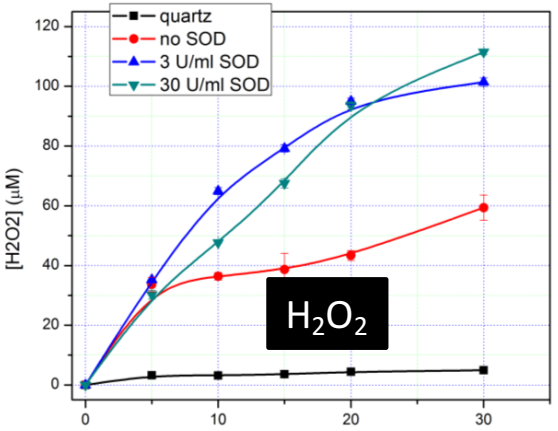
Plasma-generated metastable liquids in medicine, food processing, and agriculture.

- **Metastables in plasma-activated water**
  - Oxygen “plasma acid” composition and temporary oxidative effectiveness
  - Contribution of $ONOO^-$ and its oxidative pathways
- **Metastables in plasma-activated bio-organic solutions**
  - Suppression of peroxidation in bio-solutions
  - S-nitrosylation of thiols and non-oxidative disinfection
- **Biochemical effect of plasma-activated liquids in medicine, food processing, and agriculture**
- **Water molecules form clusters on charged and metastable species, leading to reduction in water activity of foods and to fast drying of processed materials**

Metastables in plasma-activated water:
Contribution of ONOO- and its oxidative pathways

1. **Positive Ions** create **acidity**
   - **Charge exchange mechanism:**
     $N_2^+ (O_2^+) + H_2O \rightarrow H_2O^+ + N_2(O_2)$
   - $H_2O^+ + H_2O \rightarrow H^+(H2O) + OH^\bullet$
2. **Conjugate Base (Negative Ions): ROS**
   - $e + O_2 \rightarrow O_2^-$
   - O_2^- is the primary negative ion both in gas and liquid
3. H_2O_2 is **immediately created** in both **gas** and **liquid**
   - $OH^\bullet + OH^\bullet \rightarrow H_2O_2$
4. **Nitrate and nitrite** are generated in liquid





$N_2 \xrightarrow{e} 2e + N_2^+$

$N_2 \xrightarrow{e} 2N^\bullet$

$N_2^+ + H_2O \longrightarrow N_2^+(H_2O)$

$N_2^+(H_2O) + H_2O \longrightarrow H_3O^+ + N_2 + {}^\bullet OH$

$N_2^+ + H_2O \longrightarrow HN_2^+ + {}^\bullet OH$

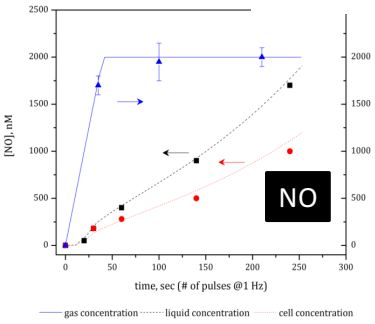
$N_2^+ + H_2O \longrightarrow {}^\bullet NO + NH_2^+$

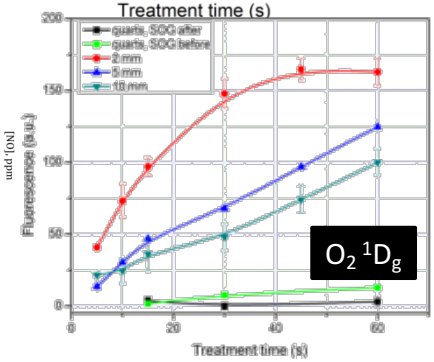
${}^\bullet NO + O^\bullet \longrightarrow {}^\bullet NO_2$

${}^\bullet NO_2 + {}^\bullet OH \longrightarrow ONOOH$

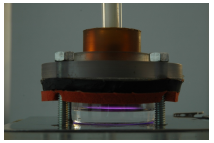
$2\,{}^\bullet NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$





