

Part 1: Plasma-Liquid Transport Processes in Convective Systems

Part 2: Fertilization of Raddishes, Marigolds, and Tomatoes Using Plasma Activated Water

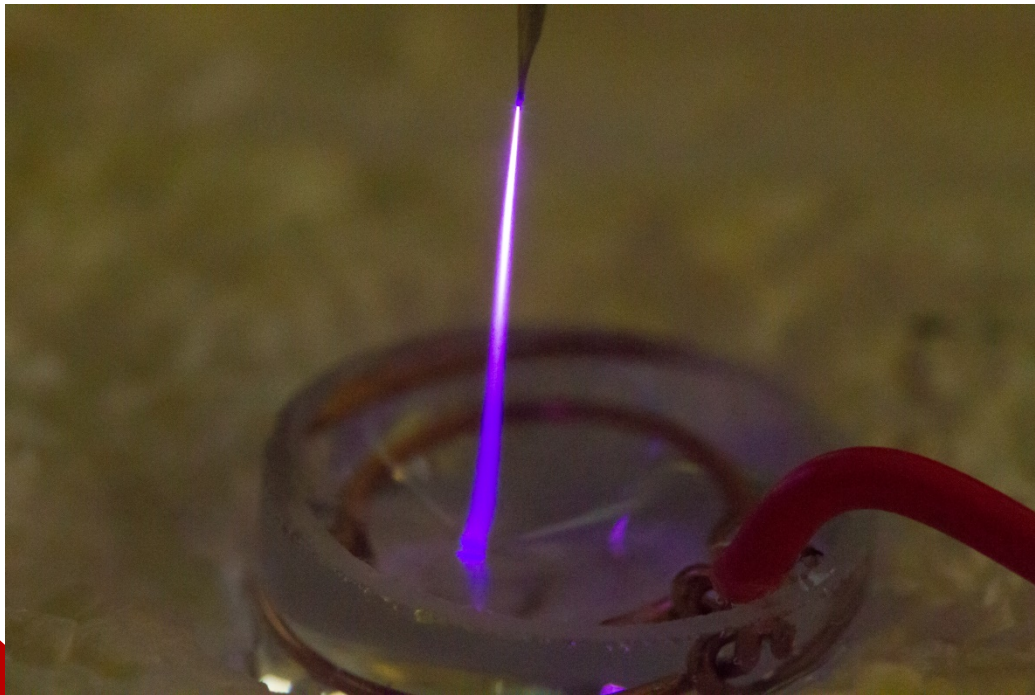
Alex Lindsay, Brandon Byrns, Carly Anderson, Brandon Curtis,
Elmar Slikboer, Detlef Knappe, William Fonteno, David Graves,
Steven Shannon

Part 1: Purpose & Overview

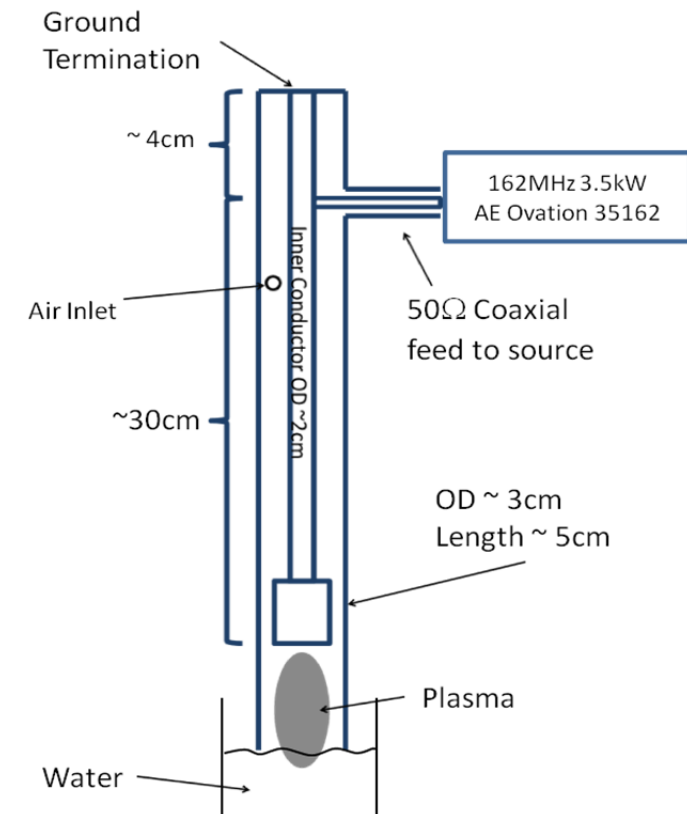
- Purpose: Gain better qualitative understanding of plasma-generated species transport at interface and in bulk solution for systems in which convection is important
 - Most sophisticated models of atmospheric plasma-liquid systems investigate DBD discharges or other plasma systems in which diffusion is dominant transport process (e.g. Tian, Wei, and Mark J. Kushner, *Journal of Physics D: Applied Physics* 47.16 (2014): 165201.)
- Talk overview
 - Momentum transport: gas phase convection induces convective currents in liquid
 - Heat transport
 - Dilute species transport without reactions
 - Dilute species transport with reactions

Model Convective Systems

- UC Berkeley: pulsed corona discharge (primary focus for current modeling)



- NCSU: 162 MHz wave-driven discharge (return to in Part 2 of talk)



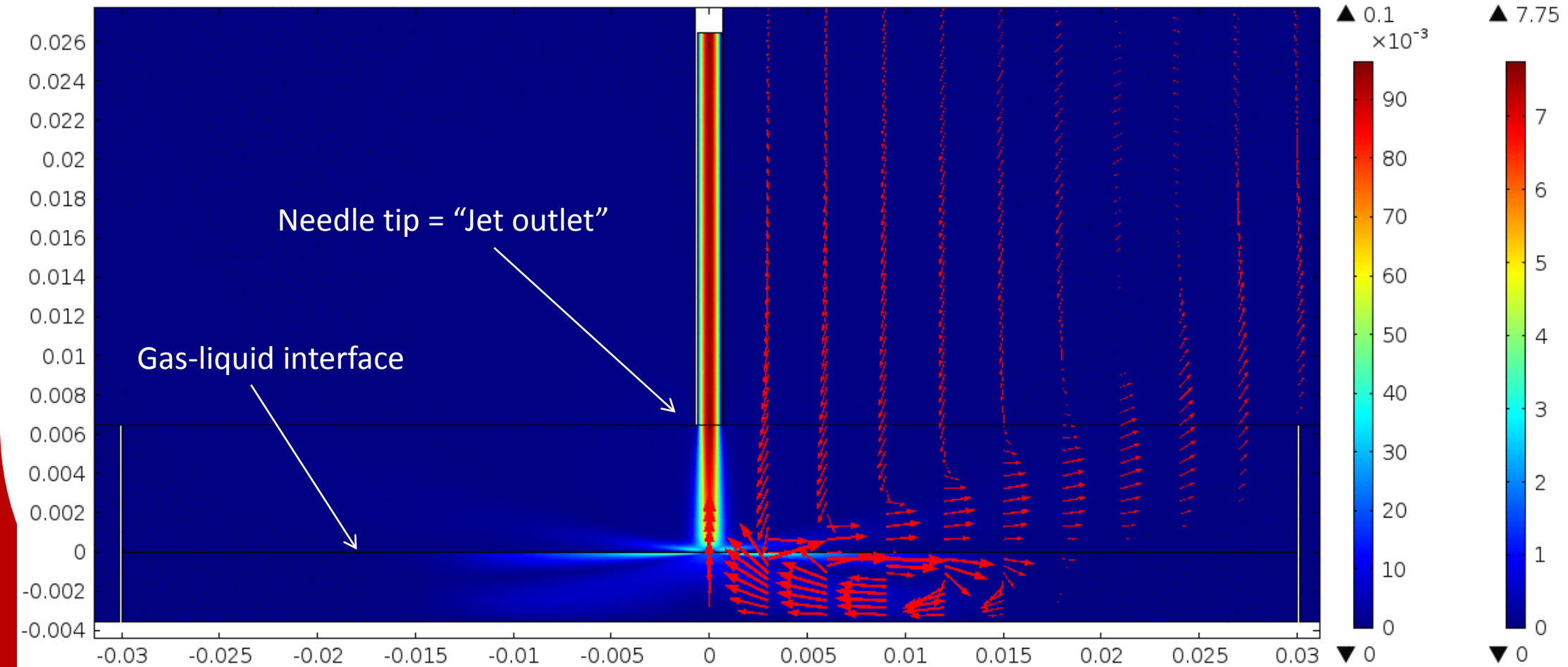
Pulsed corona inputs

- Not currently modeling plasma
- Model ionic wind using a jet with diameter = needle diameter = .6 mm
- Experimentally measure 6 kV pulses with $\sim .7$ cm gap between needle and water surface
- Zhao et. al. (J. Electrostatics 63 (2005)) modeled gas flow profiles for corona discharges
 - Interpolating from their data, obtain a maximum axial flow velocity of 7.75 m/s for 6 kV
 - Use this as maximum velocity in jet model
- With preliminary model, interested in qualitative understanding of dilute species mass transport
 - Inlet concentrations of all “plasma”-generated species based on DBD streamer-liquid model of Kushner and Tian

Fluid flow and momentum transport: velocity magnitude

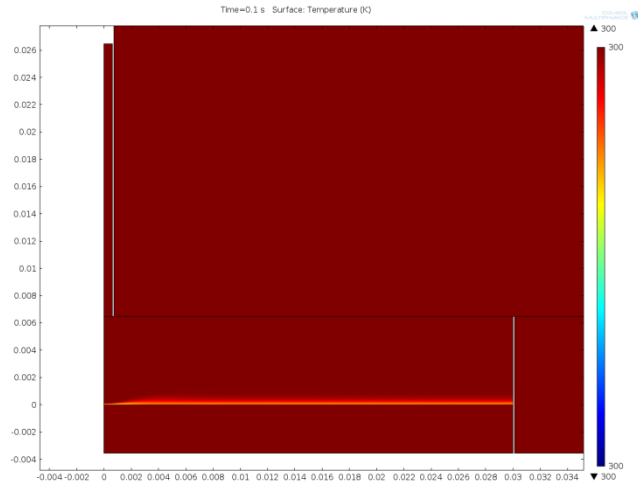
Time=150 s Surface: $(u^2+w^2)^{0.5}$ (m/s) Surface: $(u^2+w^2)^{0.5}$ (m/s) Arrow Surface: Arrow Surface:

