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Experimental Program to Model Chlorine Reactivity with Environmental Materials in Atmospheric Dispersion Models

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Overview

- Motivation:
 - Some past consequence assessments have not accounted for the reaction of chlorine with environmental materials.
 - There was a general recognition that hazard exclusion zones would be smaller if chlorine reactivity was included in the consequence assessment.
- Atmospheric modeling by dry deposition
- Past experimental data
- Current experimental program

Dry Deposition

- Chemical species dispersing in the atmosphere (e.g., gases, vapor, particulates) deposit on environmental materials including water, vegetation, buildings, etc.
- Dry deposition developed to model the effect of air pollution (low concentrations and large areas).
- Dry deposition rate proportional to the pollutant concentration; proportionality constant is the Deposition Velocity which depends on the chemical species and the atmospheric surface for air pollution.
- Simple dry deposition models do not limit the amount of pollutant that can be removed by the atmosphere.
- Little data is available for chlorine, especially at higher concentrations

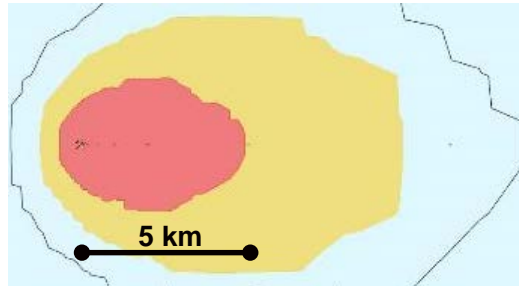
Chlorine Deposition Modeling Issues

- Extensive study of similar chemicals (nitric acid) shows dry deposition rate depends on:
 - Surface
 - Atmospheric turbulence (wind speed and atmospheric stability)
- Is there a limit to the amount of chlorine that a surface can react with? (Maximum deposition)
- Current atmospheric models are typically based on simple dry deposition (no limit of maximum deposition).
- Not currently considering reactivity of rained out chlorine (liquid chlorine on a solid surface).

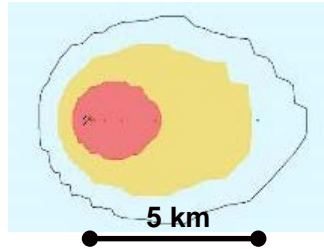
Preliminary Analysis: 17-ton Chlorine Release HPAC Footprints

Amount: 15422 kg
10 minute release
1542.2 kg/min rate

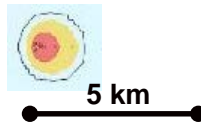
1.5 m/sec wind
F stability



Dry Deposition
Velocity = 0 cm/sec



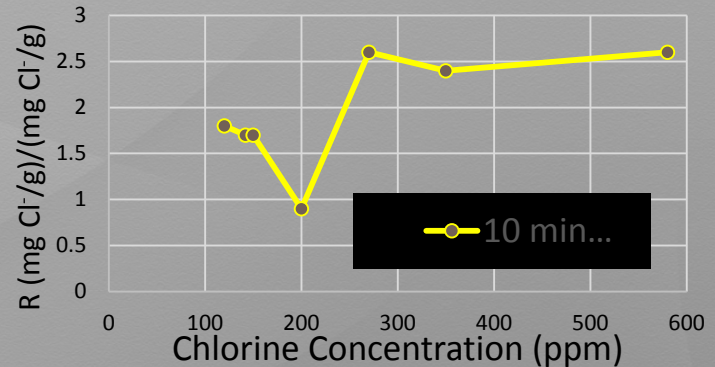
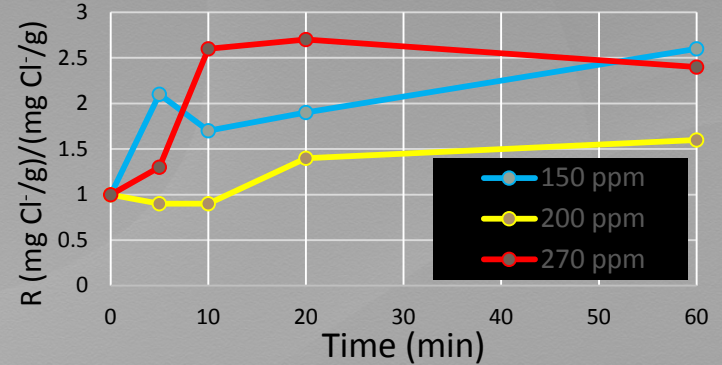
Dry Deposition
Velocity = 0.3 cm/sec