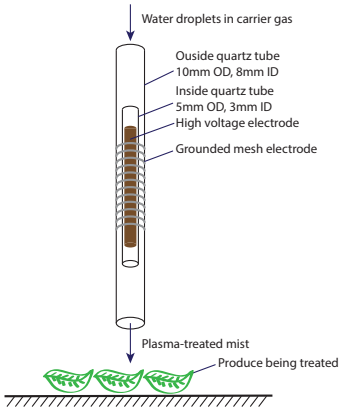
DBD

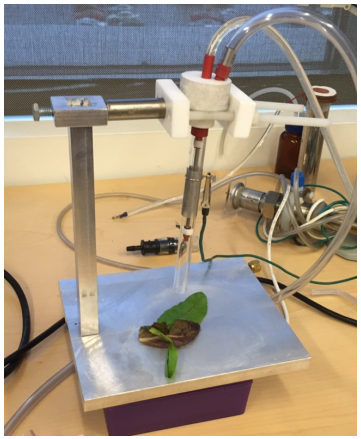


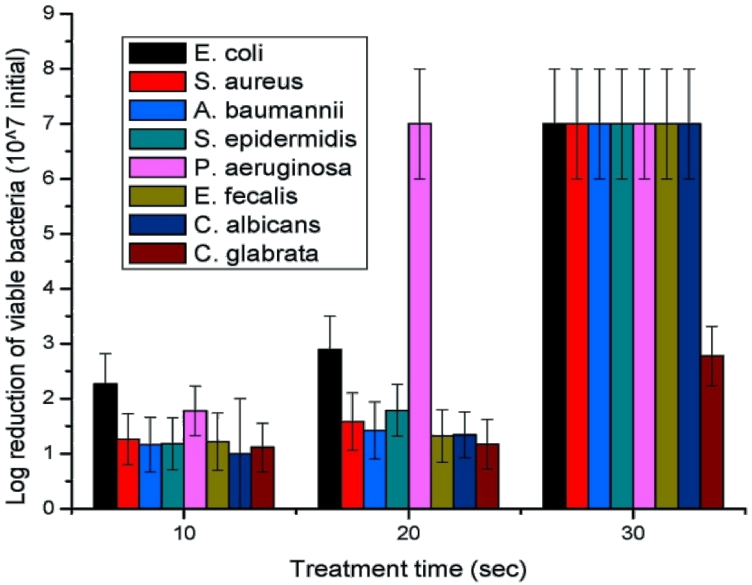
Plasma spray

Glidarc

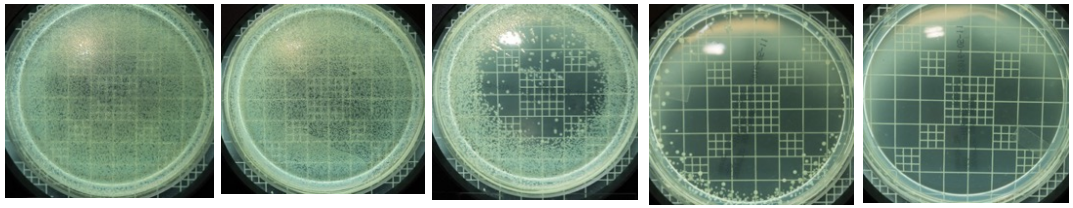
DBD mister produce treatment setup







Water flow rate: 0.18 ml/min, Complete inactivation, up to 10^7 *E.coli*



Control | 5 sec | 15 sec | 45 sec | 135 sec

$$H^+ + H_2O_2 + NO_2^- \rightarrow H^+(NOO_2^-) + H_2O$$

$$H^{\oplus}ON\text{-}O\text{-}O^{\ominus} \rightleftharpoons OH + NO2$$

$$H^{\oplus} + NO3^{\ominus}$$

$$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+}$$

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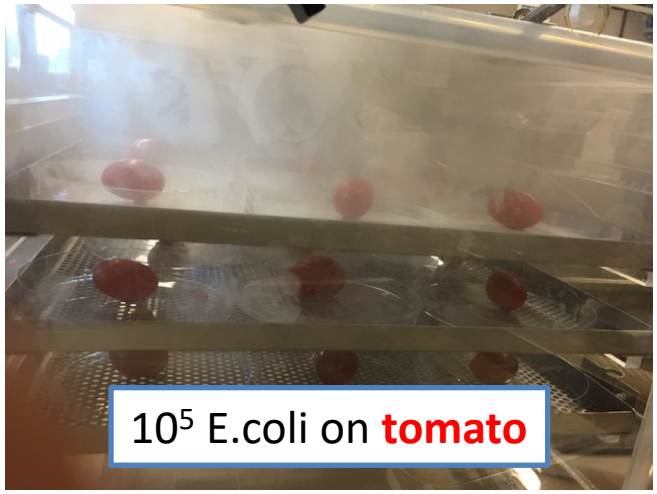
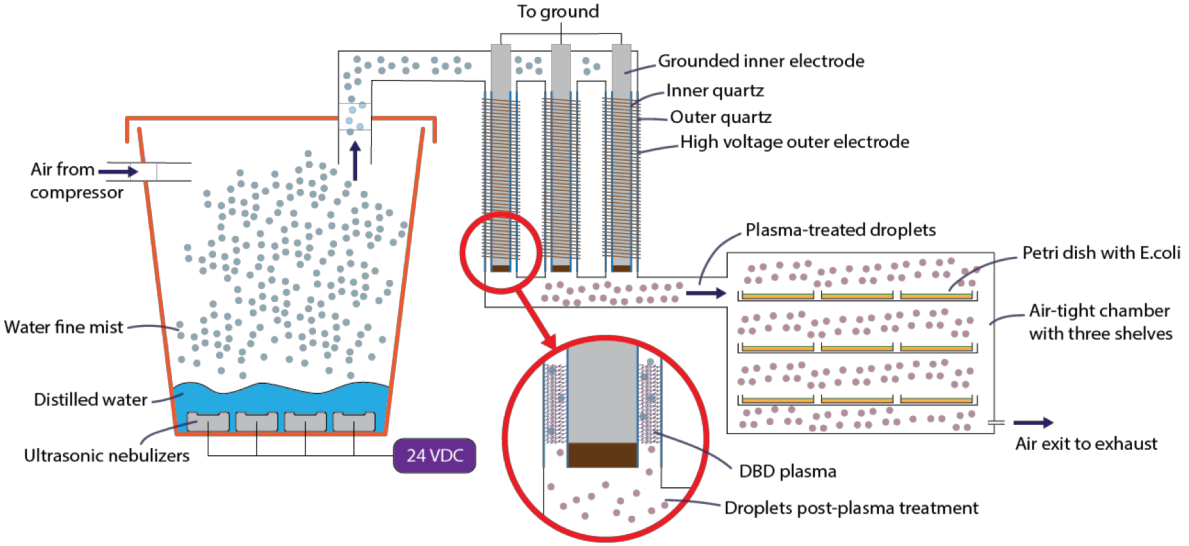
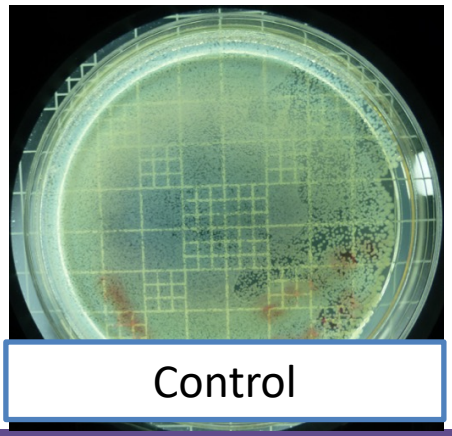
Three-pipe large-scale **4 ft³** DBD misting setup for fresh produce processing