COMSOL
MULTIPHYSICS

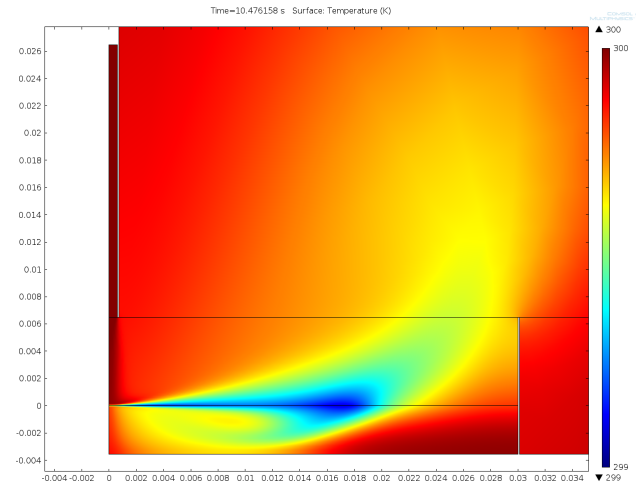


Coupled heat and mass transfer due to convection

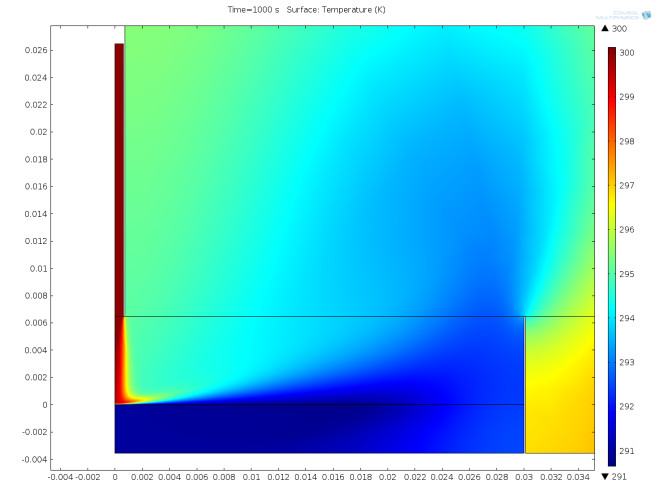
Temperature →



$t = .1 \text{ s}$

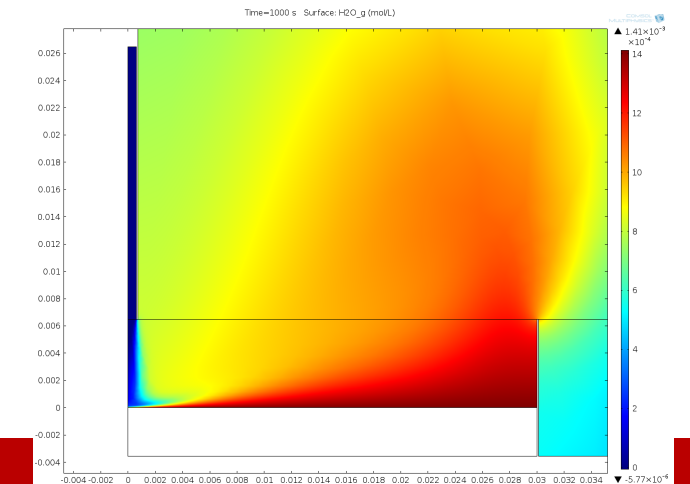
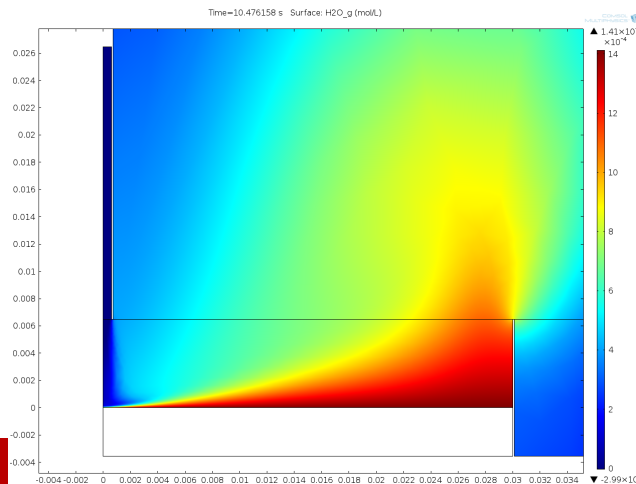
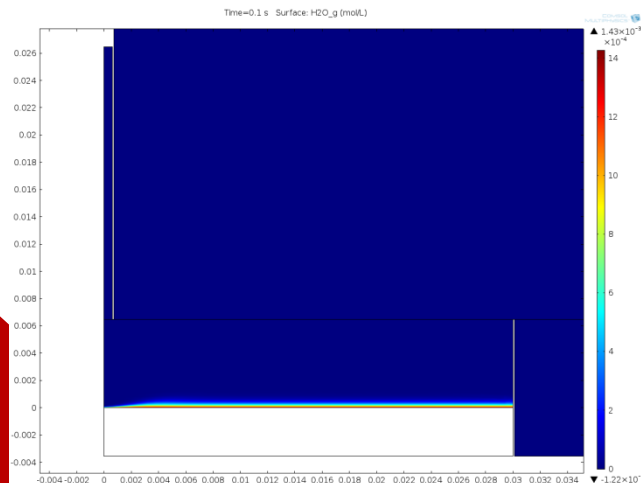


$t = 10 \text{ s}$

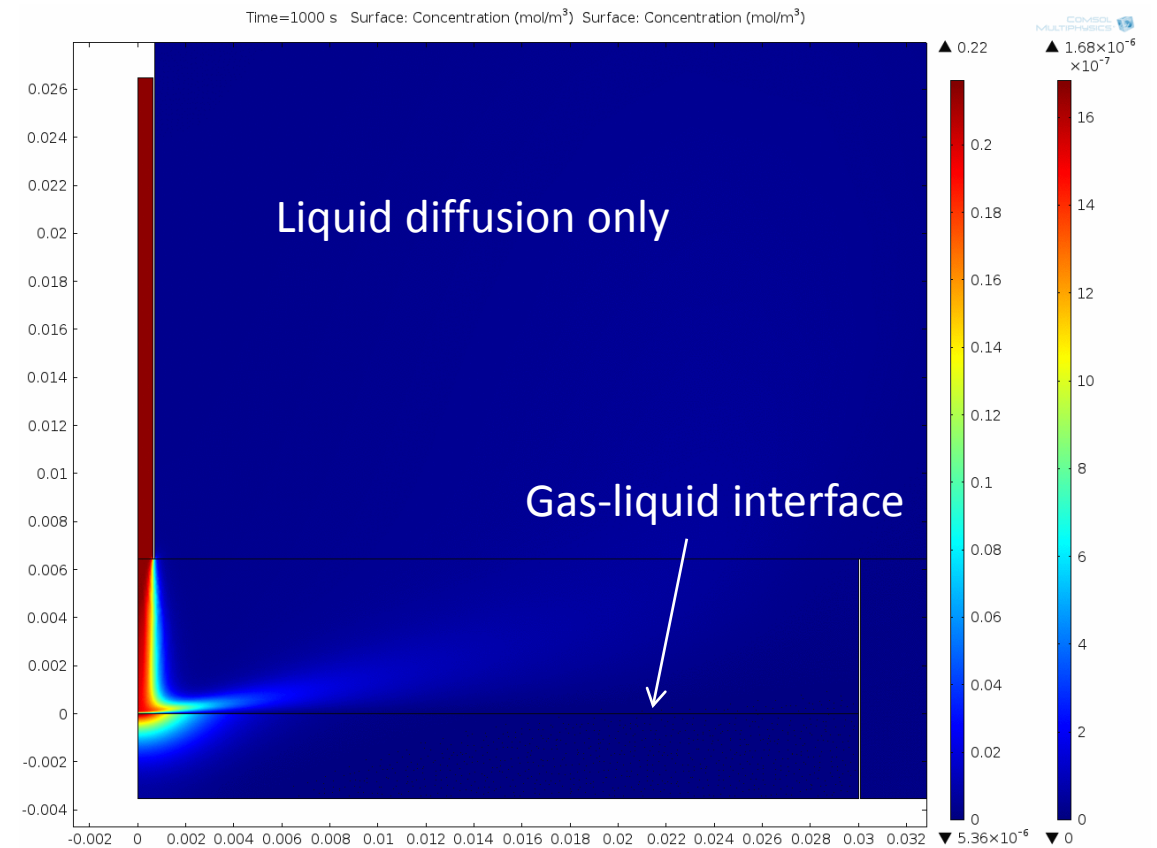
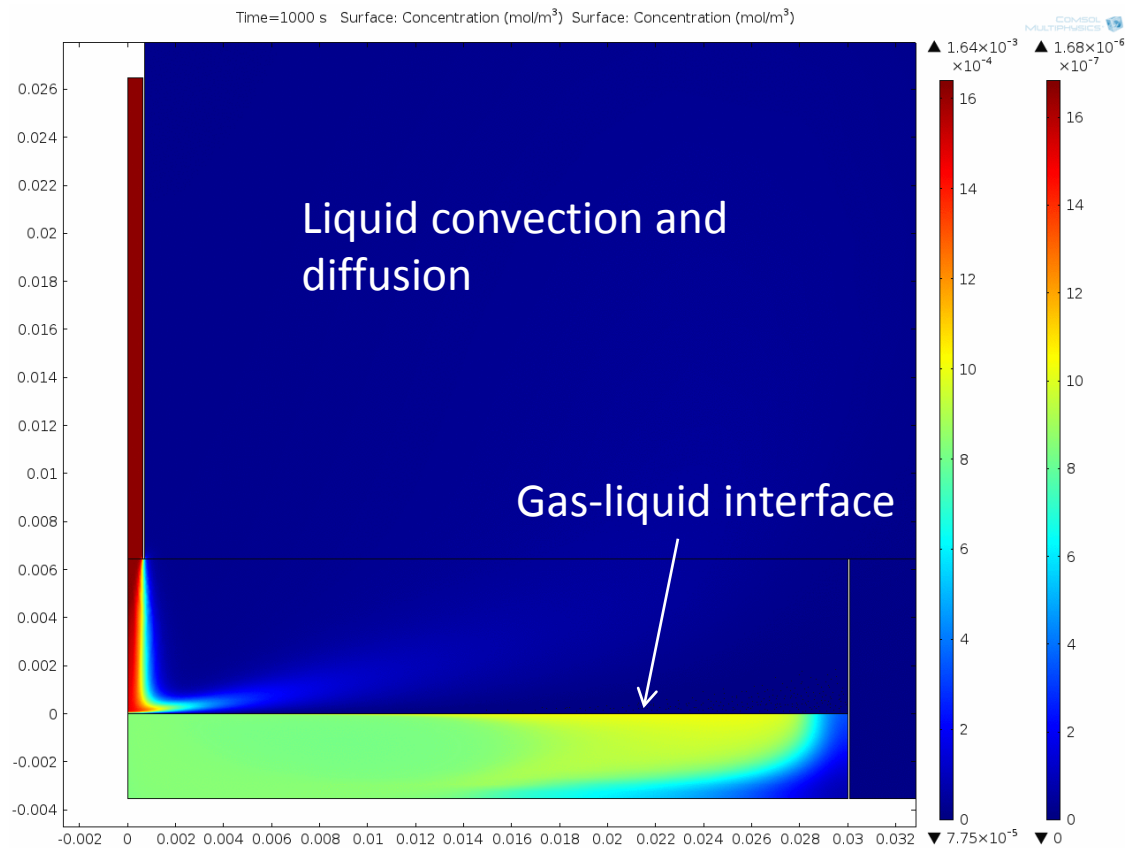