Dry Deposition
Velocity = 2.07 cm/sec

Lydiard Data

- Exposed vegetation samples to constant chlorine concentration in air.
- Measured chloride concentration in vegetation (L. perenne and T.repens) by extraction using an ion specific electrode.
- Multiple trials and averages compared with untreated samples.
- Ratio R of measured concentration in treated sample (mg Cl⁻/g dry substrate) to untreated control (average of 4.5 mg Cl⁻/g).
- For exposures over 250 ppm, maximum adsorbed is ~7 mg Cl⁻/g T.repens (white clover)



Argonne Chlorine Data

- Measured chlorine concentration decay in the gas phase in a closed system with exposed sample. The initial chlorine concentration (50 ppm) was the maximum concentration of their analytical instrument.
- Closed system exposed to high chlorine concentrations to stabilize reactivity of apparatus with chlorine. After this conditioning phase, the empty apparatus showed a repeatable chlorine (gas phase) concentration adsorption/reaction as a function of time.
- Repeated experiments were conducted with (freshly cut) vegetation samples and various soil moistures. Note that plant samples and soil tested separately.

Chlorine Surface Reaction Rate Expression

General n^{th} order (heterogeneous) reaction on a surface for chlorine can be modified using the standard approach to catalyst deactivation:

$$-r_s'' = k_s'' C^n a_s^p$$

where a_s is the surface activity. (In catalyst deactivation literature, a_s is defined to be the ratio of the rate of reaction for a catalyst pellet to the rate of reaction for a new catalyst pellet; $a_s = 1$ initially.) If $p=1$, this is equivalent to surface adsorption following a Langmuir isotherm (or the Hill Equation in biochemistry used by Argonne in their analysis).

For chlorine adsorption on a surface, the surface activity can be related to the maximum mass of chlorine that can be adsorbed by a surface M_{max}''

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

where M'' is the mass of chlorine adsorbed on a surface as a function of time.

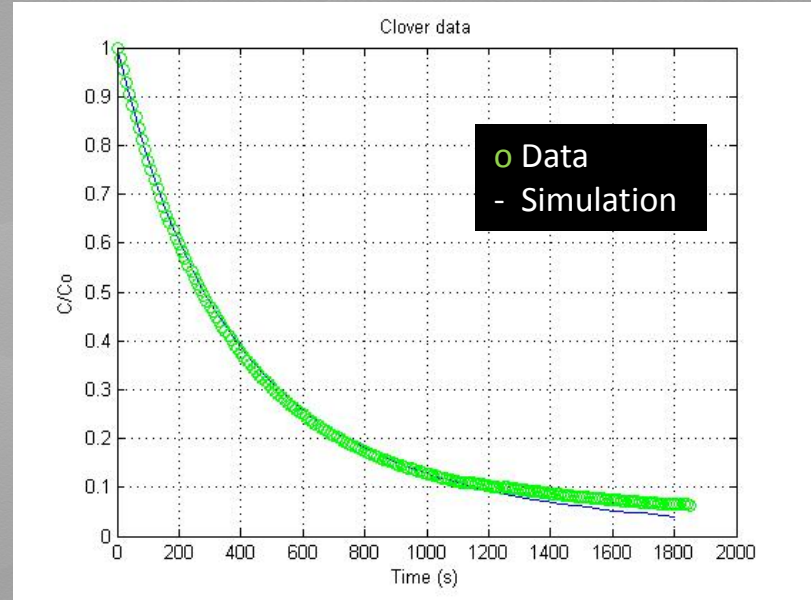
Argonne Data Analysis

Empty chamber data analyzed to determine rate and maximum adsorbed/reacted in empty chamber.