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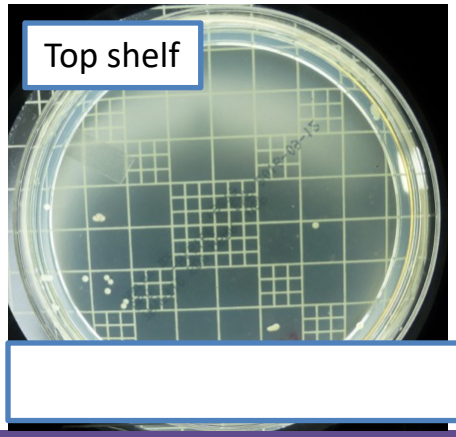
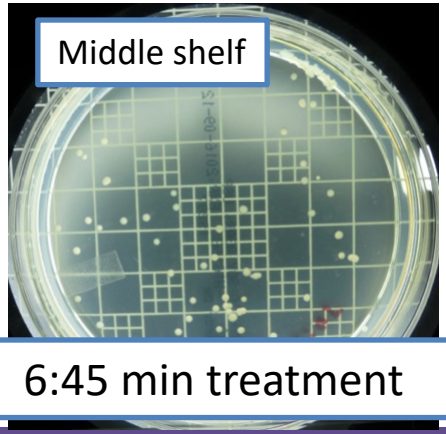
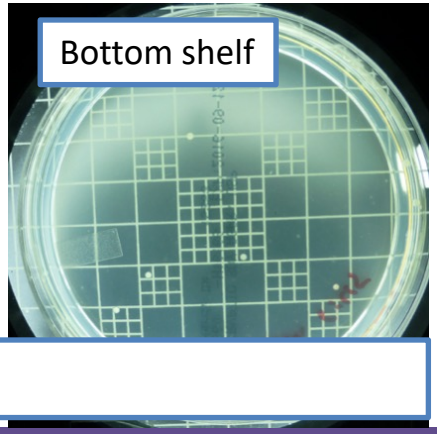