$t = 1000 \text{ s}$

H₂O(g) concentration →

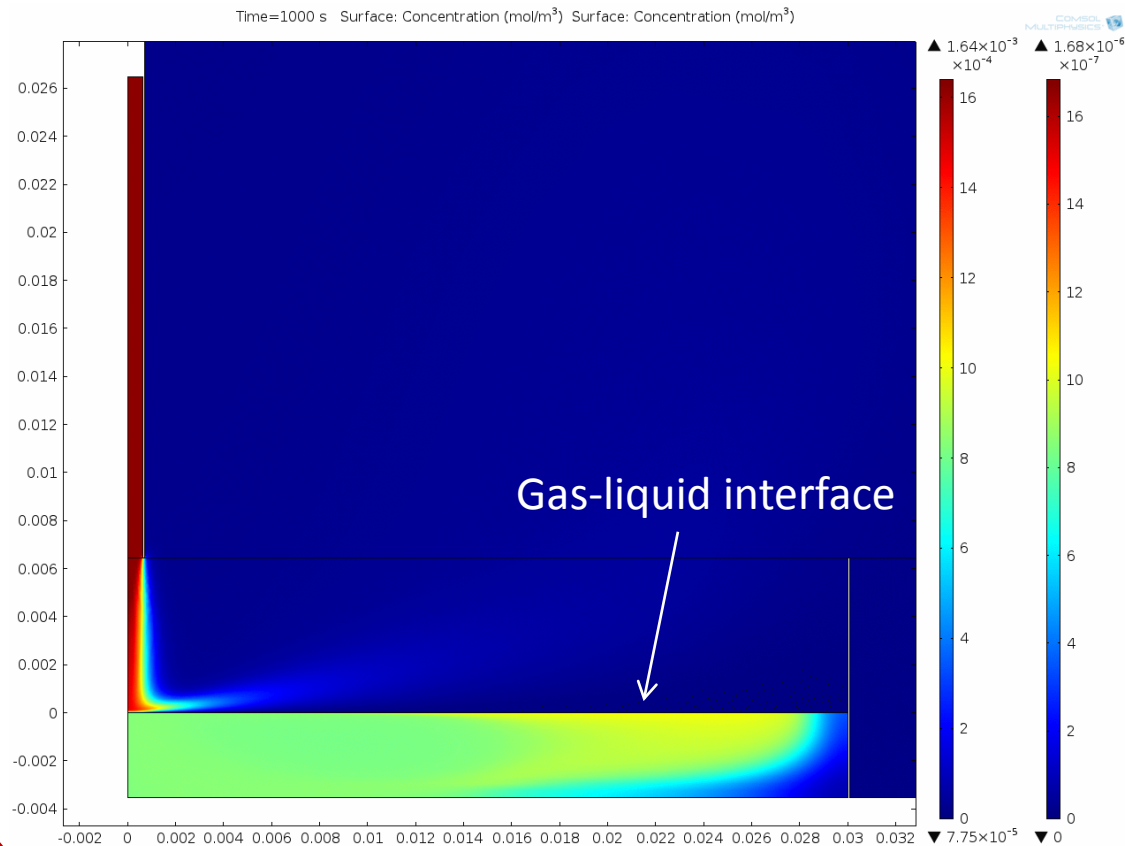


HNO_3 dissolution with and without convection (no reactions)

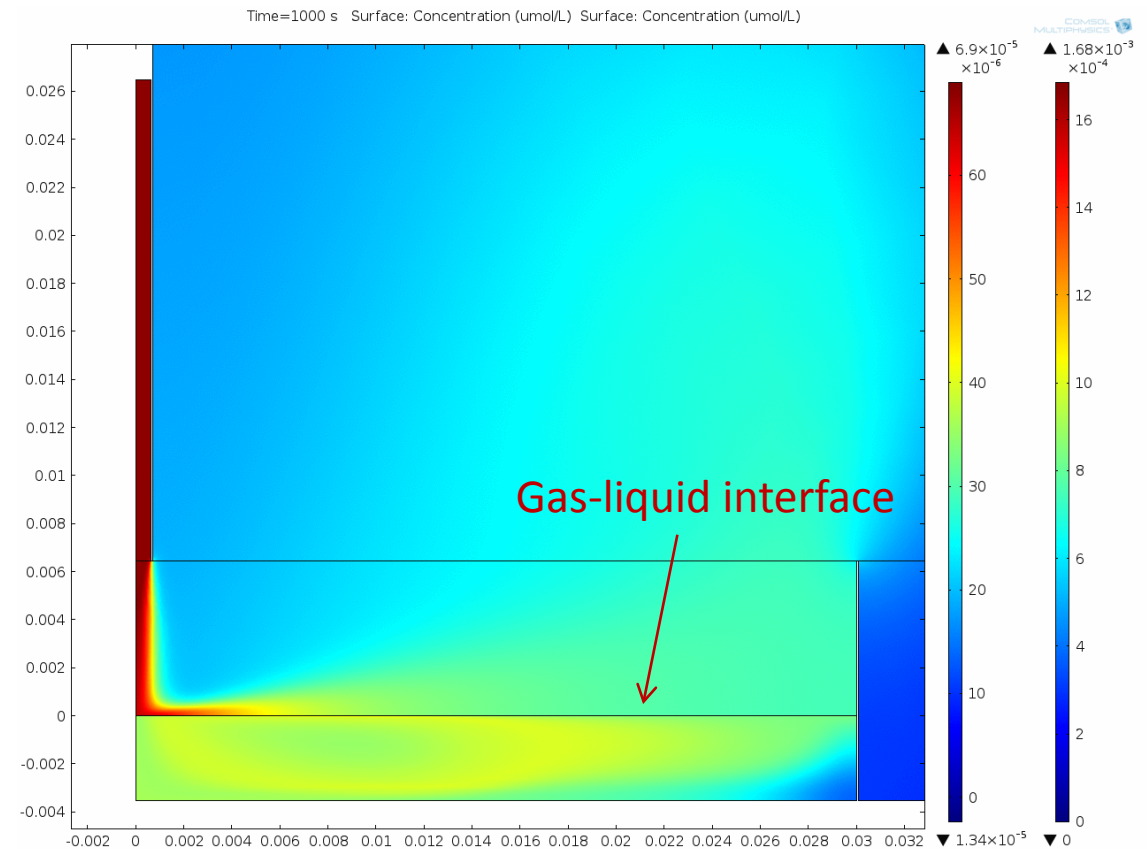


Dissolution of hydrophilic vs. hydrophobic species (no reactions)

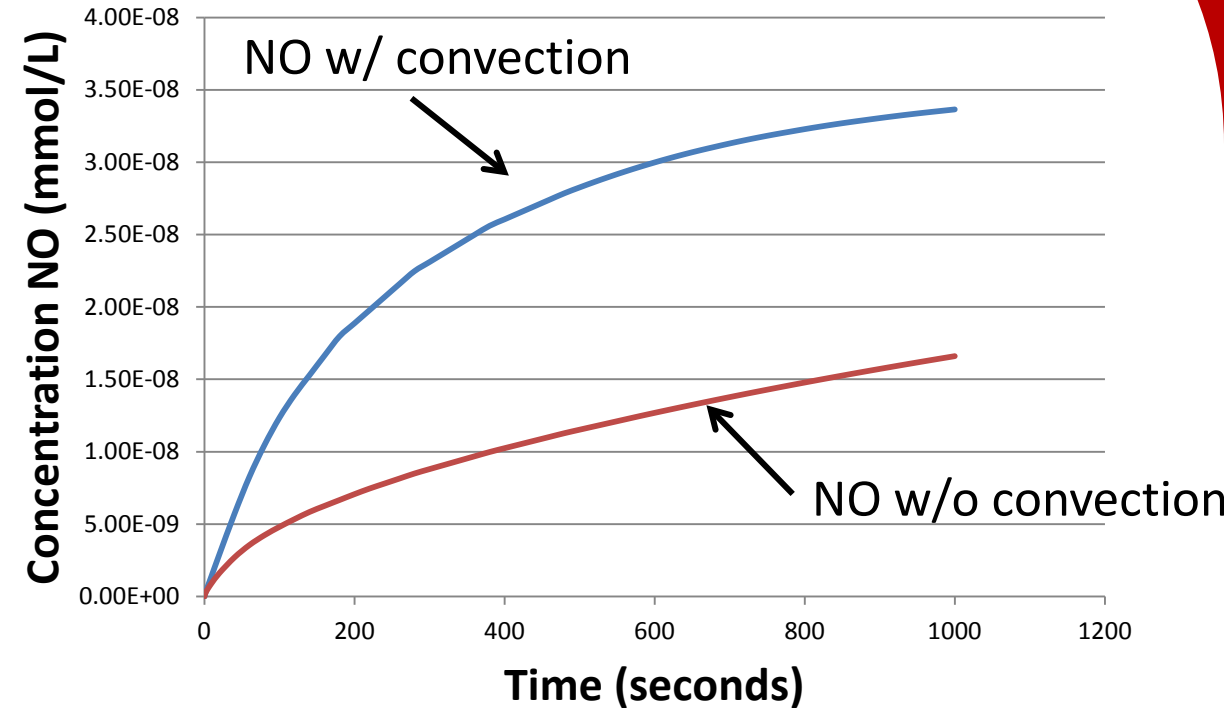
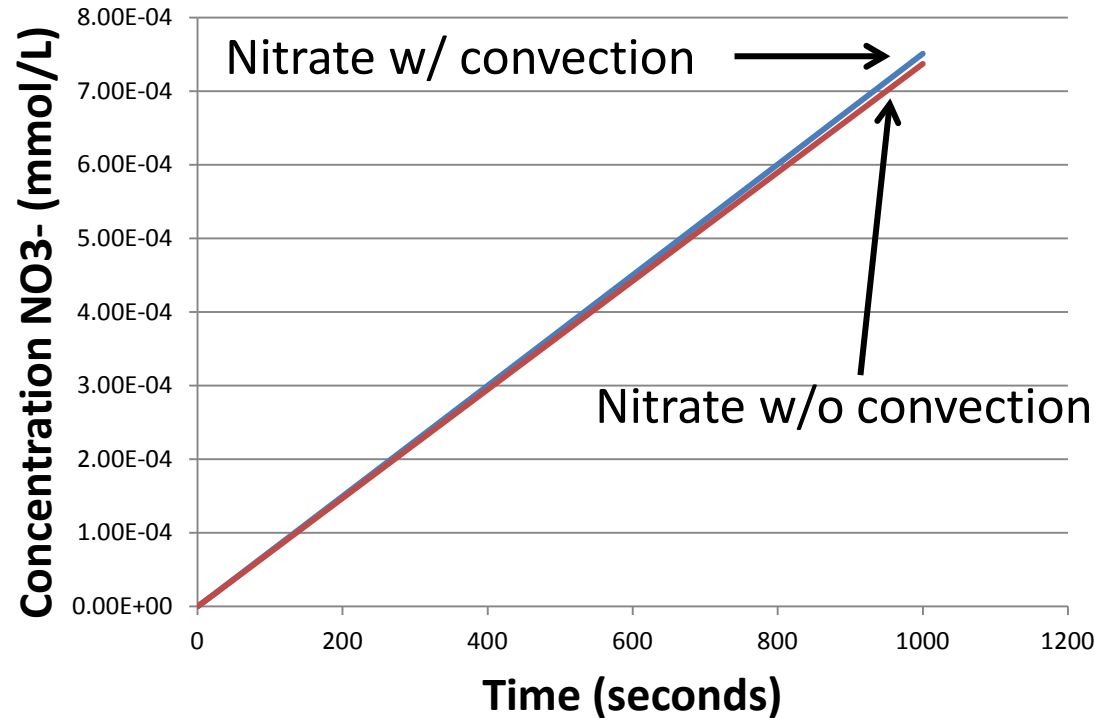
HNO₃



