

Chlorine and ammonia environmental surface reactivity and adsorption/desorption modeled as dry deposition for large-scale release consequence assessment

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Dry Deposition and Surface Chemical Reactivity

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Overview

- Model simulations with HPAC showed that a significant fraction of chlorine could be removed from a high concentration cloud in an accident
- Experience with accidents such as Graniteville supported large impact on vegetation and environment
- How to best model chlorine removal?
- Historical approach of dry deposition using resistance model to determine deposition velocity
- Experimental programs by Lydiard and Freeman et al. showed that there could be a limit to the reactivity of chlorine (and ammonia) not described by the gas concentration only

Gas Reactivity with Environmental Materials

- Dry deposition model:

$$F = V_d C_g = \frac{C_g}{R_a + R_b + R_c}$$

- The flux F is a surface reaction rate between the gas and substrate. Since both substrate (C_s) and gas (C_g) are involved, standard treatment from chemistry perspective would be a second order reaction:

$$F = k'' C_g C_s$$

So the dry deposition model has the basic assumption that substrate reaction sites far out number molecules of gas to react.

- Important consequence: While C_s may be constant during reaction, C_s would be different for different surfaces (especially different leaves). Consequently, k'' would have a different numerical value as would R_c depending on the surfaces present. This difference would likely not be accounted for using the LAI only.

Consequence Assessment Modeling

- For consequence assessment purposes involving high gas concentrations, substrate reaction sites may no longer outnumber gas molecules for reaction. (Maximum deposition)
- Lydiard and Freeman et al. have already shown that there is a limitation of the surface on reaction with a gas, but neither experimental program considered whether the boundary layer resistance could be important. To be used in atmospheric dispersion modeling, experimental program should provide a method to scale data to atmospheric flows.
- An experimental program to address consequence assessment modeling should consider both factors:
 - Maximum deposition
 - Measured turbulence levels that are comparable to the atmosphere

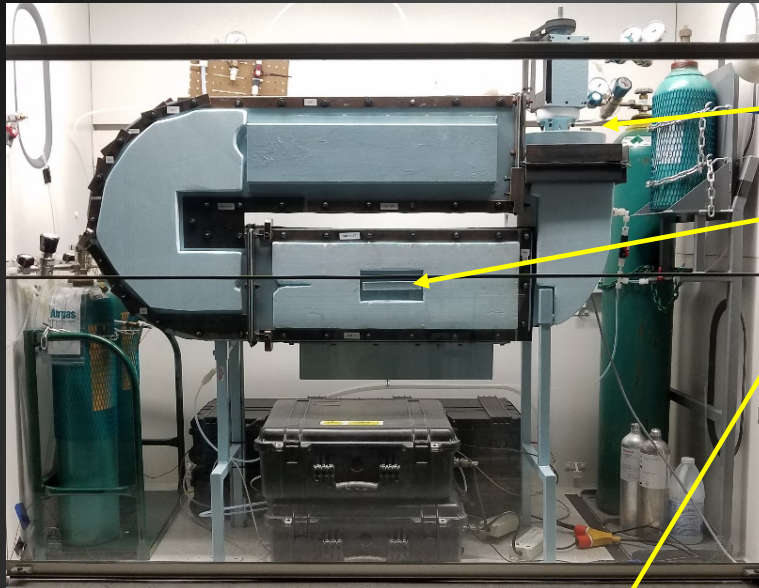
Accomplishing Objectives

- Field test program would be certain to be consistent with atmospheric conditions, but field test results are known to have many uncertainties. Cost levels were beyond the scope.
- Build a single pass enclosure where samples could be exposed to a known quantity of gas (originally chlorine), and measure the outflow mass flux of gas. Issues included:
 - Difficulty of measuring outflow gas mass flux (simultaneous concentration and velocity)
 - Analyzing experimental results (what is the concentration above plants; how does it vary along the channel; etc.)
 - Cost
- An original wood prototype was built, but this approach was ultimately abandoned. Note that this type of flow contacting pattern is referred to by engineers and chemists as a plug flow reactor (PFR).

Accomplishing Objectives (2)

- A long recognized principle of chemistry is that reaction kinetics measured under one flow condition would also be applicable under another flow condition.
- Frequently, chemical reaction data taken with a batch reactor is used in the design of a PFR.
- The inherent advantage of a batch reactor is that the concentration in the continuous fluid phase can be made constant if there is adequate mixing.
- Refined objective: provide fluid flow (and mixing) around samples that is consistent with atmospheric turbulence levels.

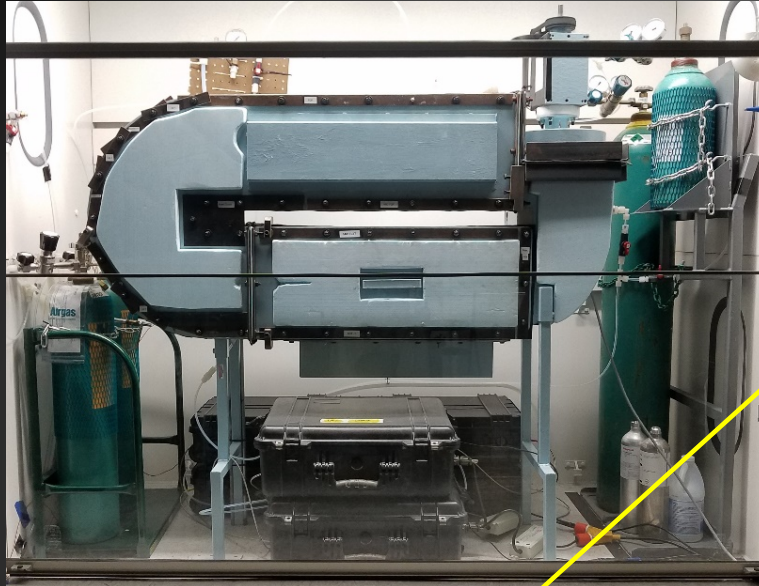
CERT Test Chamber



- Blower used to control velocity inside the test chamber.
- Working section is 75 cm long with 25 cm x 25 cm cross section.



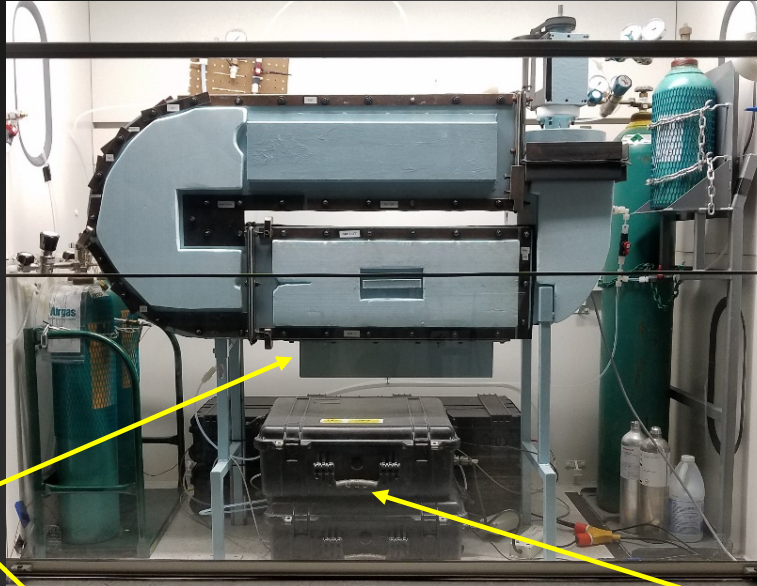
CERT Test Chamber



- Blower used to control velocity inside the test chamber.
- Working section is 75 cm long with 25 cm x 25 cm cross section.
- Apparatus internals coated with Kynar.
- Kynar injection quills, tubing, and fittings.
- Peroxide cured EDPM gasket.