Top shelf


Middle shelf


Bottom shelf

6:45 min treatment

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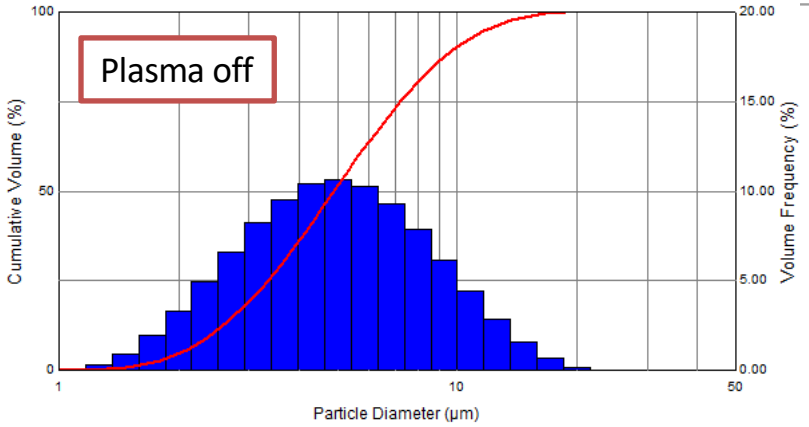
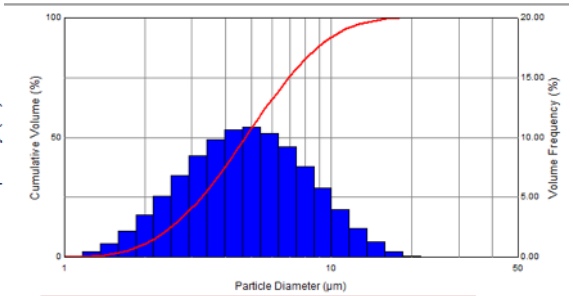
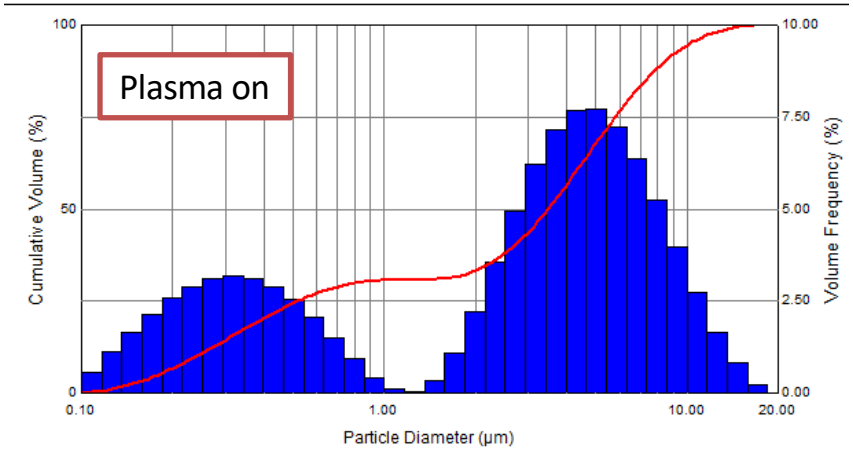
Droplet explosions and cluster formation in DBD plasma





Plasma on with biased grid

Fast condensation on ions and metastables



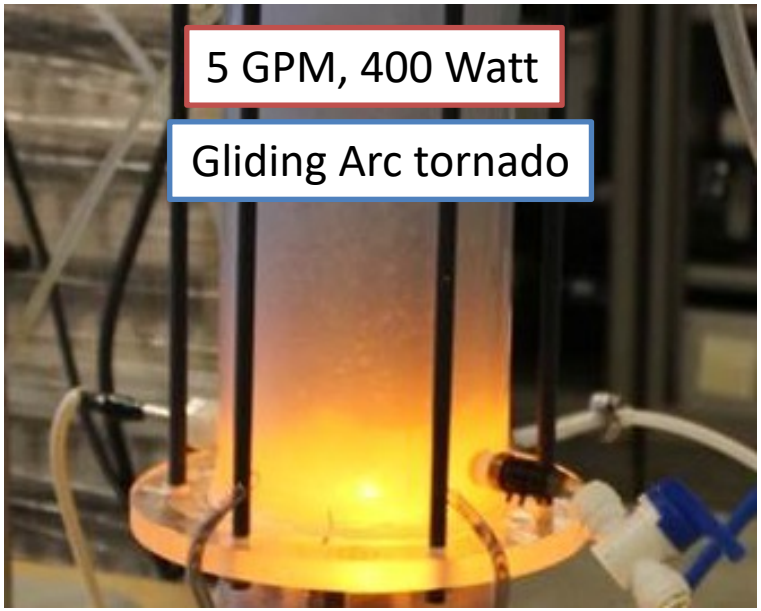
- **Large droplet explosions and**
- **Formation of water clusters on charged and metastable species**

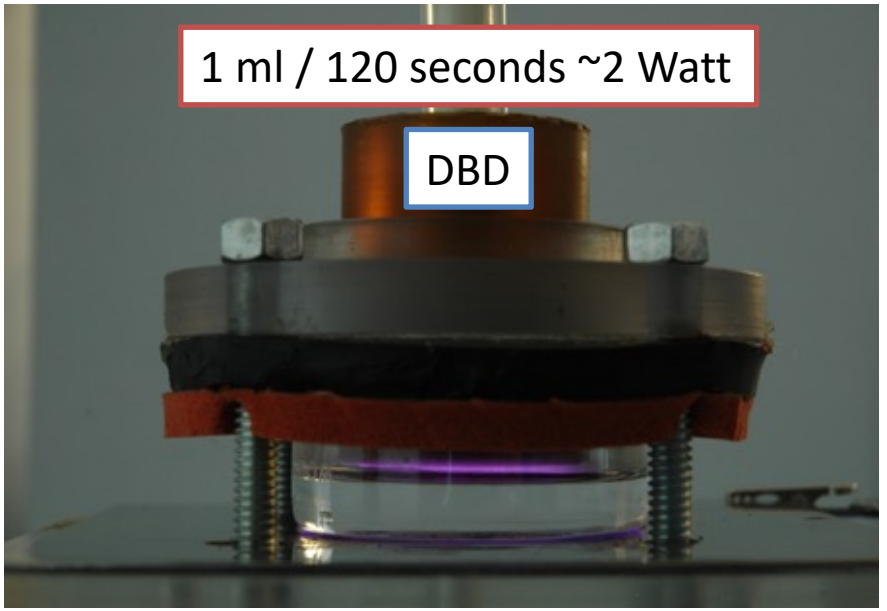
→ **High efficiency and efficacy of surface treatment, disinfection**