NO



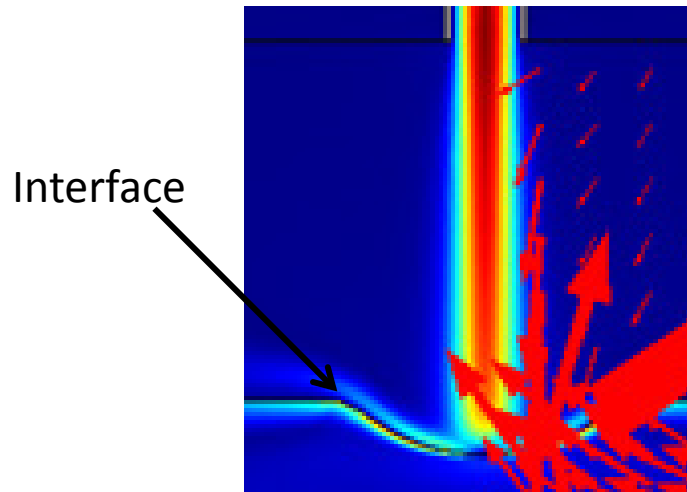
Role of convection in total species uptake



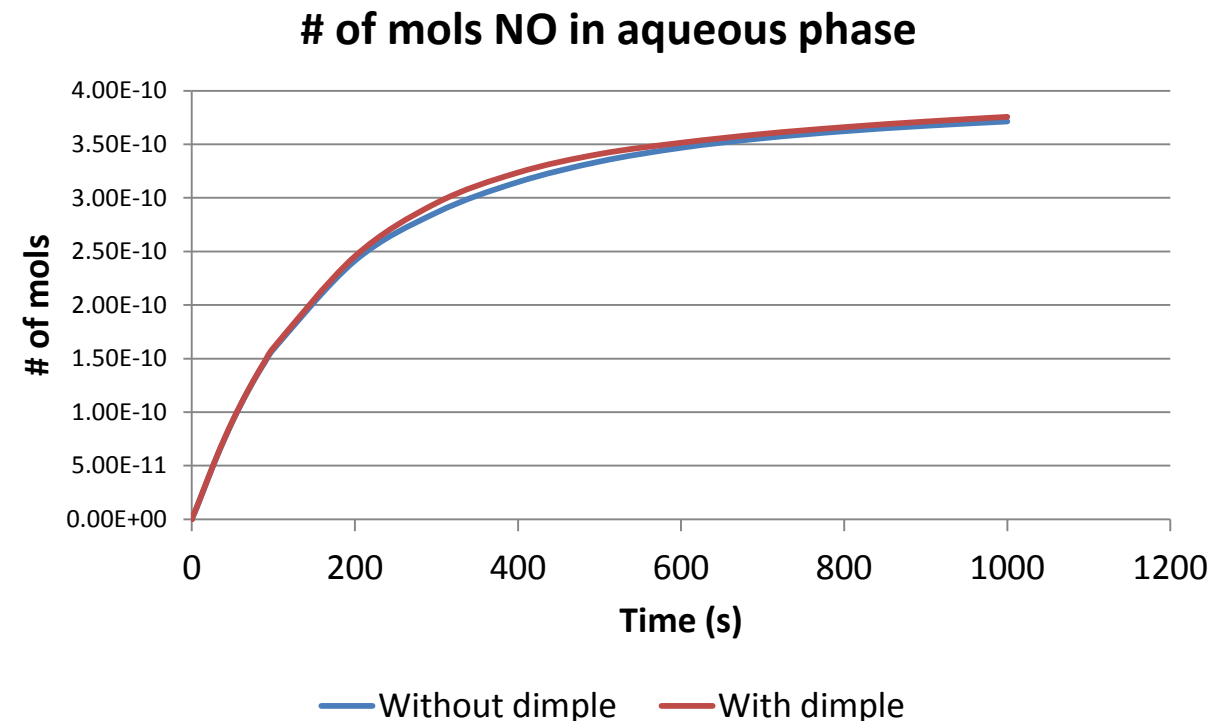
- Though concentration profiles are clearly different, including liquid convection hardly changes hydrophilic nitrate uptake rate
- However, including liquid convection increases hydrophobic NO uptake by factor of 2
- Fundamental difference in behavior between -philic and -phobic species not intuitively obvious (to me)

What about interface deformation from corona impingement?

- During experiments, visually estimate size of interface depression
- Consistent with shape determined from force balance (R.B. Banks: J. Fluid Mech., 1963 vol. 15, pp. 13–34.)
- Insert into model:



Effect of interface on species uptake: max of 3% error over simulation time → Interface deformation not important for phenomena we care about

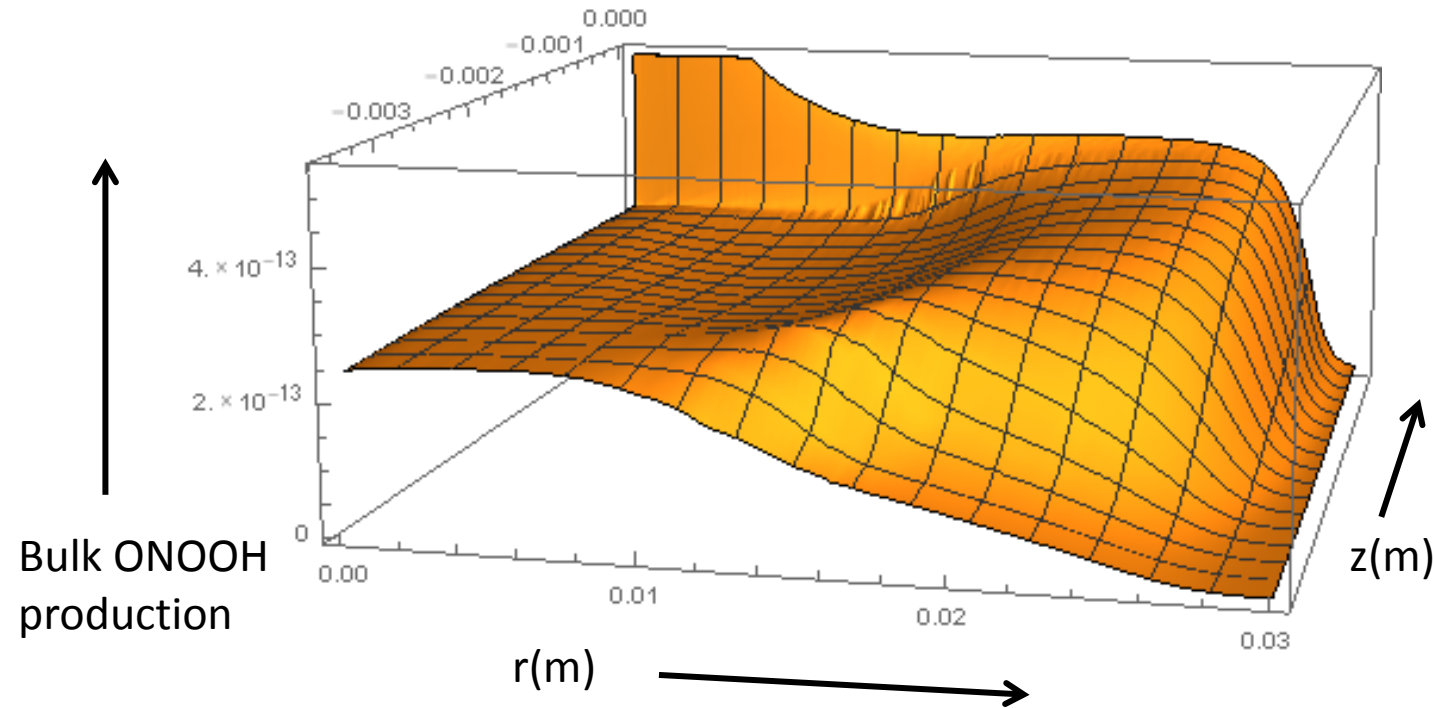


Reactions

- We use a limited reaction set focusing on NO_x species that contribute to formation of ONOOH and OH in liquid phase
- Reactive species considered:
 - NO, NO₂, N₂O₄, OH, H₂O₂, H₂O, HNO₂, NO₂⁻, HNO₃, NO₃⁻, H⁺, OH⁻, ONOOH
- Observe penetration depth of OH to be **1-10 μm**
- For applications requiring high reactivity in the bulk liquid or at some underlying substrate, we must look to less reactive pre-cursors which have time to be transported from the plasma-liquid interface to the bulk solution

- Lukes (PSST 23 (2014)) & others have postulated that OH and NO₂ radicals produced through dissociation of ONOOH may significantly contribute to bactericidal effects of plasma activated water (PAW)
- Key reaction for bulk ONOOH production:
 - $\text{H}_2\text{O}_2 + \text{H}^+ + \text{NO}_2^- \rightarrow \text{ONOOH}$
- While discharge is on, liquid convection and high concentrations of reactants in vicinity of streamer lead to inhomogeneous bulk production of ONOOH
- Post-discharge, production should homogenize
- Large gradients at interface raise following questions: Do we have non-ideal solution thermodynamics at surface where species concentrations (including ions) can be significantly higher? What effect could this have on Henry's law coefficient and solvation rates? What about heats of solvation? → Area of future research

Bulk ONOOH



Summary

- Convection leads to significant coupled heat and mass transfer at gas-liquid interface
 - Depending on impinging gas temperature, possible to observe significant changes in liquid temperature → affects bulk solution kinetics
 - Inhomogeneous distribution of water vapor above water surface → likely to affect type and quantity of plasma-generated species
- Convection plays key role in spatial distribution of aqueous species
 - Also significantly increases volume averaged uptake of hydrophobic species (effect not observed for hydrophilic species)
- Inhomogeneous bulk production of ONOOH while discharge is on due to higher reactant concentrations near streamer and within convective loop
 - Should homogenize post-discharge

Future Work

- Incorporate plasma model for more accurate description of gas phase composition and heat transfer between phases
- Relative importance of surface vs. bulk reactive species production
- More details of interface and aqueous phase:
 - Double layers
 - Electrochemical reactions at electrode
 - Non-ideal solution thermodynamics?
 - Heating from solvation
 - Photons
 -

Part 1: Plasma-Liquid Transport Processes in Convective
Systems

Part 2: Fertilization of Raddishes, Marigolds, and Tomatoes
Using Plasma Activated Water

