ANL Surface Reactivity Experiments for Key TIH materials

David F. Brown

Wade Freeman

Bill Haney

Argonne National Laboratory

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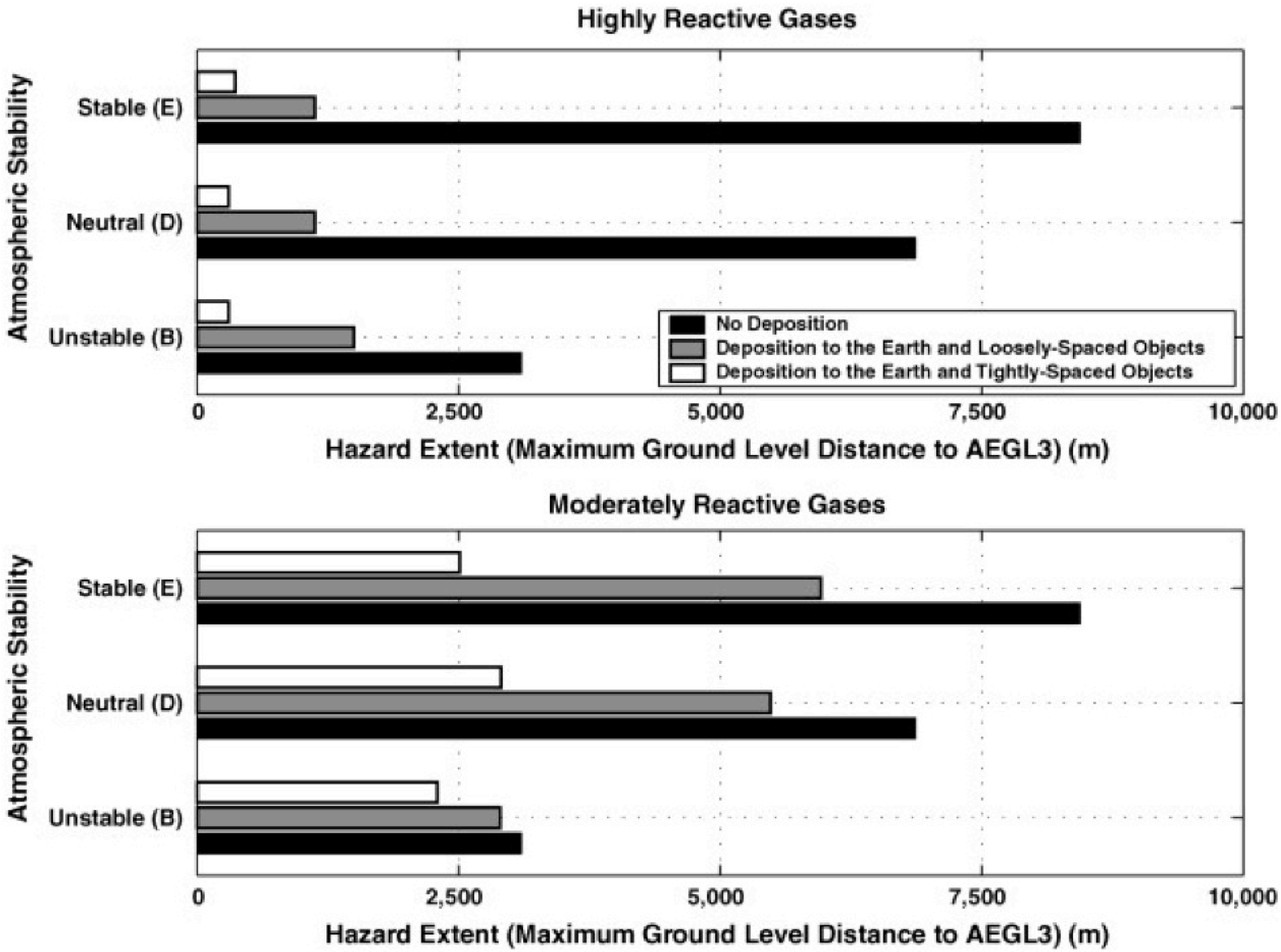
Motivation for the Research