→ **Reduction in water activity of foods and fast drying of processed materials**

Scale-up, production of more plasma-treated water, requires higher power

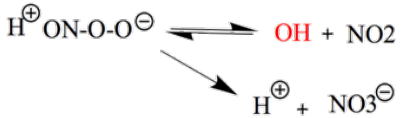
Increasing temperature generates more acidity but destroys peroxides.



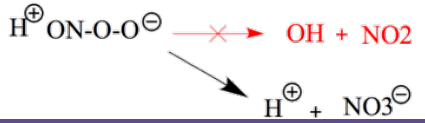


Temp ºC	Reaction time
1 ºC	10 sec
20 ºC	0.3 sec
30 ºC	0.03 sec
50 ºC	1 msec
80 ºC	30 µsec

At low temperature:



At elevated temperature:



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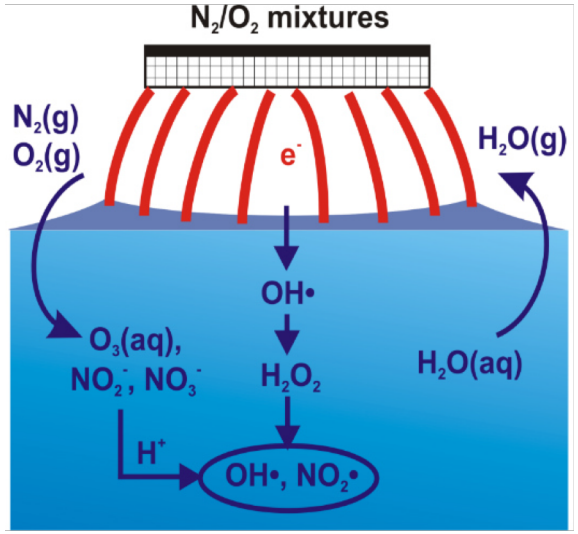
For AGR industry, high power is needed and temperature follows power

Acidic decomposition of NO_2^-

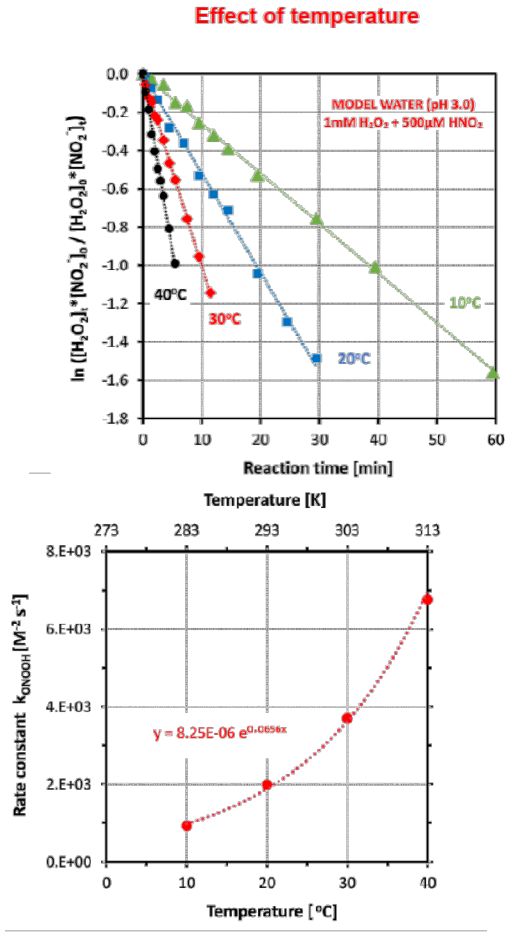
$$2\,NO_2^- + 2\,H^+ \leftrightarrow 2\,HNO_2 \xrightarrow{pH < 3.5} NO\bullet + NO_2\bullet + H_2O$$

Peroxynitrite formation via NO_2^-/H_2O_2

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



- Lukes et al. Plasma Sources Sci. Technol. 23 (2014) 015019
- Lukes P., Dolezalova E., Laurita R., Colombo V., 6th International Conference on Plasma Medicine (ICPM-6) Bratislava, Slovakia, Sept. 4-9, 2016