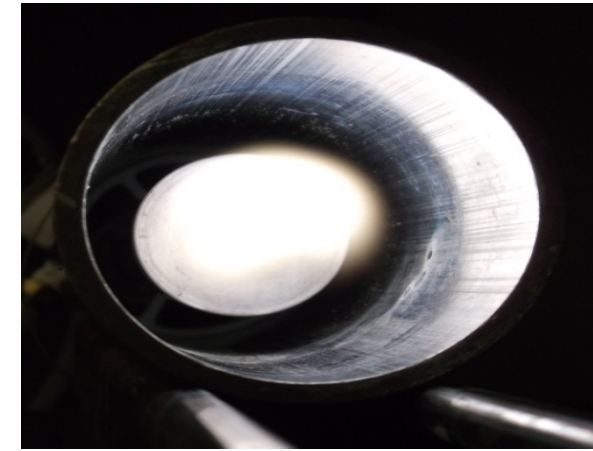
Part 2 Purpose: Distributed Fertilizer Production

- As distributed sources of energy (solar, wind) and electricity continue to advance, there is a growing opportunity for distributed and locally controlled production of fertilizer
- For remote regions or regions with poor infrastructure, costs of delivering essential nitrogen fertilizer can be high
- Far-reaching goal is to develop renewably-powered source of fertilizer capable of assisting farmers with poor access to centralized fertilizer producers or who desire greater control over their fertilizer supply/use

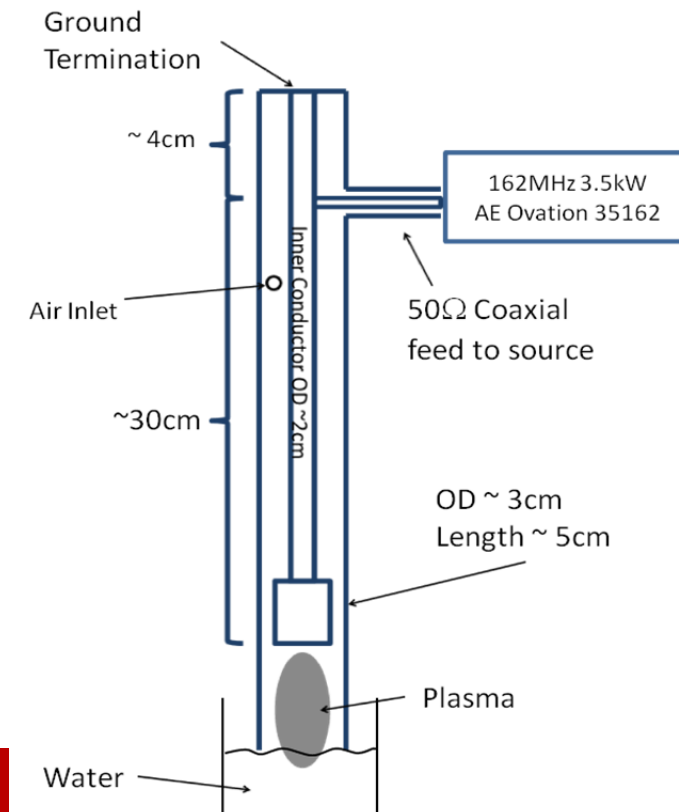


Agro-chemicals

- Important nitrogen species in plant life cycle:
 - Ammonium: NH_4^+
 - Nitrate: NO_3^-
 - Nitrite: NO_2^-
- We readily create these species in an air plasma at atmosphere
 - Source design: Byrns, Brandon, et al. "A VHF driven coaxial atmospheric air plasma: electrical and optical characterization." *Journal of Physics D: Applied Physics* 45.19 (2012): 195204.



NCSU
162 MHz
coaxial
plasma
source in
air



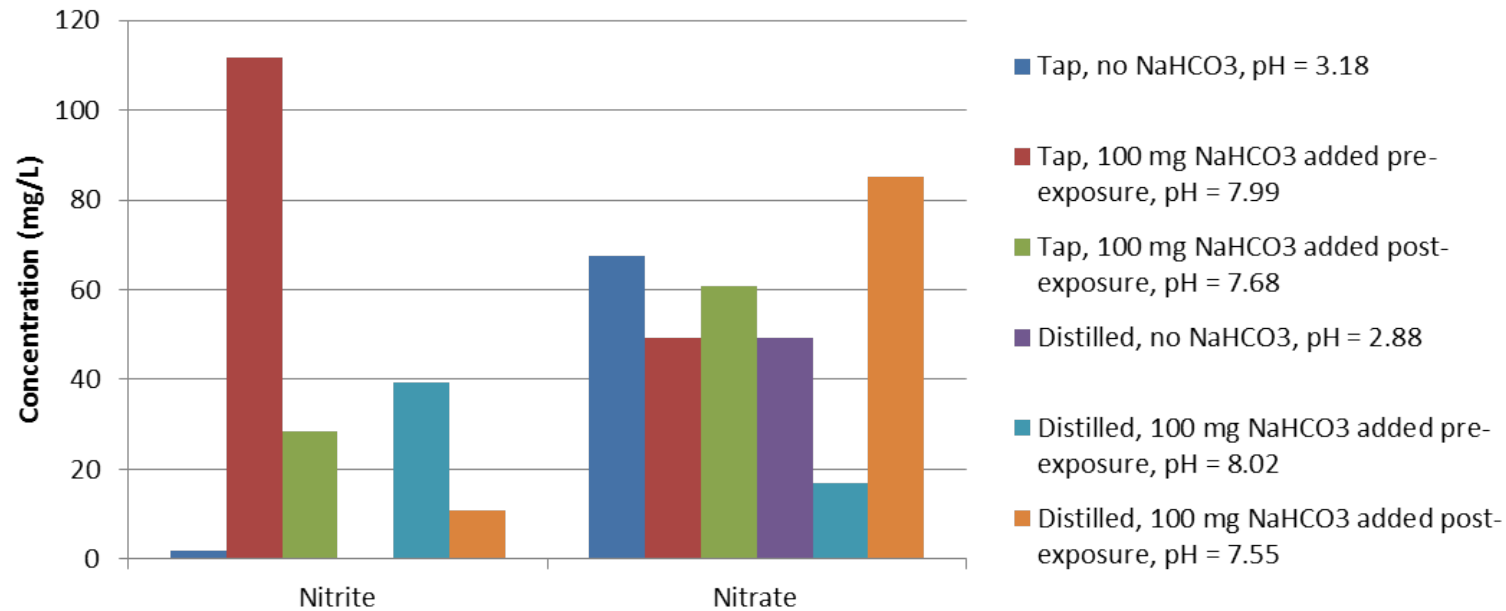
Source set-
up for PAW
generation

Part 2: Overview

- Observed nitrogen species in water as function of plasma/solution conditions
 - Effect of dissolved NaHCO_3
 - Plasma power
 - Gas flow rate
- Effects of Plasma Activated Water (PAW) on plant species



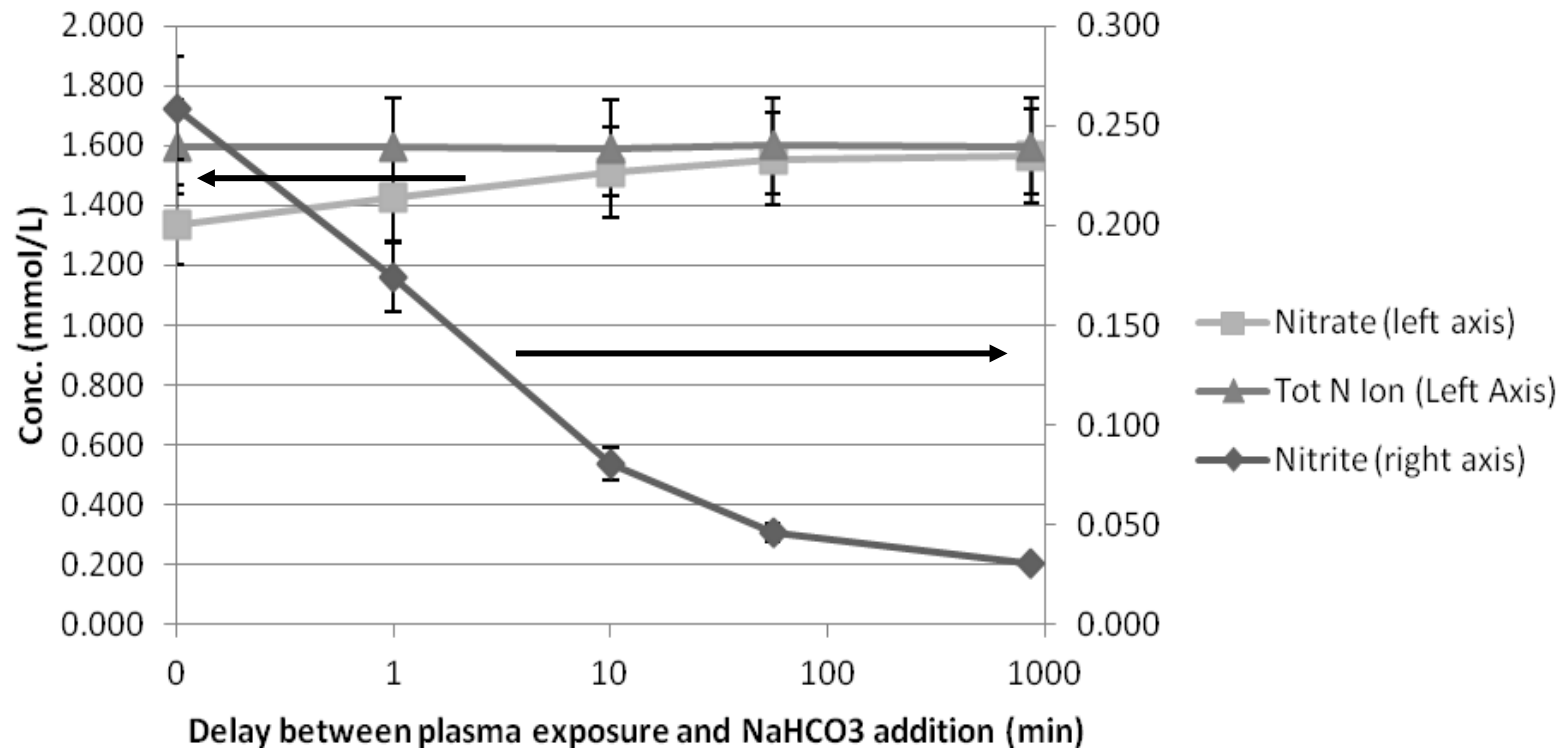
[NO_x] and NaHCO₃



- Adding baking soda before exposure dramatically increases nitrite concentration
 - Decreases nitrate concentration
- Adding immediately after exposure produces similar but lesser effects....

$[\text{NO}_x]$ and NaHCO_3

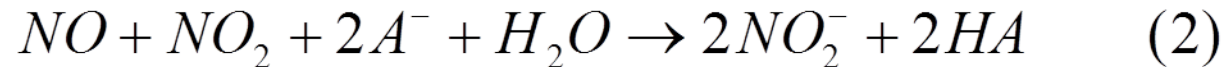
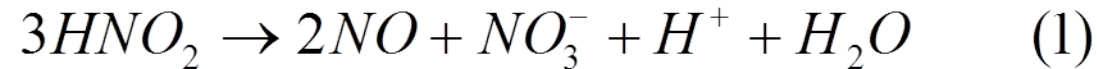
- Tagging on to that last data point, what happens if we wait to add baking soda post-exposure?