CERT Test Chamber



Box for samples



- Blower used to control velocity inside the test chamber.
- Working section is 75 cm long with 25 cm x 25 cm cross section.
- Apparatus internals coated with Kynar.
- Kynar injection quills, tubing, and fittings.
- Peroxide cured EDPM gasket.
- JAZ instruments for gas phase concentration measurements
- Velocity and turbulence profiles measured with LDV
- Target u'/U : In the atmosphere, $\sigma_u/u_* \approx 2.4$; $u_*/U \approx 1/10$ to $1/15$; so $u'/U \approx 16$ to 24% . Turbulence levels used to determine boundary layer resistance.

Overall Process

- Condition the empty chamber by repeatedly exposing it to gas until the gas removal in the empty chamber is repeatable.
- Test samples of materials; different samples of materials are tested at different velocities.
- Repeat measurements in the empty chamber to ensure behavior is consistent with past experiments
- Analyze the data for each sample type. For example, rye grass should be the same for different velocities, so all of the rye grass data was analyzed together.

For Experiments with Samples

- Load sample to be tested in test section and seal the side panel.
- Calibrate Jaz: 1000 ppm and 100 ppm for chlorine in air gas standards; for ammonia in air 100, 500, and 1000 ppm
- Charge the chamber with pure gas so that the concentration is nominally 1000 ppm.
- After 30 to 60 min of sample exposure, stop the test by venting the chamber contents.
- Calibrate Jaz after the test.
- Remove the tested sample.

Maximum Deposition

- To model impact of surface reaction limitation, maximum deposition modeled with activity (simple model of catalyst poisoning)

$$a_s = (M_{max}'' - M'')/M_{max}'' = 1 - (M''/M_{max}'')$$

where M_{max}'' is the maximum mass of gas that can react per unit sample surface area and M'' is the mass of gas that has already reacted with the surface during an experiment.

- Initially, $a_s = 1$ (no gas has yet reacted with the surface), but as the reaction at the surface continues, a_s gets smaller and approaches 0.
- Surface reactivity resistance with gas $r_c = \frac{1}{k_s'' a_s}$ for first order reaction and surface activity a_s

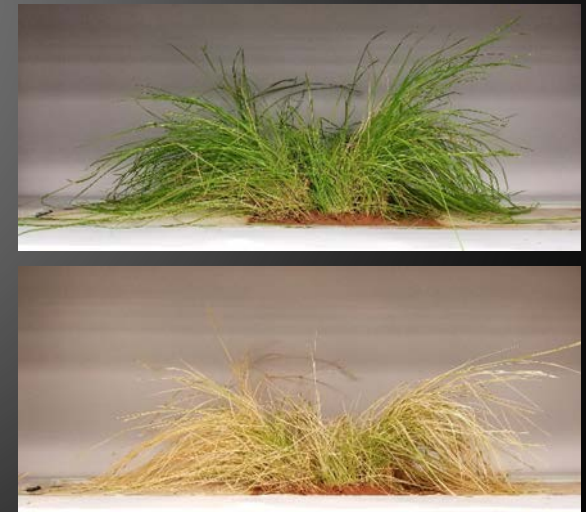
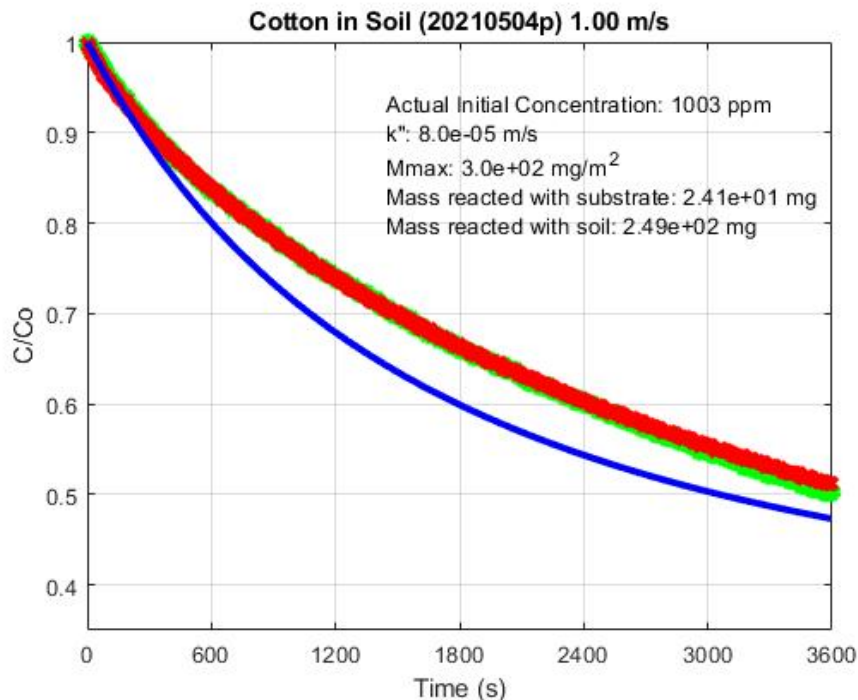
Experiments

2019/20 Experiments

- Maple Jeffersred (leaves only)
- Sugar Maple (leaves only)
- Norway Spruce (sample to first major branch)
- Bare soil used for live plants
- Rye grass in soil
- White clover in soil
- Pilot tests (Pansy and White clover)

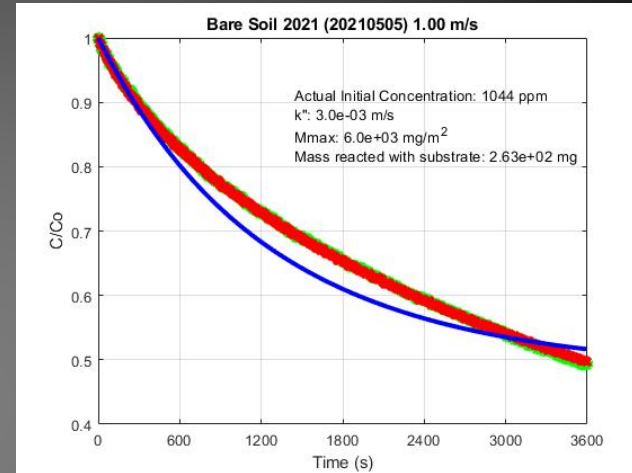
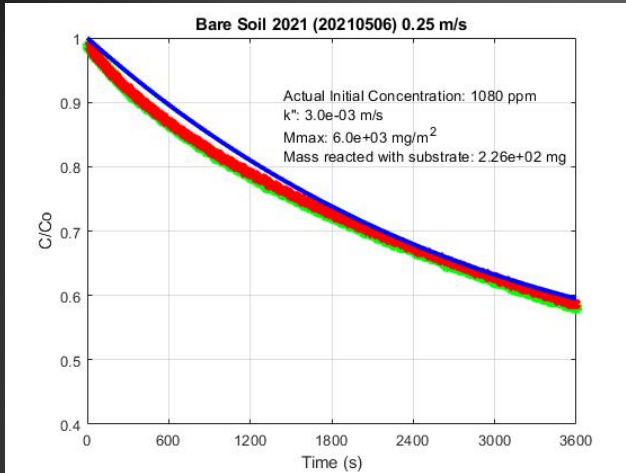
2020/21 Experiments