- Reactivity and surface deposition of materials recognized as a gap in current understanding of hazardous material releases
- Multiple studies have shown that distances to AEGL-3 concentration thresholds are significantly reduced if simple surface deposition (reactivity with surface matter) is included
- Much of this effect is driven by vegetation uptake – an effect strong enough to lead some to suggest that greenbelts and other vegetation around potential release sites
- Deposition is conceptually easy to implement and had been incorporated is CASRAM for the 2016 ERG. This utilizes many surface parameters already included in our scenario analyses
  - Land use/season
  - Vegetation parameters such as leaf area index
  - Atmospheric boundary layer properties

Example Results from Literature



From: Michael Dillon, *Role of Deposition in Limiting the Hazard Extent of Dense Gas Plumes,* Journal of Hazardous Materials, 2008

Key Application Issues

- Surface reactivity is not well characterized, even for major commodities
  - Appears important for many materials, though saturation or destruction of organic material at high chemical concentrations may limit reactivity in the near field
  - Values in the literature are often anecdotal
  - Additional mitigation effects include photolysis and other atmospheric chemical reactions – can expressed in terms of a chemical half life which can be 20 min or less
- 170 separate chemicals and mixtures considered in our ERG analysis. Will eventually need a method that addresses not just major commodities but all TIH materials
  - Uniform methodologies across the range of materials in the ERG analysis would be ideal – **only 6 materials considered to date: chlorine, ammonia, sulfur dioxide, hydrogen chloride, carbon monoxide, hydrogen sulfide**
  - Like other aspects of the problem, could be treated statistically.

Key Application Issues (cont.)

- Purpose for experiments and use of data acquired
  - Calculate a deposition velocity v_d using a ***surface depletion resistance*** R_c