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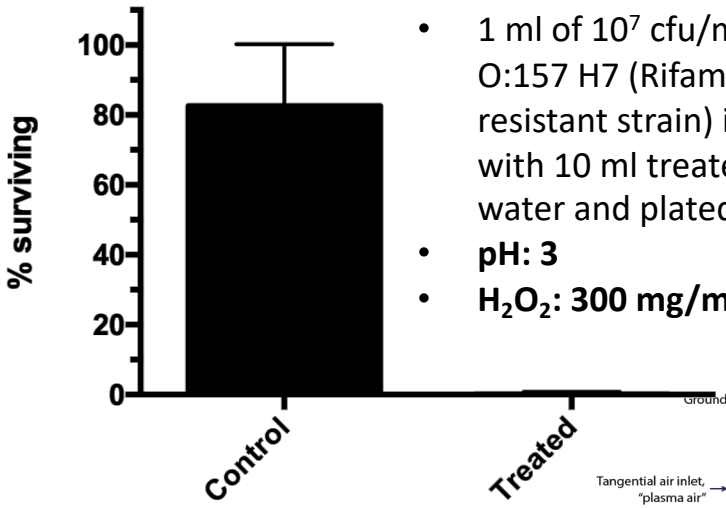
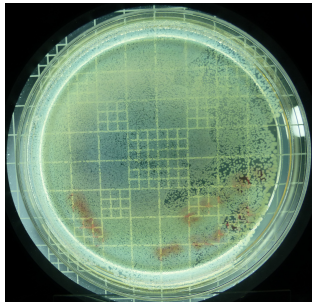
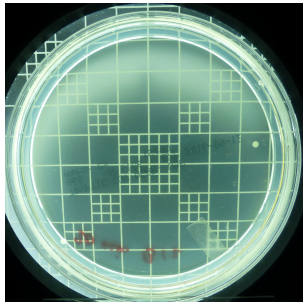
Sterilization by washing with actively-cooled plasma-treated water



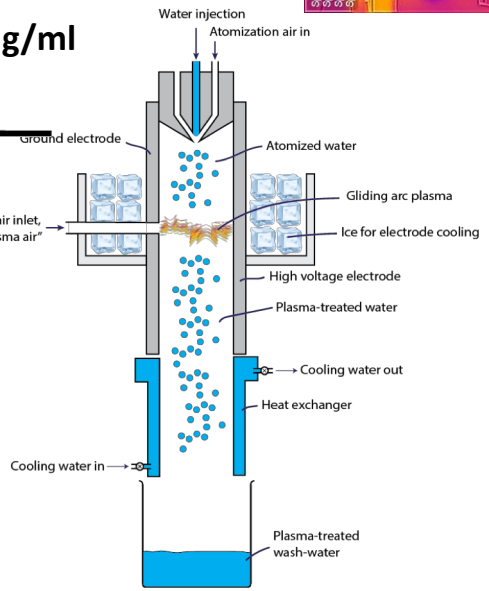
- 1 ml of 10^7 cfu/ml *E.coli* O:157 H7 (Rifampicin resistant strain) is mixed with 10 ml treated tap water and plated
- **pH: 3**
- **H_2O_2: 300 mg/ml**