- Longer we wait to add NaHCO_3 , the smaller its effect on solution chemistry, e.g. we observe the small nitrite and large nitrate concentrations seen when no NaHCO_3 is added to the solution

[NO_x] and NaHCO₃ Theory

- Two potentially important reactions to consider (taken from Greenwood's *Chemistry of the Elements*)



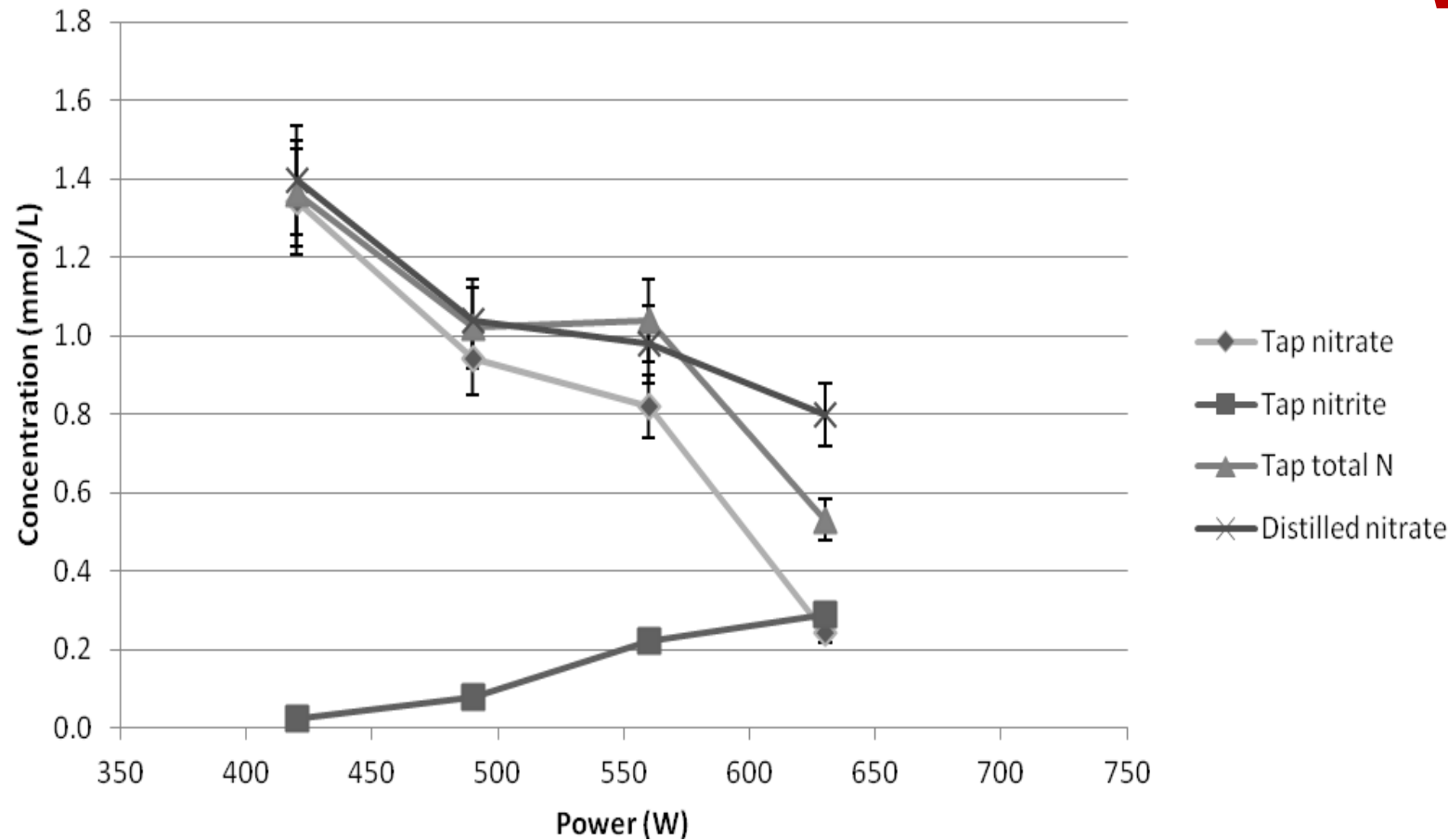
- Reaction 1 occurs readily at acidic pH
- Reaction 2 is generic representation of industrial process for producing nitrite
 - Greenwood: “NaNO₂ is made by absorbing ‘nitrous fumes’ in aqueous alkali or carbonate solutions”

[NO_x] and NaHCO₃ Theory

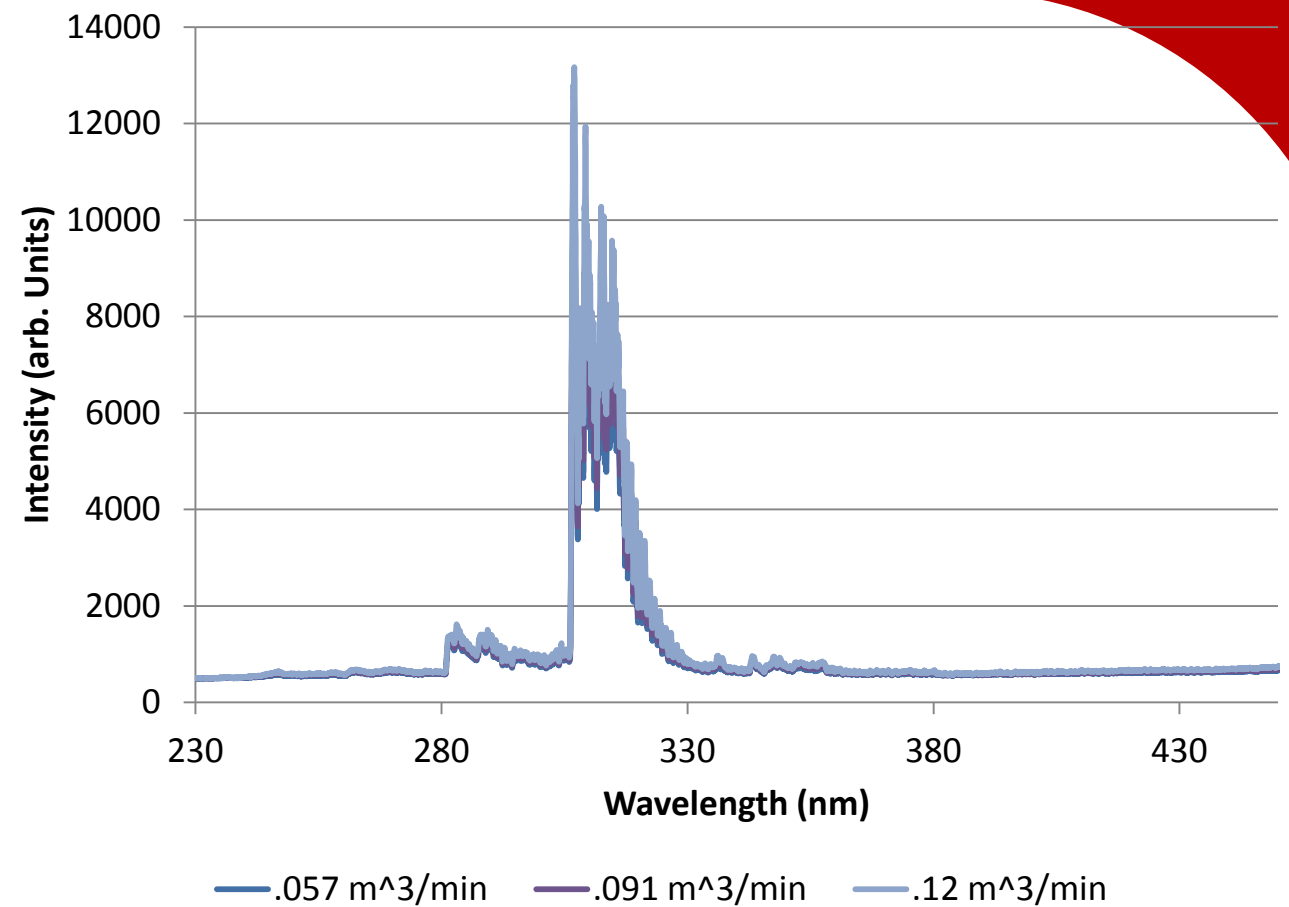
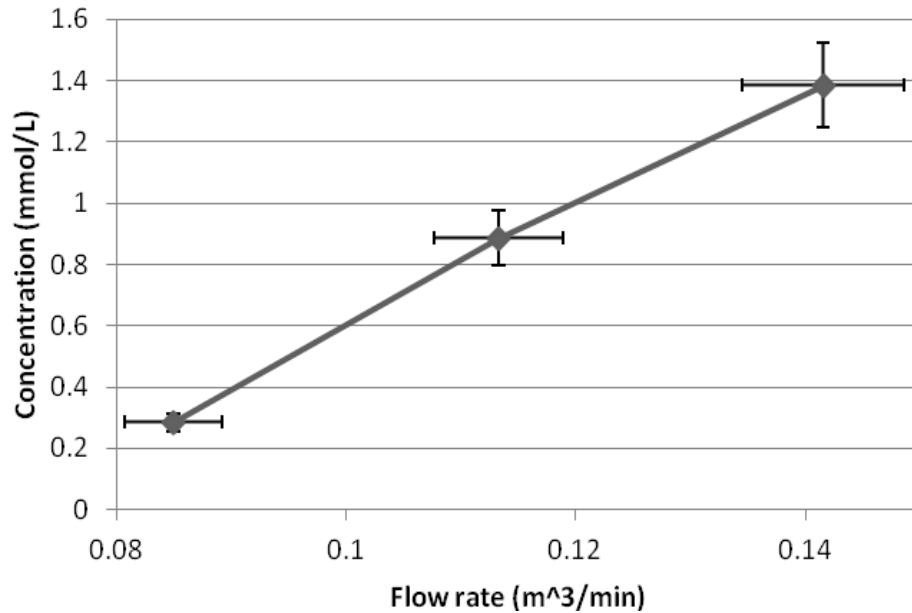
- Plasma generates NO and NO₂ which reacts with bases such as carbonate in solution (reaction 2)
- Explains sharp spike in nitrite concentration when NaHCO₃ added pre-exposure
 - Moreover, because neutral pH is maintained throughout, disproportionation of nitrous acid inhibited, decreasing nitrate production (reaction 1)
- If base added post-exposure while NO and NO₂ remain in solution, more nitrite will be produced
 - However, NO and NO₂ eventually volatilize...explains why adding NaHCO₃ days after exposure does not increase nitrite (reaction 1)
 - Moreover, if delay is long, there is sufficient time for all HNO₂ to disproportionate and form NO₃⁻ (reaction 2)

[NO_x] vs. Dissipated Power

- Treatment times scaled such that deposited energy constant for each experiment
- Interestingly, increasing power favors:
 - More nitrite
 - Less nitrate
- No current good hypothesis as to why