- Built environment materials: crushed limestone, asphalt, and concrete
- Bare soil (different) used for live plants
- Crop plant species in soil: sorghum, cotton, and soybeans
- North American shrubland materials: red twig dogwood and viburnum winterthur
- Playa sample from Dugway Proving Ground from before the 2015 JR2 tests

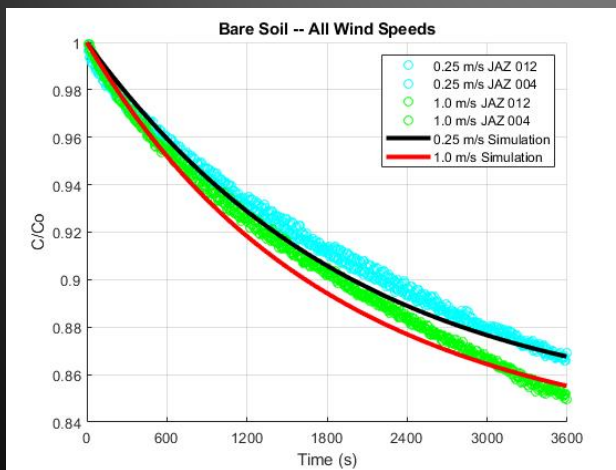


Bare Soil

- New soil ($k''=3.0 \times 10^{-3}$ m/s; $M_{\max} = 6,000$ mg/m²)



- Previous soil ($k''=1.0 \times 10^{-3}$ m/s; $M_{\max} = 4,500$ mg/m²)

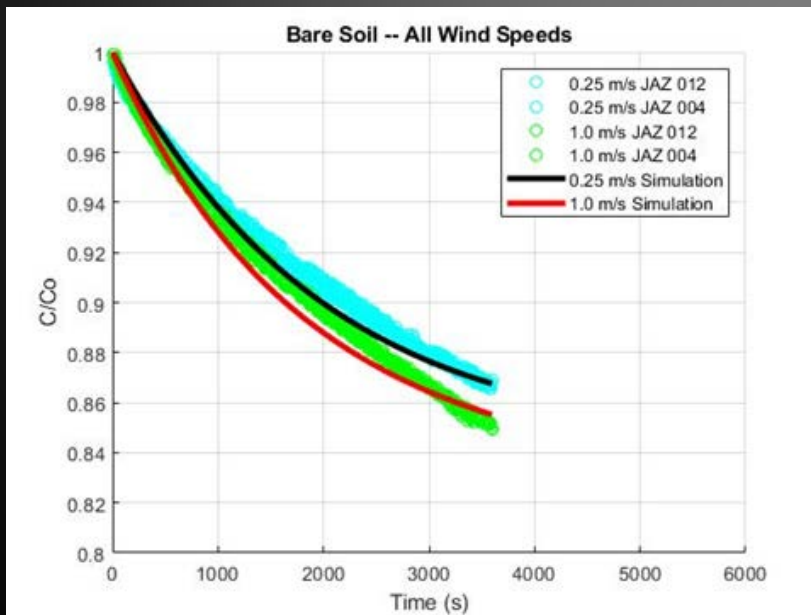


Boundary layer resistance model adequate for deposition to horizontal surface.

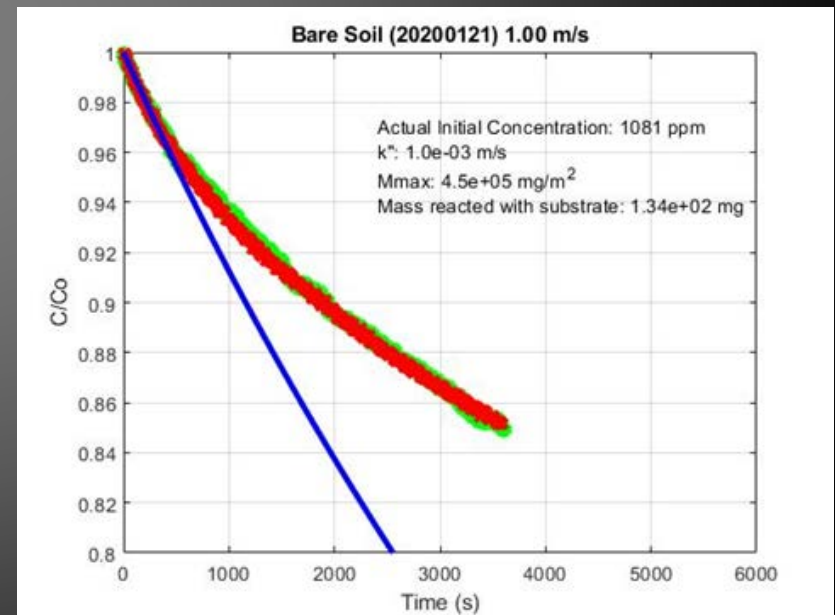
Bare Soil – Sensitivity Analysis

- Bare soil tests had constant surface area, so importance of maximum deposition easily demonstrated:

With maximum deposition included in the model

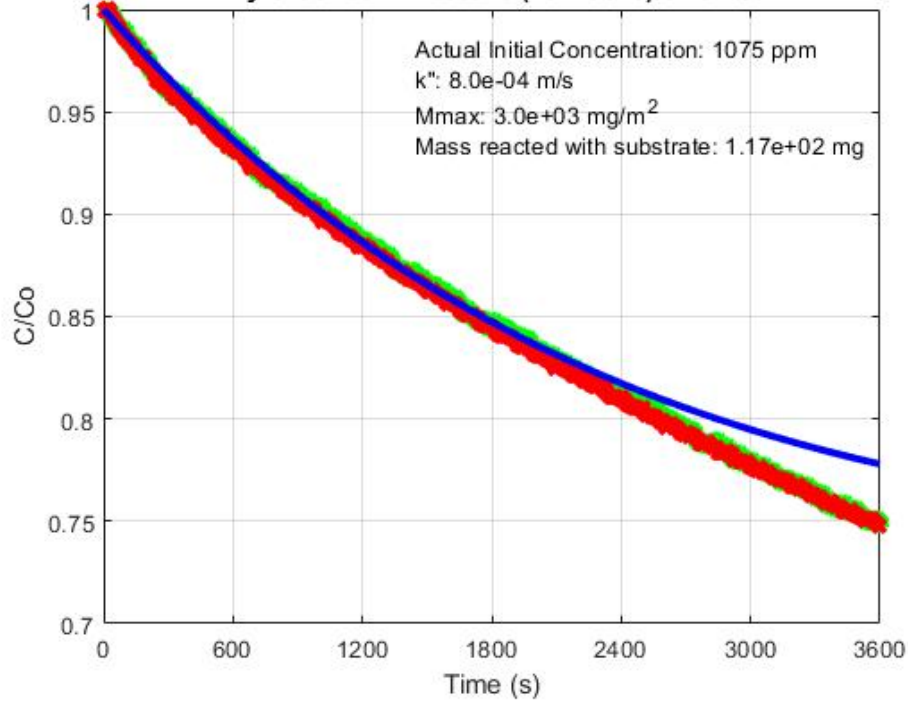


Without maximum deposition included in the model

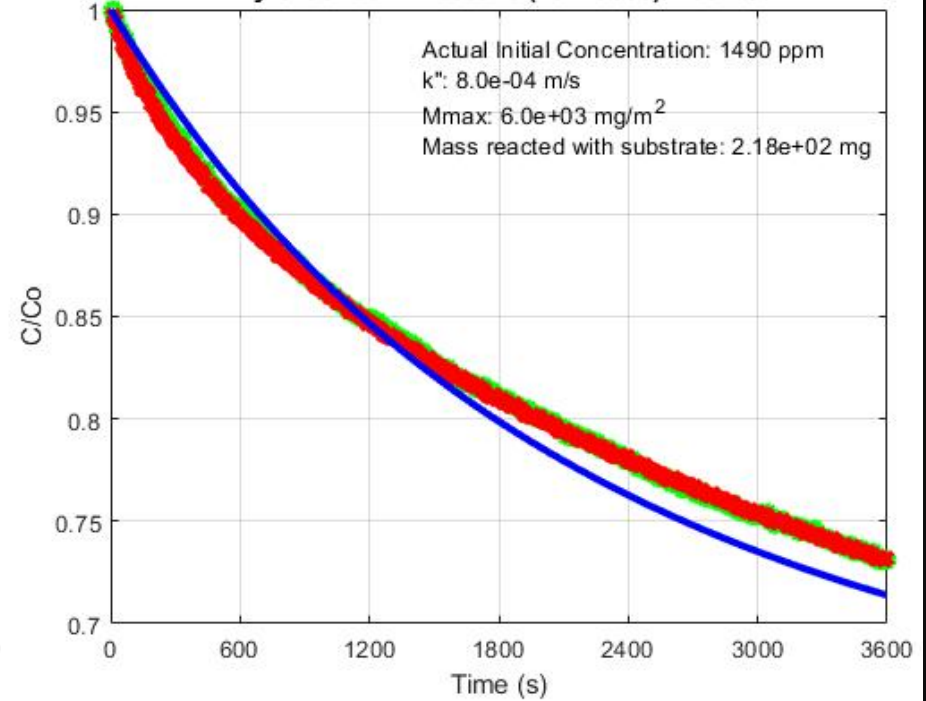


Crushed Limestone

Dry Crushed Limestone (20210310) 0.25 m/s

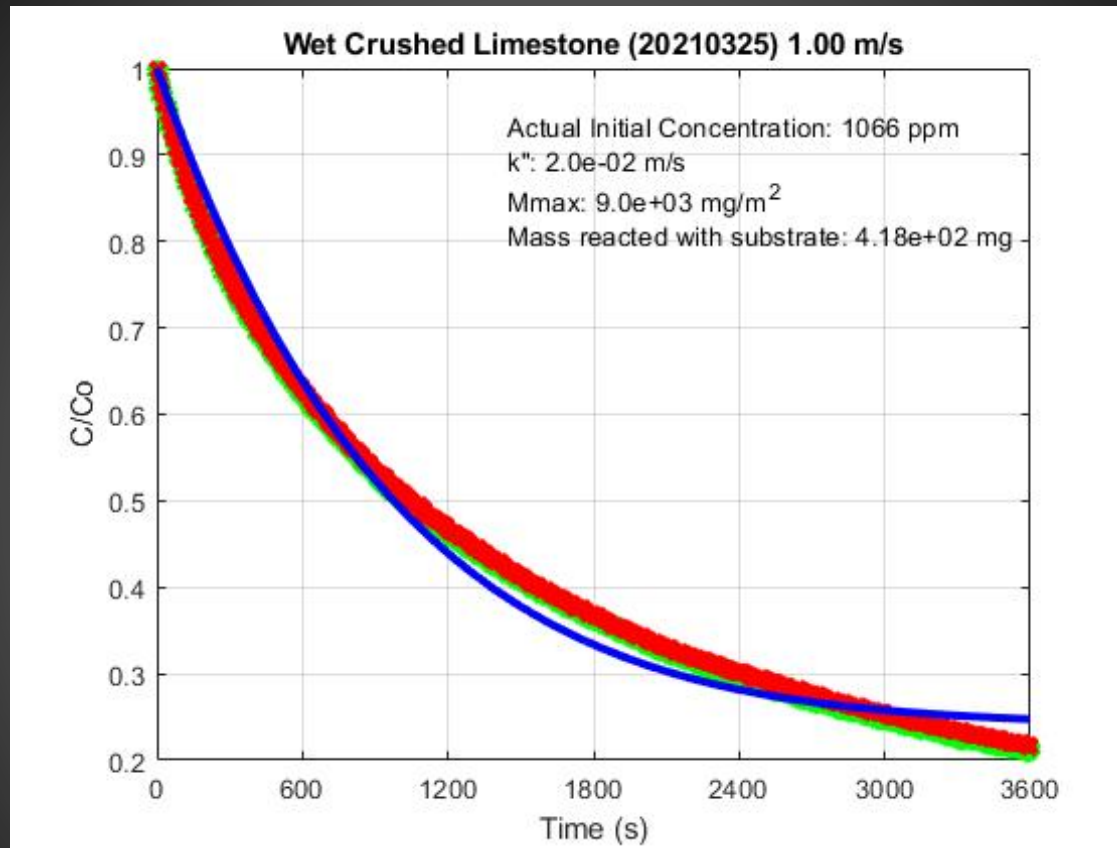


Dry Crushed Limestone (20210305) 1.00 m/s



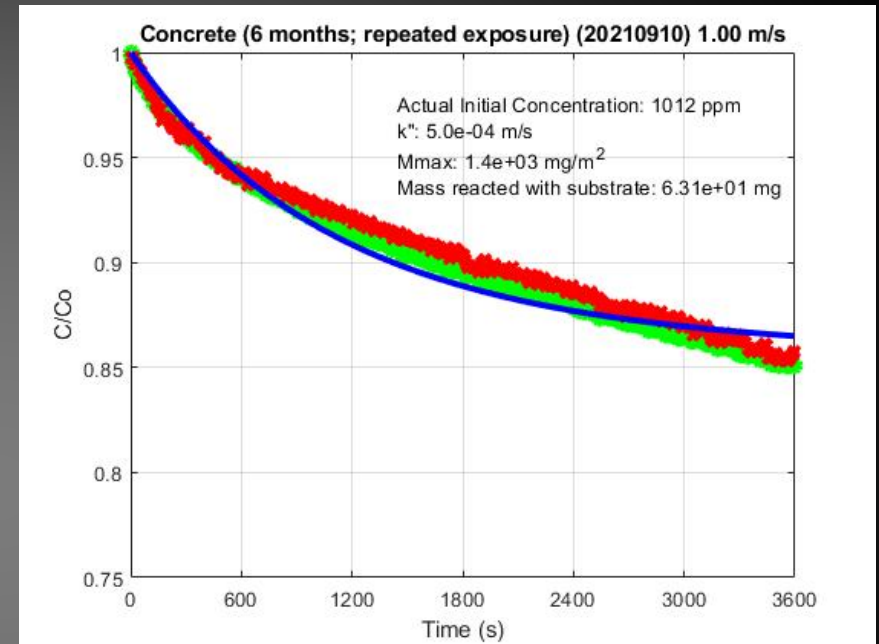
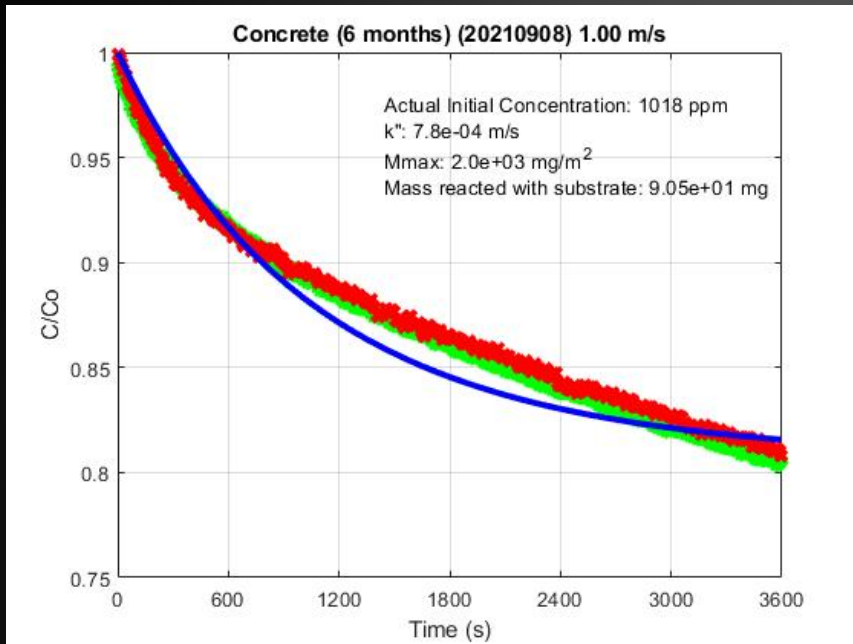
- Dry crushed limestone showed variability in maximum deposition.
- Samples were very dusty, so one test conducted with washed limestone with comparable measured parameters.

Crushed Limestone



- Wet limestone tested by immersing in water for 1 min in a mesh, drained without drips for 2 minutes, then loaded for experiment. k_s'' increased by a factor of 25. M''_{\max} roughly doubled.

Concrete



- Concrete tested after 45 days and 6 months. Concrete aged 6 months showed significantly less reactivity
- Concrete sample exposed a second time
 - k_s and M_{max} were reduced.
 - Does this indicate adsorption/desorption? (Reversible deposit of gas on surface during exposure and return to gas phase when in fresh air.)

JR2 Trial 5 Witness Board



Post-test image indicates chlorine visibly adsorbed on gravel pad surface.

Impact on rate chlorine travels downwind?

If maximum deposition of crushed limestone is 6000 mg/m^2 , then only $\sim 90 \text{ kg}$ on gravel pad, but important to emergency responders

Surface Area Determination

- In chamber experiments, the surface area of plant samples was measured with a flatbed scanner. The samples were dried, and the dry mass was used to estimate the area of plant samples used in the experiments.
- Leaf Area Index (LAI) has long been estimated for plants and crops and is defined to be the leaf area divided by the plan area (area of ground on which the plants live).
- Material Area Index (MAI) can be defined similarly for built environments as the surface area of the material divided by the plan area.