With empty chamber characterized, concentration data including exposed samples fit to kinetic model for closed test chamber to determine for samples:

- Maximum amount of chlorine reacted
- Rate of reaction (kinetic) constants

Analysis shows surface activity model fits data well. First order reaction worked well.



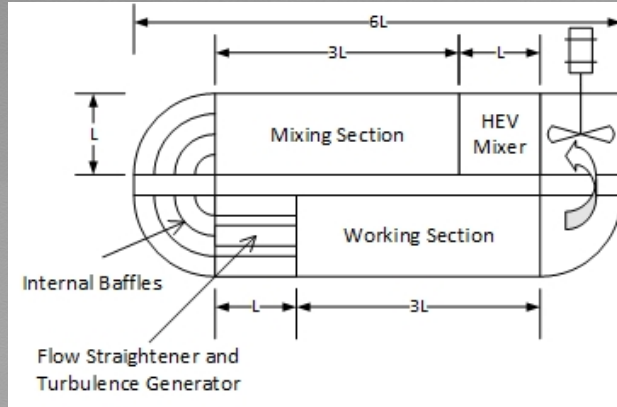
Analysis of plant and soil data – 1st order

Material	Reaction Order	Kinetic Constant k_s " (m/s)	M_{\max} " (mg/m ²)
White Clover	1	3.0×10^{-3}	700
Shamrock	1	7.7×10^{-4}	5000
White Spruce	1	1.18×10^{-3}	5000
Soil (0% moisture)	1	5.4×10^{-3}	5000
Soil (2% moisture)	1	5.0×10^{-3}	1000
Soil (4% moisture)	1	5.7×10^{-3}	600
Soil (8% moisture)	1	7.1×10^{-3}	600

Argonne Data Conclusions

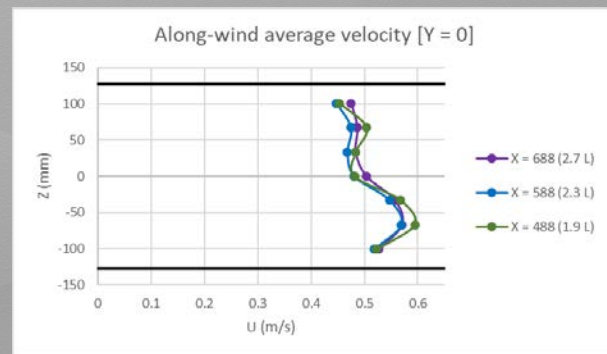
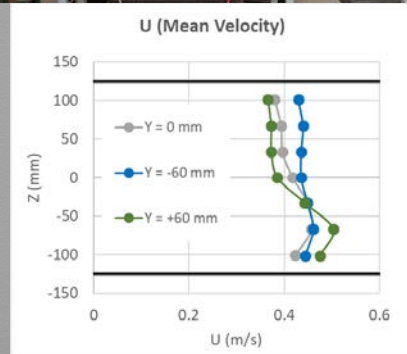
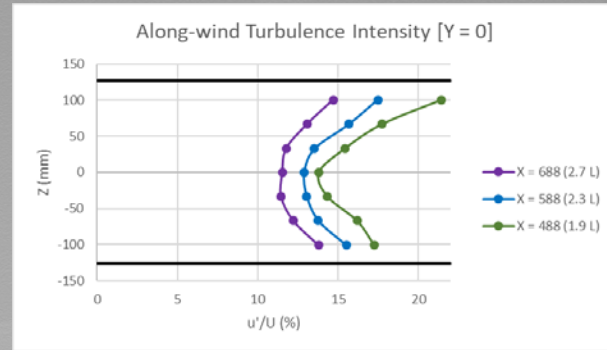
- First order reaction rate is reasonable to use to describe chlorine reactivity with tested samples.
 - Would the same rate expressions be suitable at higher concentrations (where reactivity is more important)?
 - Is the maximum deposition approximately the same at higher initial concentrations?
- Argonne assumed that velocity was such that complete mixing was assured and atmospheric and leaf boundary layer resistances could be neglected.
 - How does velocity (and/or turbulence intensity) impact the reactivity measurements?