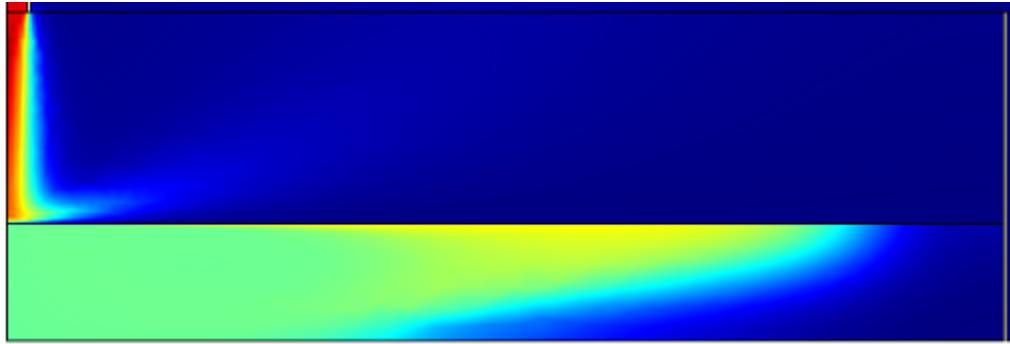


$[\text{NO}_3^-]$ vs. Gas Flow



- Left plot shows significant increase in dissolved nitrate as gas flow is increased
- Change in uptake takes place while OES spectra remain the same
- Since core plasma chemistry appears to remain unchanged, increase in uptake could be attributed to enhanced mass transfer from plasma to liquid → increased spreading of nitrate over the interface increases surface area for mass transfer

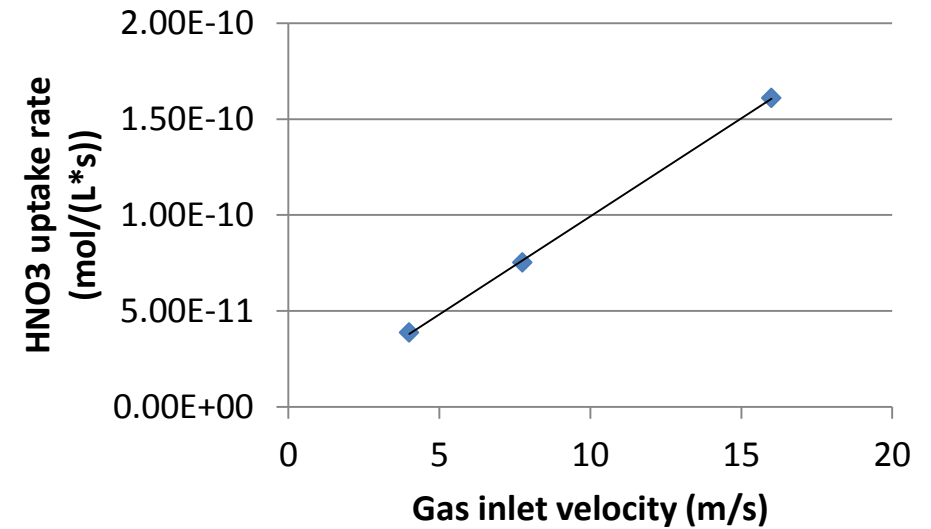
Back to Part 1 Model for a second...



HNO₃ profile at 17 minutes for inlet velocity = **4 m/s**



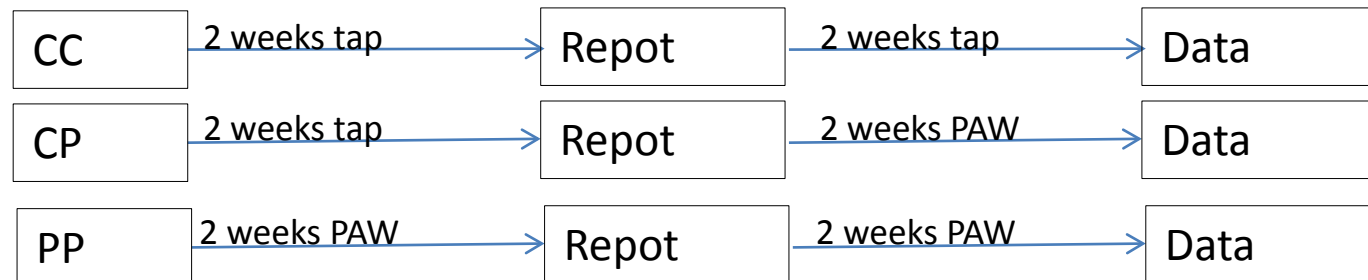
HNO₃ profile at 17 minutes for inlet velocity = **16 m/s**



- Admittedly different geometry from NCSU system, but qualitatively similar
- A little difficult to see, but higher flow does lead to greater HNO₃(g) spreading over interface
- Leads to greater HNO₃(aq) uptake as seen in top right graph

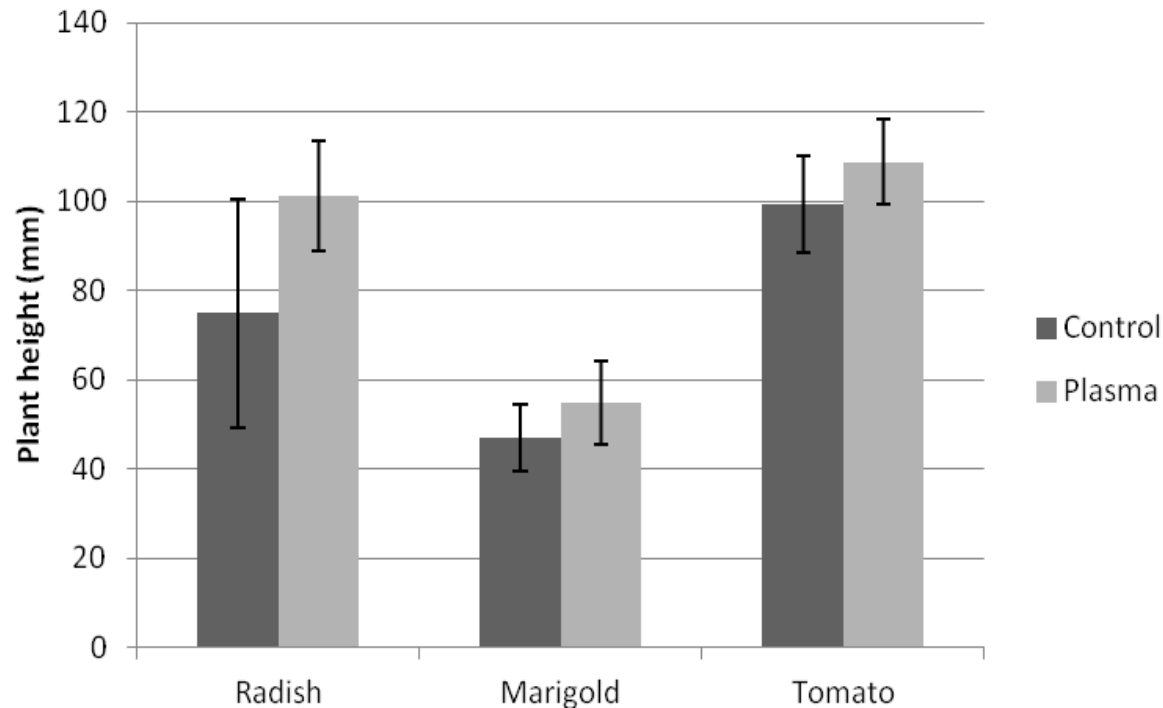
From basic science to application: PAW for Fertilizer

- Ran 4-week fertilizer experiment in collaboration with Horticulture department
 - Weeks 1-2: seedling or germination phase
 - Weeks 3-4: “growth” phase
- Treated tomatoes, radishes, and marigolds
- 3 treatment types



- PAW treatment solution: 4-5.6 ppm nitrite, 113-120 ppm nitrate (generated from distilled water)

Final Seedling phase data (1/2 way point of experiment)



Welch's two-tail t-test. Numbers shown are p-values. It is common to choose $p < .05$ to denote statistically significant differences between distributions

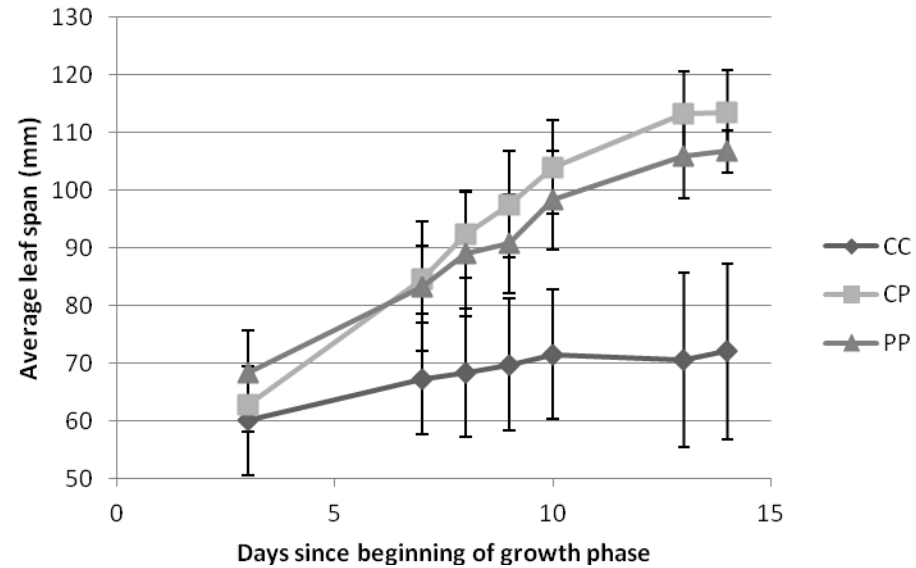


Radish	Marigold	Tomato
.054	.243	.219

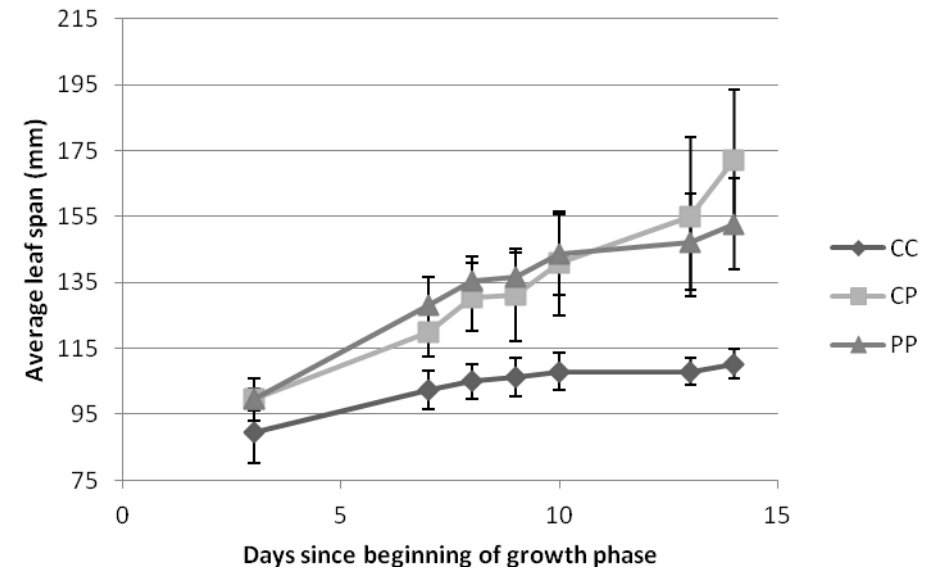
- At $\frac{1}{2}$ way point, plasma groups are taller than controls across all plant types, but not enough for standard statistical significance