Summary of Chlorine Kinetic Parameters

Material	2019/20 Study		2020/21 Study		Estimated:
	k_s'' (cm/s)	M_{max}'' (mg/m ²)	k_s'' (cm/s)	M_{max}'' (mg/m ²)	Maximum V_d (cm/s)
White Clover	0.0055	500			0.33
Rye Grass	0.018	3,000			0.39
Soil (~10% moisture)	0.10	4,500			0.10
Cotton			0.0080	300	0.34
Sorghum			0.060	1,800	0.60
Soybeans			0.10	1,800	0.80
Soil (~10% moisture)			0.30	6,000	0.30
Norwegian Spruce	0.017 to 0.0017	1,000			0.39 (1.15)
Jeffersred Maple	0.0015	2,000			0.31 (0.38)
Sugar Maple	0.00032	2,000			0.30 (0.32)
Red Twig Dogwood			0.018	4,000	0.39
Viburnum Winterthur			0.018	1,200	0.39
Crushed Limestone			0.080	4,500	0.08
Crushed Limestone (wet)			2.0	9,000	2.0
Asphalt			0.015	1,500	0.02
Concrete			0.078	2,000	0.08
Playa (unexposed)			0.14	6,000	0.14

★ Maximum V_d assumes plant LAI=5 (LAI=50) and largest k_s'' for soil; ignores boundary layer resistance and maximum deposition. Maximum V_d will decrease during exposure.

Chlorine Conclusions

- Maximum deposition is important to consider in dry deposition/chemical reaction for high concentration consequence assessment. Many consequence assessments are made for low wind speeds and stable atmospheres where clouds would linger over terrain for a long time which would overestimate chlorine removal if maximum deposition is not taken into account.
- The measured maximum deposition velocities for chlorine are generally around 0.3 to 0.6 cm/s which is significantly less than has been recommended in the past for air pollution concentration levels of chlorine. Deposition velocities are frequently dominated by soil reactivity.
- The dry deposition/reactivity model used here accounts for turbulent transfer from bulk concentration to reactive surfaces in a manner consistent with characterization of aerodynamic resistance used in current air pollution models. However, similarity theory between turbulent mass and momentum transfer requires use of the Schmidt number as used here.