Recirculating Test Chamber



- Working section is 75 cm long with 25 cm x 25 cm cross section.
- Apparatus internals coated with Kynar.
- Peroxide cured EDPM gasket.
- Kynar injection quills, tubing, and fittings.
- JAZ instruments for gas phase concentration

Test Chamber



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%

Testing

Experiments at multiple velocities (0.25, 0.5, and 1 m/s) with initial chlorine concentration of ~1000 ppm

Test Materials

- Bare soil (single moisture)
- Clover in soil
- Rye grass in soil
- Spruce (PVDF mount)
- Maple leaves (PVDF mount)

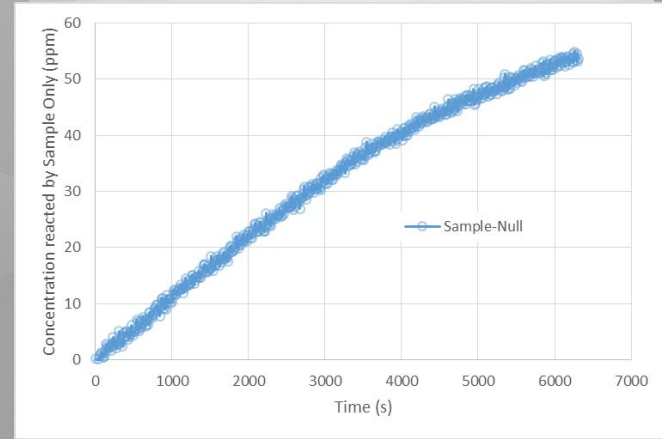


Chlorine gas phase concentrations measured with JAZ instrument. Chloride concentrations in test materials measured using ion chromatography.

Maple Testing

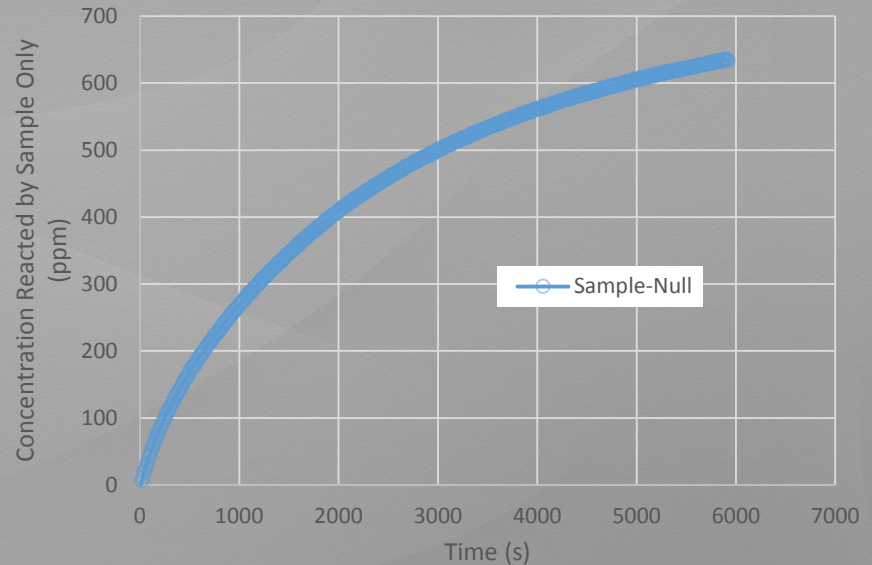
Autumn Blaze and Sugar Maple

- All 3 speeds complete
- Reduction in concentration due to sample measured, but small consistent with observations of leaf damage
- Rate of reaction decreases indicating limit to total chlorine that can be reacted for a given sample.
- Leaf area determined from flat bed scanner correlated to leaf mass.