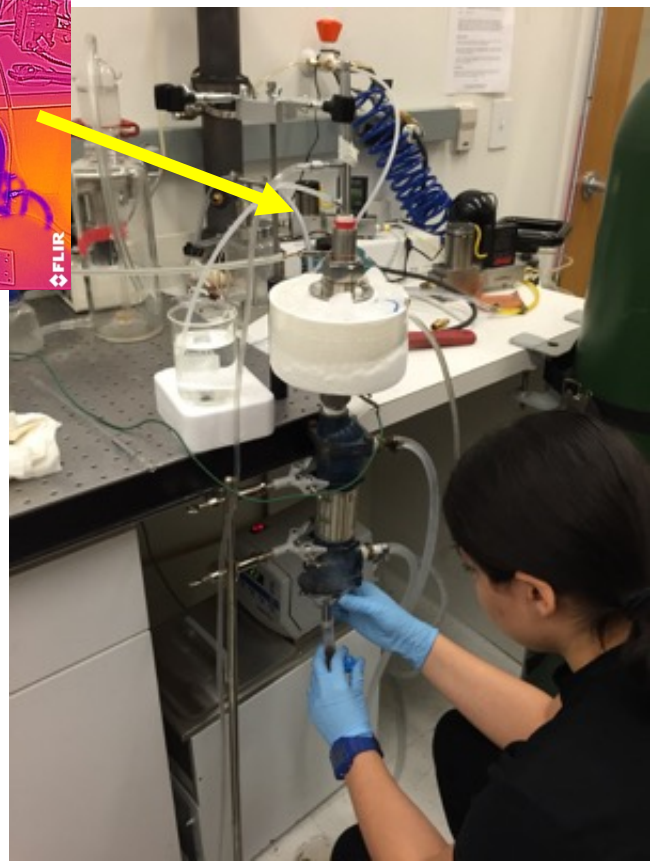


Control



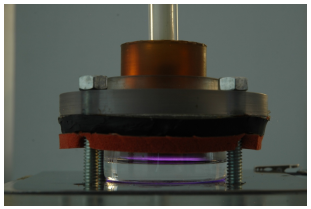
Treated



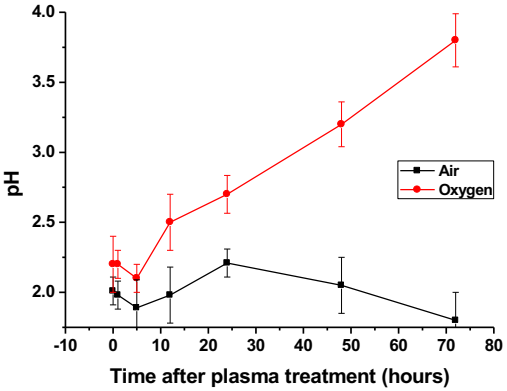


Metastables in *oxygen plasma*-activated water: plasma acid

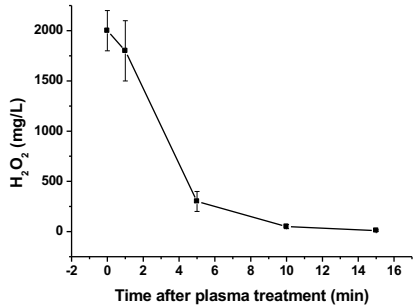
1. **Positive Ions** create **acidity**
   - **Charge exchange mechanism:**
     N_2^+ (O_2^+) +H_2O → H_2O^+ +N_2(O_2)
   - $H_2O^+ + H_2O \rightarrow H^+(H2O)+OH^\bullet$



2. **Conjugate Base (Negative Ions)**
   - $e + O_2 \rightarrow O_2^-$
   - O_2^- is the primary negative ion both in gas and liquid
   - **H_2O_2** may be present in small concentration and may participate

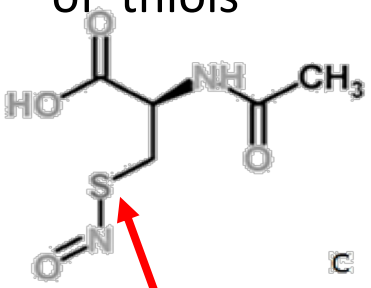


- Plasma acid in oxygen is not too stable
- Nitric/nitrous acid presence could stabilize plasma acid
- Usual for metastable substances

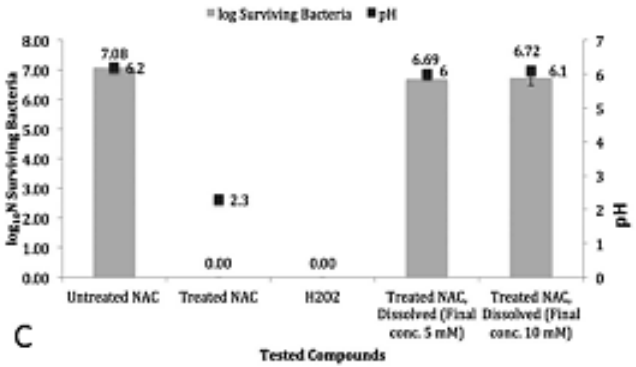


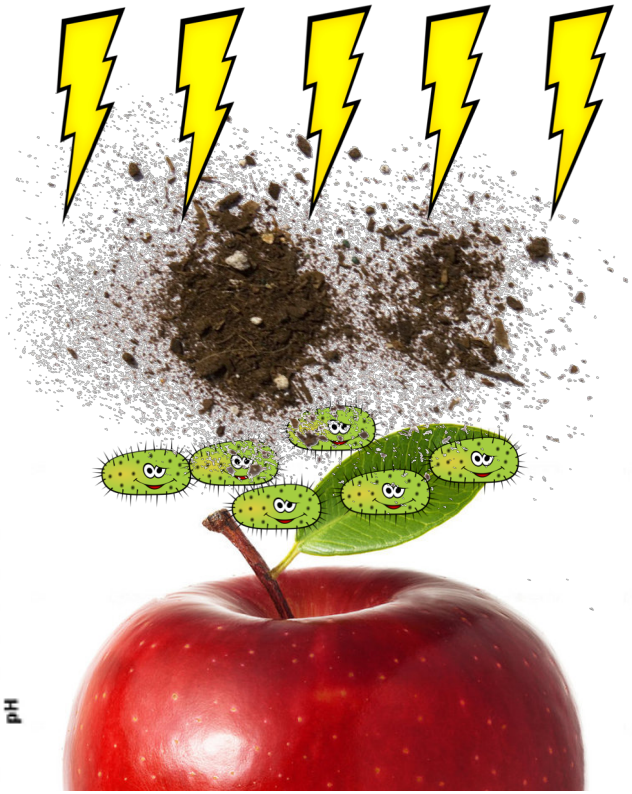
Metastables in plasma-activated bio-organic solutions (NAC → SNAC)