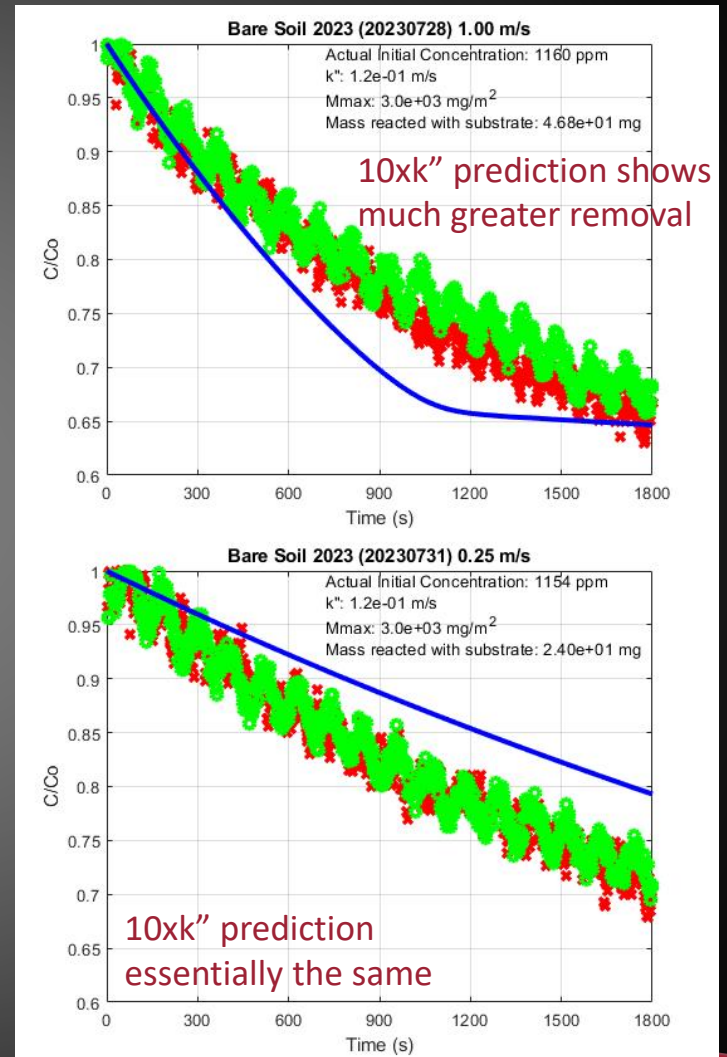
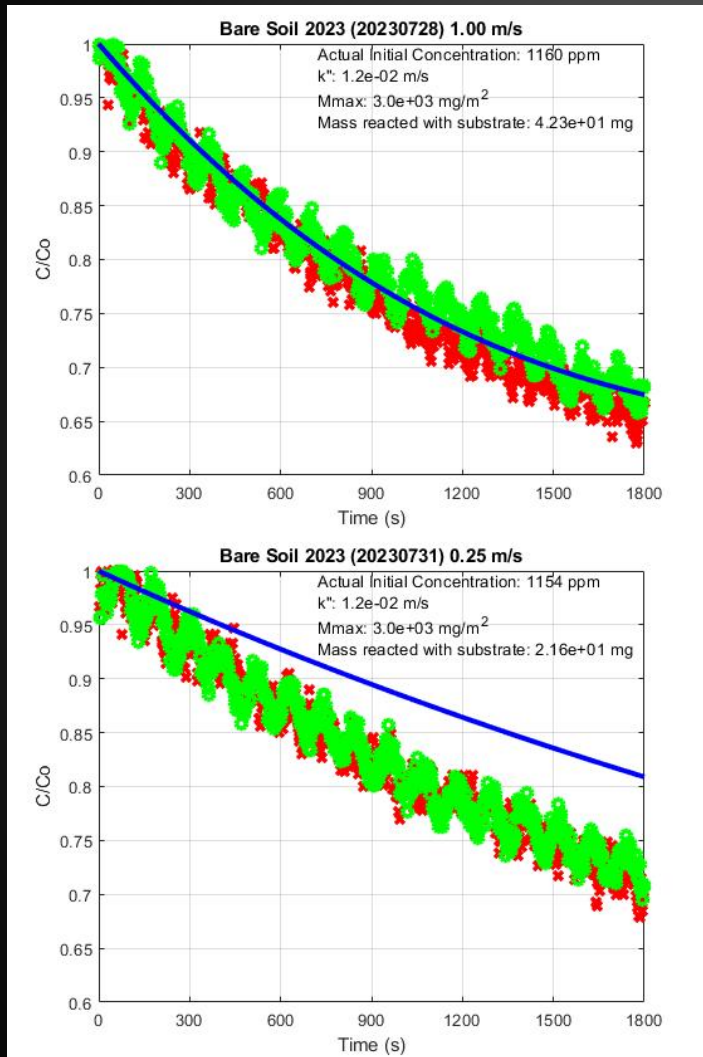
Chlorine Conclusions (2)

- There is a clearly demonstrated effect of adsorption/desorption in surfaces exposed to chlorine in addition to (irreversible) surface reaction.
- Water significantly enhances the chlorine reactivity rate and maximum deposition for crushed limestone. Chlorine is not very soluble in water, but the presence of water clearly did not act as a resistance to reactivity. "Wet" chlorine (chlorine gas mixed with humid air) is known to be very corrosive in comparison to chlorine free of water (e.g., for materials such as carbon steel). Will open water that includes other reactive surfaces under water (e.g., plants, bottom, algae, fish) prove effective at removal of chlorine from a passing cloud? Surface water (swamp) was present near the chlorine release at Graniteville, SC.

Ammonia

- Ammonia tests conducted with rye grass and clover planted in soil. Soil tests considered different soil moistures
- Ammonia reacted faster with empty apparatus and soil surfaces than chlorine
- Faster reacting ammonia showed that previous boundary layer resistance used in chlorine analysis was too large.