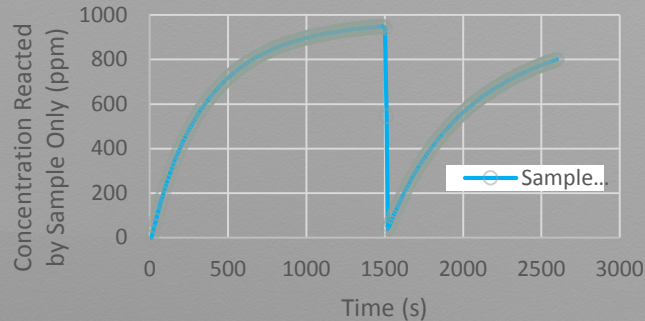
Spruce Testing

- Initial high speed test showed severe damage and significant chlorine concentration reduction
- Significantly less impact at lower speeds
- Subsequent tests pointed to importance of sunlight on previous day.
- Needle area determined from flat bed scanner and model of needle as an oblate spheroid correlated to needle mass.



Pansy Demonstration

Demonstration to help identify procedure issues (high speed only)
Severe, visible damage to plants consistent with concentration reduction (two charges of chlorine equivalent to 2000 ppm).



Note importance of having sufficient chlorine in experiments to react with all available reaction sites in treated sample. Effect of limiting amount of chlorine is included in analysis.

Conclusions

- Including the effect of reactivity of environmental surfaces with chlorine is important for proper hazard assessment.
- Previous experiments have shown that surfaces may become saturated with chlorine and unable to react with additional chlorine (maximum deposition). The reaction of chlorine with environmental materials can be effectively modeled as a first order reaction provided there is excess chlorine.
- An experimental apparatus has been built and characterized for exposing environmental materials to up to 1000 ppm chlorine under conditions that can readily be applied in atmospheric dispersion models. Current testing is underway to potentially extend that range to 10,000 ppm.

Conclusions (2)

- Spruce and Maple test have been completed. The maximum reactivity of Spruce seems to depend on stomata activity, but this is unverified.
- A demonstration with Pansy samples indicated that ground cover plants can be very effective at removing chlorine.
- Data processing is in progress to relate reactivity to vegetation area for use in operational atmospheric dispersion models. However, current models do not account for the maximum deposition.

Acknowledgements

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Data Analysis

- Measure concentration decay due to adsorption in empty apparatus
- After removing effect of empty apparatus surfaces, series resistance model between bulk concentration C_∞ and reactive surface ($C = 0$): r_1 bulk phase mass transfer to interface concentration; r_2 interface concentration governs surface reaction rate

$$\left(\begin{array}{c} \text{mass flux} \\ \text{based on reactive area} \end{array} \right) = \frac{C_\infty}{r_1 + r_2}$$

- Chilton-Colburn analogy relates momentum transfer to mass transfer to find $r_1 = \frac{Sc^{2/3}}{U} \left(\frac{U}{u_*} \right)^2$ where U is the bulk velocity (cross sectional area averaged velocity), u_* is the friction velocity, and Sc is the Schmidt number.
- Chemical reaction describes $r_2 = \frac{1}{k_s'' a_s}$ for first order reaction and surface activity a_s

Data Analysis (2)

- Rearranging rate expression:

$$\frac{C_{\infty}}{\left(\frac{\text{mass flux}}{\text{based on reactive area } A} \right)} = \frac{1}{U} \left(\frac{U}{u_*} \right)^2 + \frac{1}{k_s'' a_s}$$

- Use $\frac{C_{\infty}}{\left(\frac{\text{mass flux}}{\text{based on reactive area } A} \right)}$ as dependent variable (when C_{∞} is based on unreacted initial chlorine charge when $a_s = 1$), and $\frac{1}{U}$ as independent variable.
- As $\frac{1}{U} \rightarrow 0$, y intercept is $\frac{1}{k_s'' a_s}$
- M_{max}'' is found from fit of gas phase chlorine concentration time history and independently from ion chromatography measurements