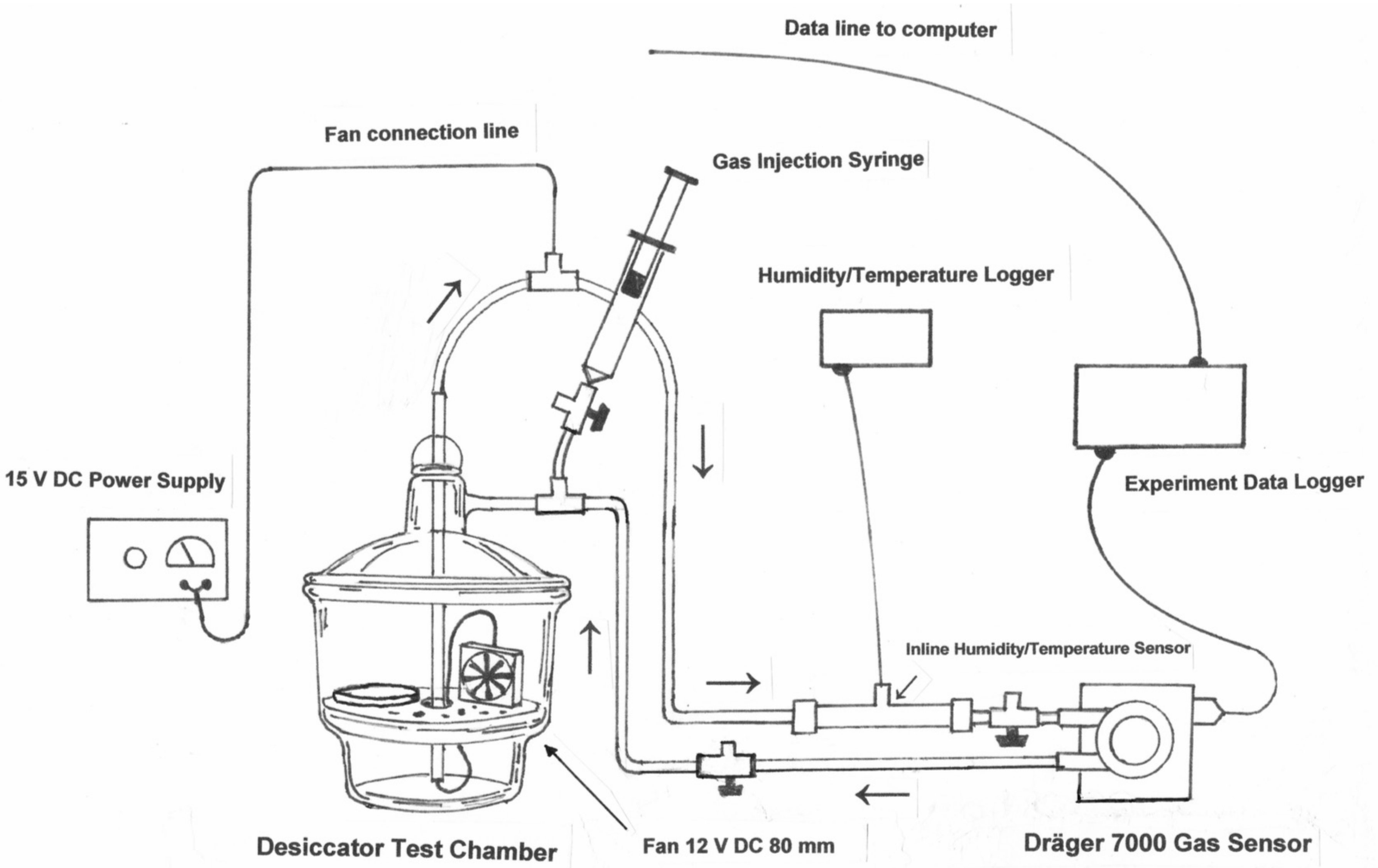
$$v_d = \frac{1}{R_a + R_b + R_c}$$

  - R_a is atmospheric resistance , R_b is surface boundary layer resistance (these are readily estimated using atmospheric turbulence parameters already used within the modeling framework)
  - R_c could be roughly estimated for highly reactive, moderately reactive, etc. (e.g., Jonsson et al. 2005; Dillon, 2009) – we have derived these values experimentally

Technical Approach

- Use several glass desiccators as sealed reaction vessels
- Inject toxic gas into sir-filled system; fill vessel to a prescribed concentration
- Use Draeger chemical detection sensors to measure gas concentration as a function of time, and allow to react over 1-2 hours to determine depletion rate
- For each chemical run tests for
  - Empty vessel
  - 4 bare soil types
  - 4 vegetation types
  - Water
- Vessel also has a small fan to keep the chamber well mixed – minimizing aerodynamic and boundary layer resistances (R_a and R_b)

Experimental Apparatus



Experimental Apparatus

Two identical set-ups including glass chamber, Draeger chemical sensor, tubing, and syringe for injection of target chemical

Experimental Apparatus

Analysis Method

- Recall: We wish to calculate a deposition velocity v_d using a ***surface depletion resistance*** R_c
- To estimate this, we calculate a deposition velocity from the known chlorine loss, then use