Soil Tests – 4% moisture



Calculation of r_b

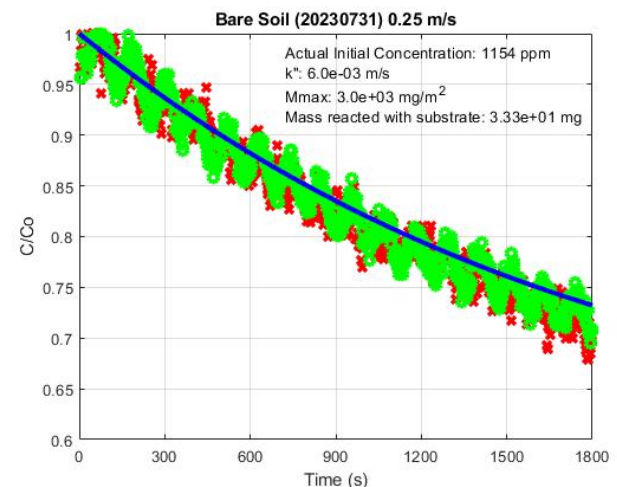
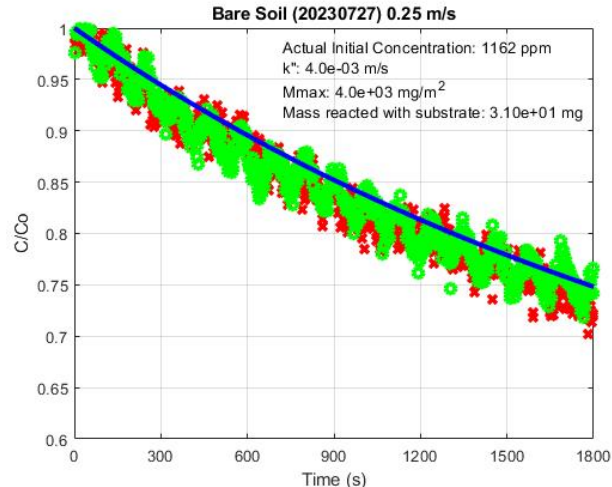
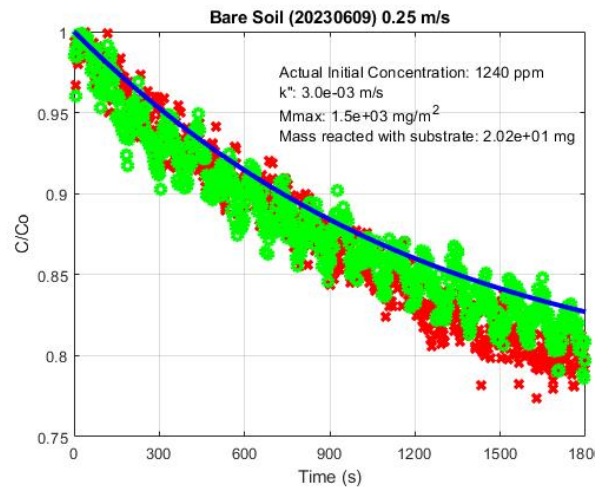
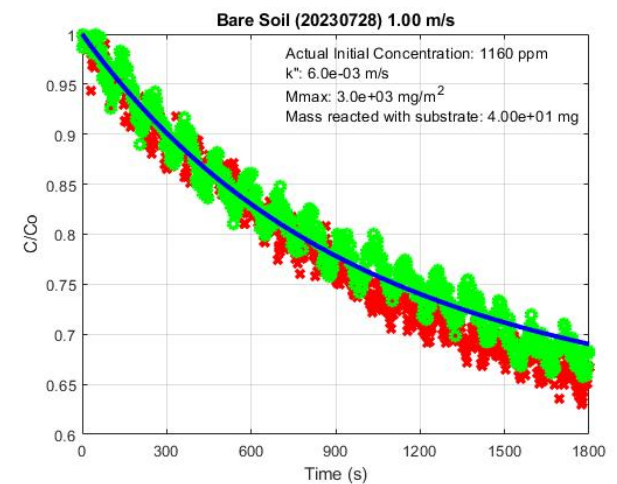
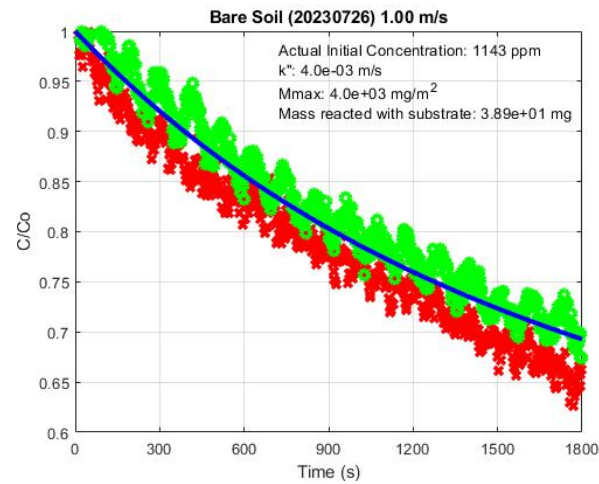
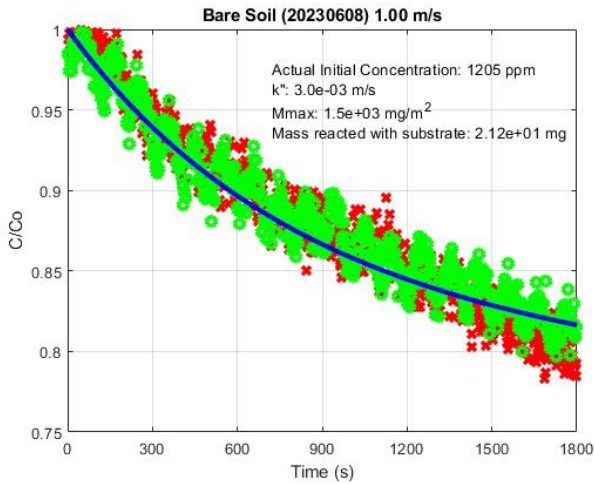
- Boundary layer resistance to interface: Chilton-Colburn analogy relates momentum transfer to mass transfer to find $r_b = \frac{Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)^2$ where U is the bulk velocity (cross sectional area averaged velocity), u_* is the friction velocity, and Sc is the Schmidt number.
- Traditional treatment of $R_b = 5Sc^{2/3}/u_* = \frac{5Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)$
- In these experiments, $\left(\frac{U}{u_*} \right) = \left(\frac{\sigma_u}{u_*} \right) \left(\frac{U}{\sigma_u} \right)$ where the first term is taken to be 2.4 (Panofsky and Dutton) for atmospheric flow, and the second term is the reciprocal of the along-wind turbulence intensity measured in the apparatus (~ 0.15). So, $\left(\frac{U}{u_*} \right) \approx \frac{2.4}{0.15} = 16$.
- Using this approximation, $R_b = 5Sc^{2/3}/u_* = \left(\frac{5}{16} \right) \frac{Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)^2$
- Would factor of (1/3) improve agreement?

Modified r_b

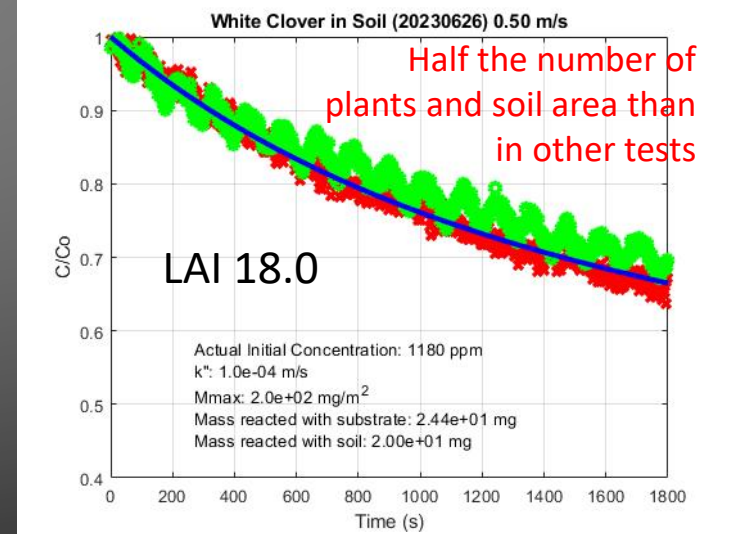
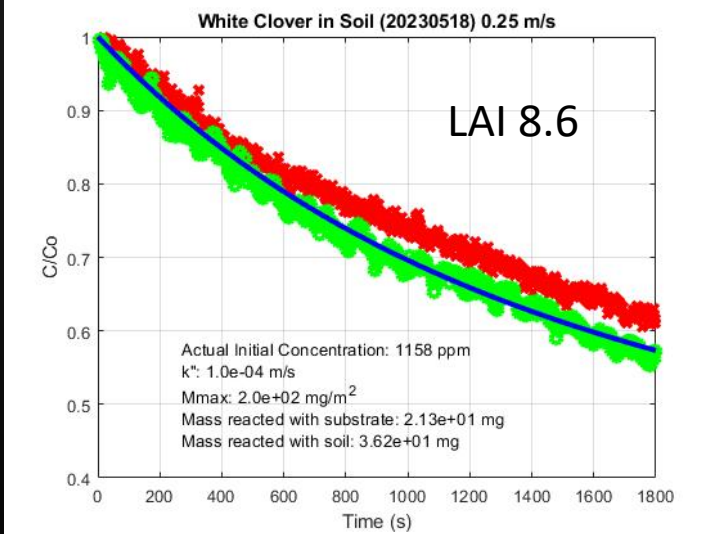
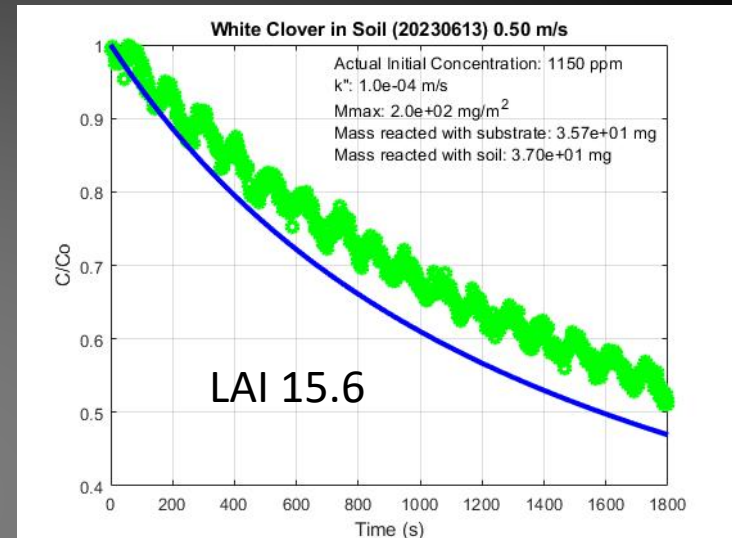
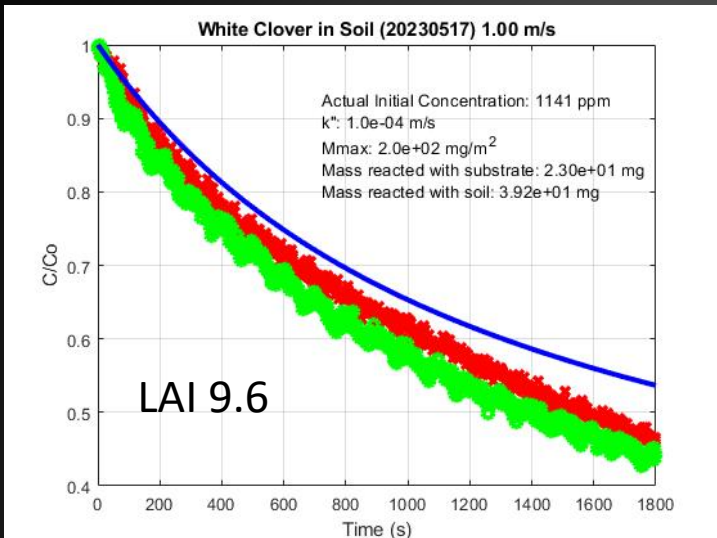
20%