- Biological buffers and antioxidants are everywhere in AGR systems and block action/effects of peroxides and ONOO-; exceptional role of tyrosine
- Non-oxidative plasma disinfection: through plasma-NO stimulated S-nitrosylation of thiols



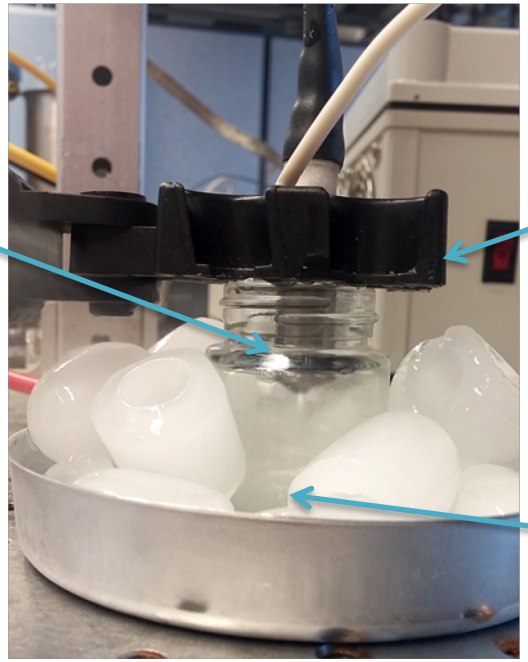
S-Nitrosylation of NAC (SNAC production)

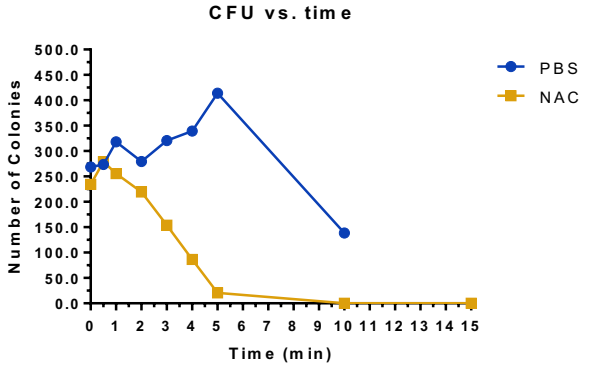




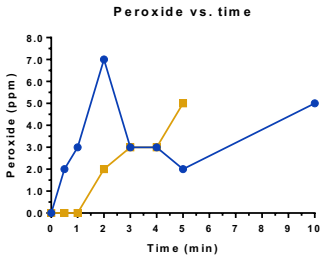
Metastables in plasma-activated bio-organic solutions (NAC → SNAC): applications

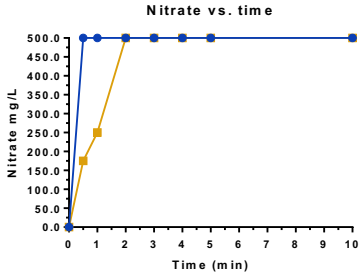
- Parameters:
- 6 SLPM compressed air
- Electrode is 3 cm above the solution
- Rotating Spark

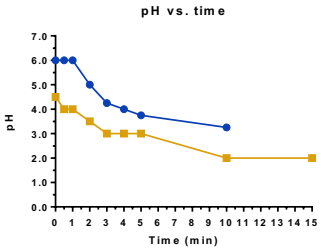




Non-oxidative inactivation of *E.coli* O157:H7 by Plasma Treated NAC Solution







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Goals

- **Non-oxidative disinfection** in medicine, food processing, and agriculture: disinfection in presence of high organic load
- **Scale-up of oxidative disinfection** flowing water treatment systems:
  - DBD misting with air, oxygen, nitrogen
  - Air plasmatron with cooling: high throughput
- Analysis of **water cluster formation** and influence on disinfection, water activity of foodstuffs, surface drying

Approach

- Analyze effect of increasing COD on disinfection
- Analyze water cluster formation rate and its effects on disinfection
- Transition from DBD to GlidArc by understanding the disinfection mechanisms

Outcomes/Deliverables

- Mechanism of non-oxidative disinfection in presence of organic load
- Mechanism of oxidative disinfection
- Understanding of appropriate approach for scale-up of DBD-based misting systems and GlidArc-based high-throughput systems

Project Timeline and Duration

Task / month	1	2	3	4	5	6	7	8	9	10	11	12
Non-oxidative disinfection in medicine, food processing, and agriculture: disinfection in presence of high organic load	x	x	x	x	x	x						
Scale-up of oxidative flowing water treatment systems: - DBD misting with air, oxygen, nitrogen - Air plasmatron with cooling: high throughput		x	x	x	x	x	x	x	x	x		
Analysis of water cluster formation and influence on water activity of foods, surface drying					x	x	x	x	x	x	x	x

Project Budget

Item	Cost
Student stipend	$ 20,000.00
Supplies	$ 10,000.00
Purchased services	$ 3,000.00
Equipment	$ 5,000.00
Travel	$ 2,000.00
Project total*	**$ 40,000**

*C-PEAB leadership recommends not to exceed $40,000/year unless discussed with IAB