Growth phase data (2-4 weeks)

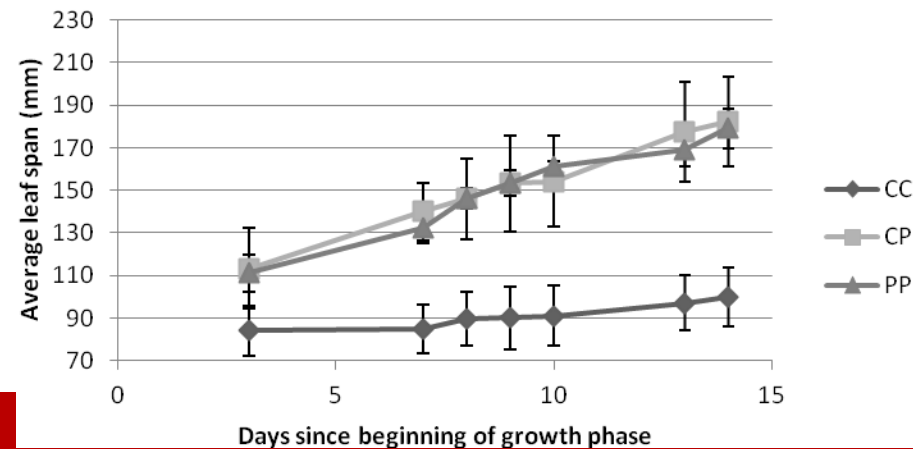
Marigolds



Tomatoes

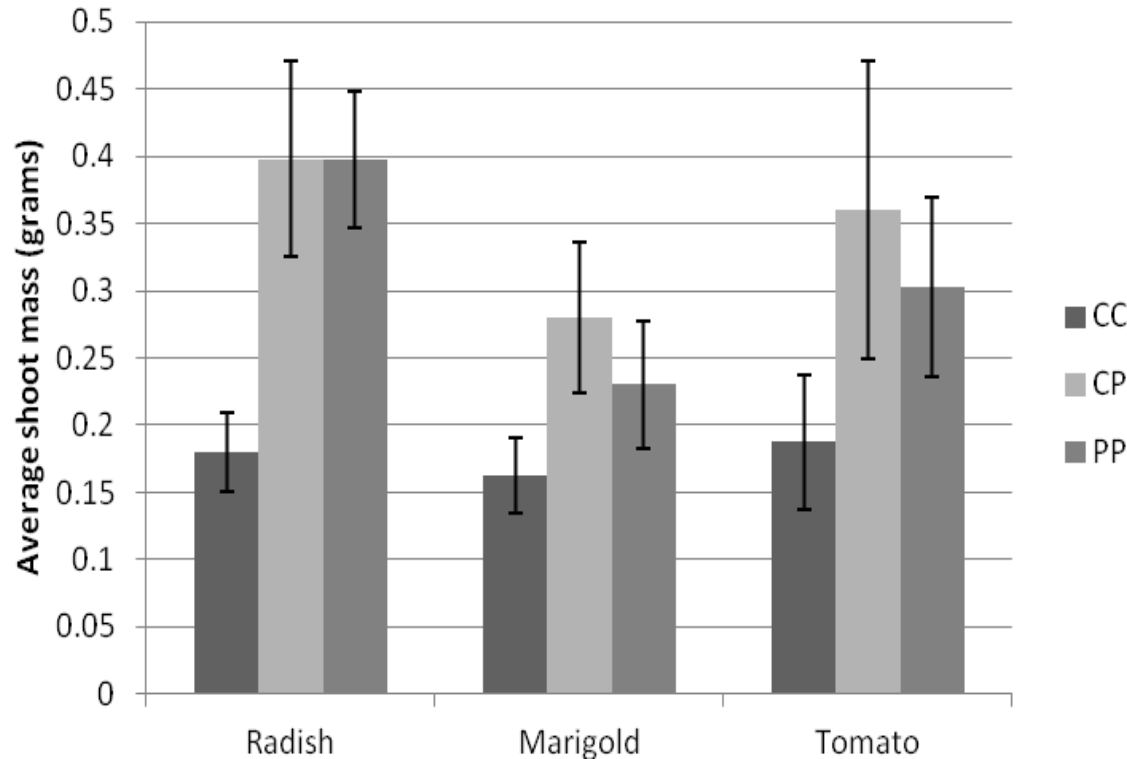


Radishes



Final growth phase results

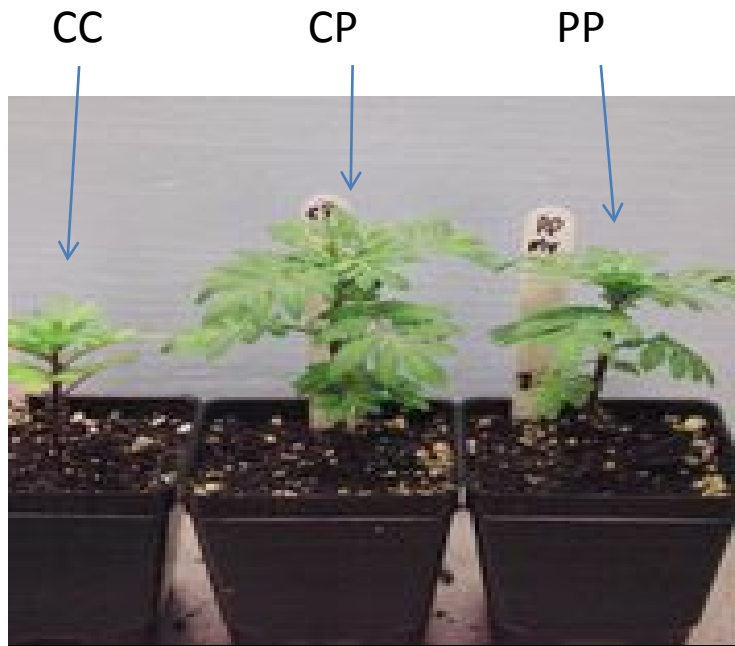
Welch's two-tail t-test. Numbers shown are p-values.



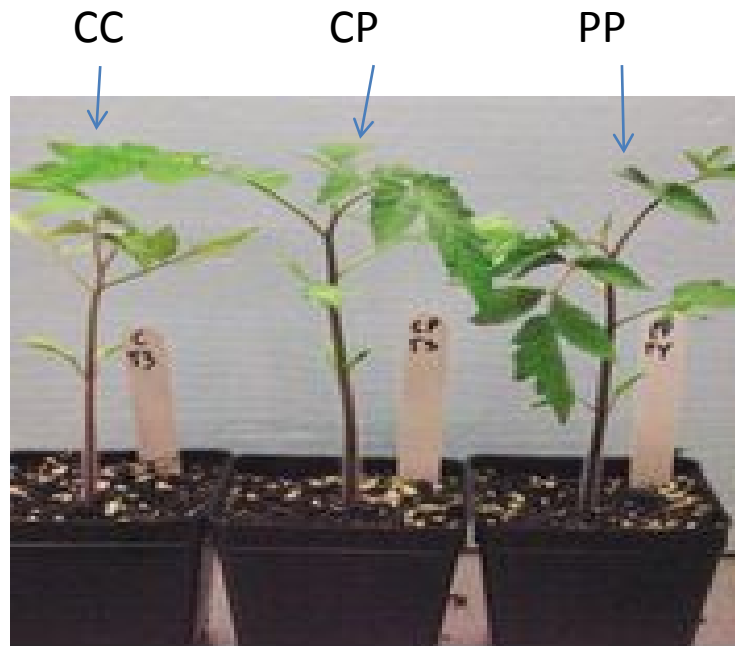
Shoot Mass	PP vs. CP	PP vs. CC	CP vs. CC
Radish	1.000	0.001	0.005
Marigold	0.224	0.060	0.017
Tomato	0.414	0.035	0.044

- Plants treated with PAW during weeks 3 & 4 are all significantly larger in shoot mass than control treated plants with the exception of CC vs. PP marigolds
- No statistically significant difference in root masses

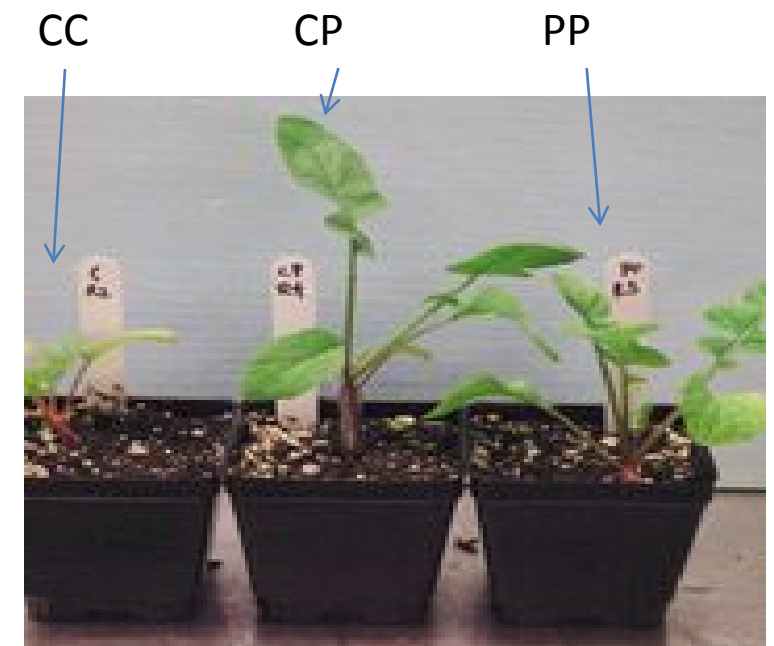
Final photos



Marigolds



Tomatoes



Radishes

Conclusions

- PAW treated plants showed slightly larger growth than control group in seedling phase, but not enough for significance
- PAW treated plants showed significantly larger growth than control groups during growth phase
- As expected, PAW capable of promoting plant growth
- Can achieve some level of control of nitrite and nitrate concentrations using gas phase knobs (power, flow rate) and solution composition (NaHCO_3)

Future Work & Acknowledgments

- **Our focus: back to basic science** → Model VHF discharge
 - Surface wave?
 - Gain greater understanding of gas phase chemistry: why more nitrite and less nitrate with increasing power?
- Incorporate and expand transport models from Part 1 (Berkeley system) to treat the NCSU system
 - Explore reactions with NaHCO_3 and other non-plasma generated aqueous species
- **Commercial development:** Discovered last month that Scandinavian start-up also using PAW for fertilizer but with added step:
 - Mix naturally acidic PAW with manure in order to lower manure pH
 - Fixes volatile ammonia in manure to non-volatile ammonium
 - Now have NH_4NO_3 : two moles of N instead of one!
 - They're still trying to figure out best plasma system for generating nitrate pre-cursor NO: this is where basic plasma physics and chemistry come into play
- Acknowledgments:
 - David Black
 - Wesley King
 - Asish Andhavarapu
 - Advanced Energy

THANKS!