12%

4%



White Clover



Summary with Revised r_b for Ammonia

Material	Wind Speed (m/s)	k'' (cm/s)	Mmax (mg/m ²)	Maximum V_d (cm/s)
Clover	1.0	0.010	200	0.35
	0.5	0.010	200	0.35
	0.25	0.010	200	0.35
Rye Grass	1.0	0.008	80	0.34
	0.5	0.008	80	0.34
	0.25	0.008	80	0.34
Soil (20%)	1.0	0.3	1500	0.3
	0.25	0.3	1500	0.3
Soil (12%)	1.0	0.4	4000	0.4
	0.25	0.4	4000	0.4
Soil (4%)	1.0	0.6	3000	0.6
	0.25	0.6	3000	0.6

Maximum V_d assumes plant LAI=5 and; ignores boundary layer resistance and maximum deposition. Maximum V_d will decrease during exposure.

Ammonia Conclusions

- Revised r_b needed to be consistent with soil data.
- Because of the high (double-sided) Leaf Area Index (LAI) of plants tested, plants and soil removed roughly equal amounts of ammonia.
- Estimated values of k'' for ammonia on rye grass and clover are comparable to chlorine.
- Maximum deposition for ammonia on rye grass and clover is very low.
- In ATD models, k'' can be used to estimate deposition velocity for ammonia. If the model can estimate the amount deposited (which HPAC can do), this amount can be compared to the maximum to determine if the model may be over-predicting dry deposition.
- Additional ammonia testing beneficial to interpretation of field test data.

Acknowledgements

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- Initial phase of chlorine experiments also supported by Defence Research and Development Canada (DRDC) and Transport Canada
- Witness board video downloaded from Utah Valley University website: <https://www.uvu.edu/es/jack-rabbit/>

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Questions?

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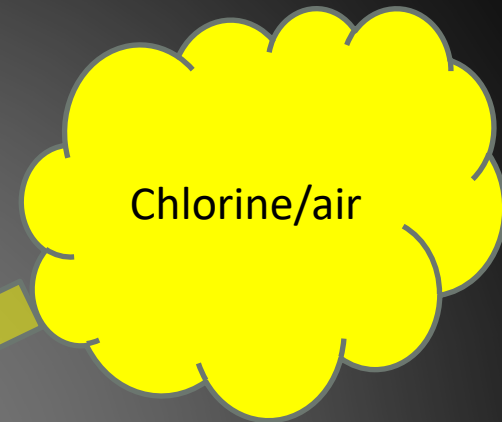
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Empty Chamber

- At the chamber surface, the chlorine concentration must be less than the concentration in the chamber.
- The rate this reaction takes place is proportional to the chlorine concentration in the chamber as well as the surface area in the chamber.
- The proportionality constant is the reaction rate constant k_s'' .



Boundary Layer Resistance

Reaction

But what if there is a maximum amount of chlorine that can react with the surface?

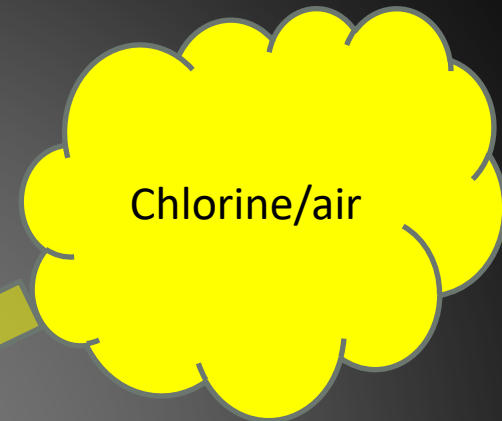
Chamber surfaces, gasket edges, etc.

- A chlorine molecule that reacts on the surface has to travel to the surface from the gas farther away from the surface.
- This travel is not instantaneous but can be modeled as a Boundary Layer Resistance r_b .
- Chilton-Colburn analogy was used to find

$$r_b = \frac{Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)^2$$
 where U is the bulk velocity (cross sectional area averaged velocity), u_* is the friction velocity, and Sc is the Schmidt number (property of the gases)

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Boundary Layer Resistance

Reaction

Reaction resistance:

$$r_c = \frac{1}{k_s'' a_s}$$

Chamber surfaces,
gasket edges, etc.

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Single Sample

The Boundary Layer Resistance is the same for

$$\text{all surfaces: } r_b = \frac{Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)^2$$

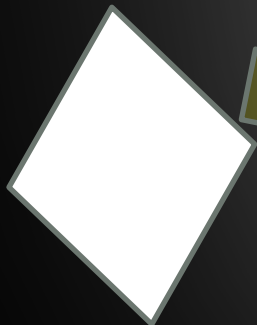
Chlorine/air

Reaction resistance for each

$$\text{surface: } r_c = \frac{1}{k_s'' a_s}$$

Parallel removal pathway for each surface.

With three surfaces such as plants in soil inside chamber, there are three parallel removal paths.



Chamber surfaces,
gasket edges, etc.



Single Sample Surface

Reaction resistance for each

$$\text{surface: } r_c = \frac{1}{k_s'' a_s}$$