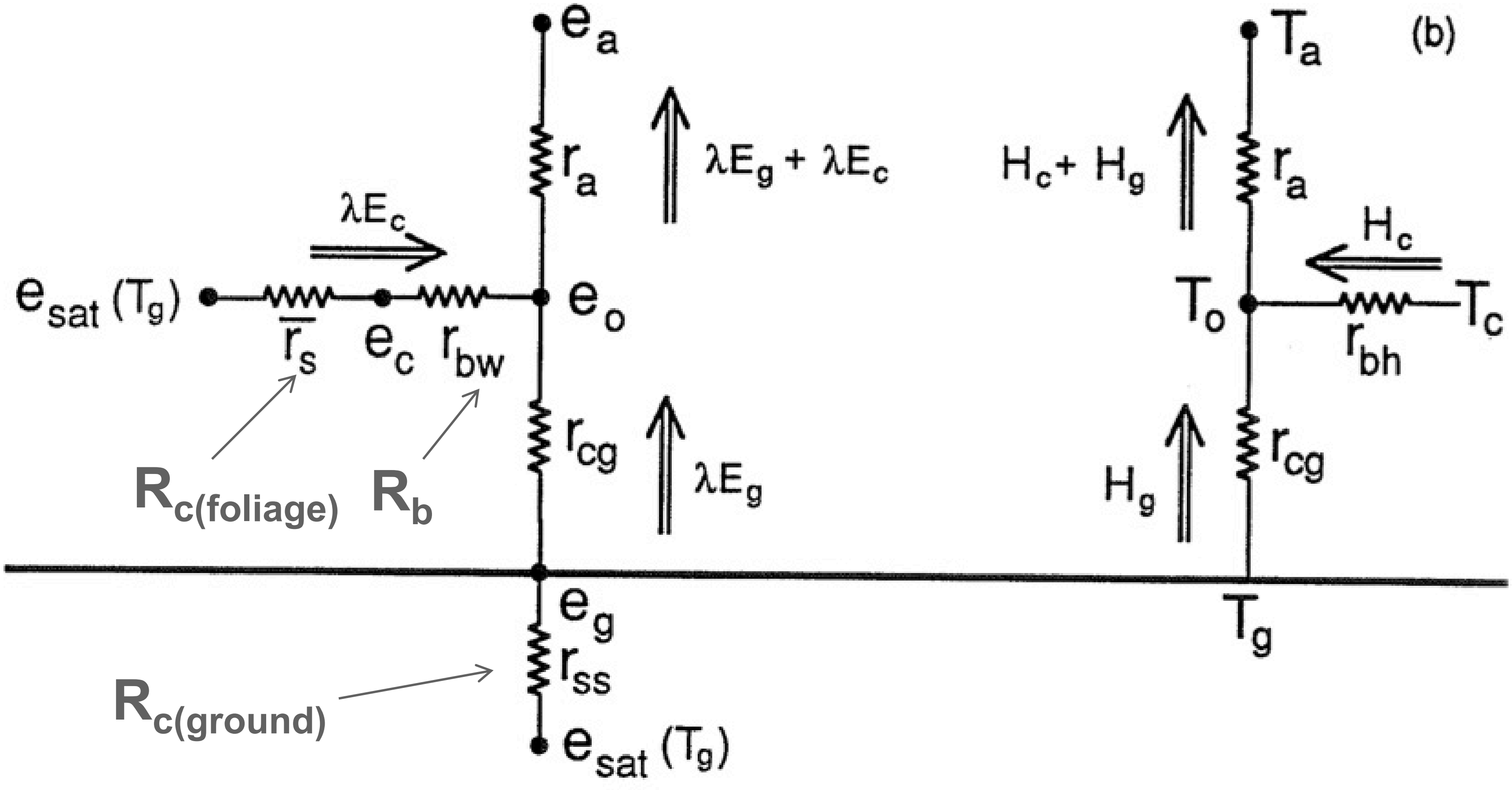
$$v_d = \frac{1}{R_a + R_b + R_c}$$

~ 0 ~ 0

$$\frac{dC}{dt} V = C v_d A$$

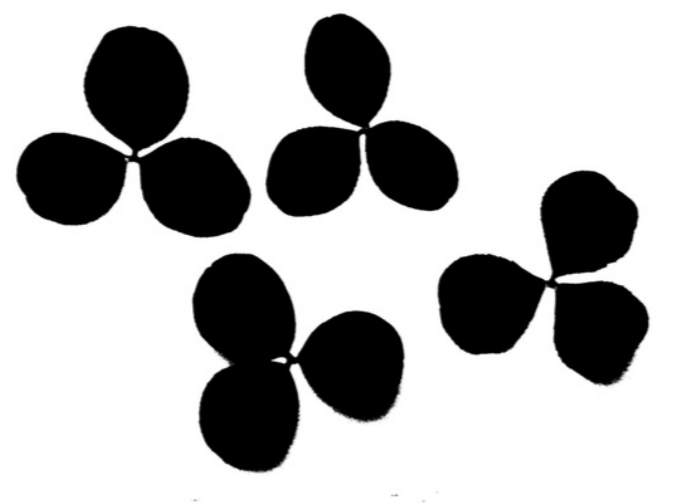
- C = measured concentration, V = volume, A is area of reaction
- Estimate A (area) – 10 cm petri dish with leaves – need total leaf area

Resistance Analogy to Sensible and Latent Heat Fluxes



Determination of Leaf Area

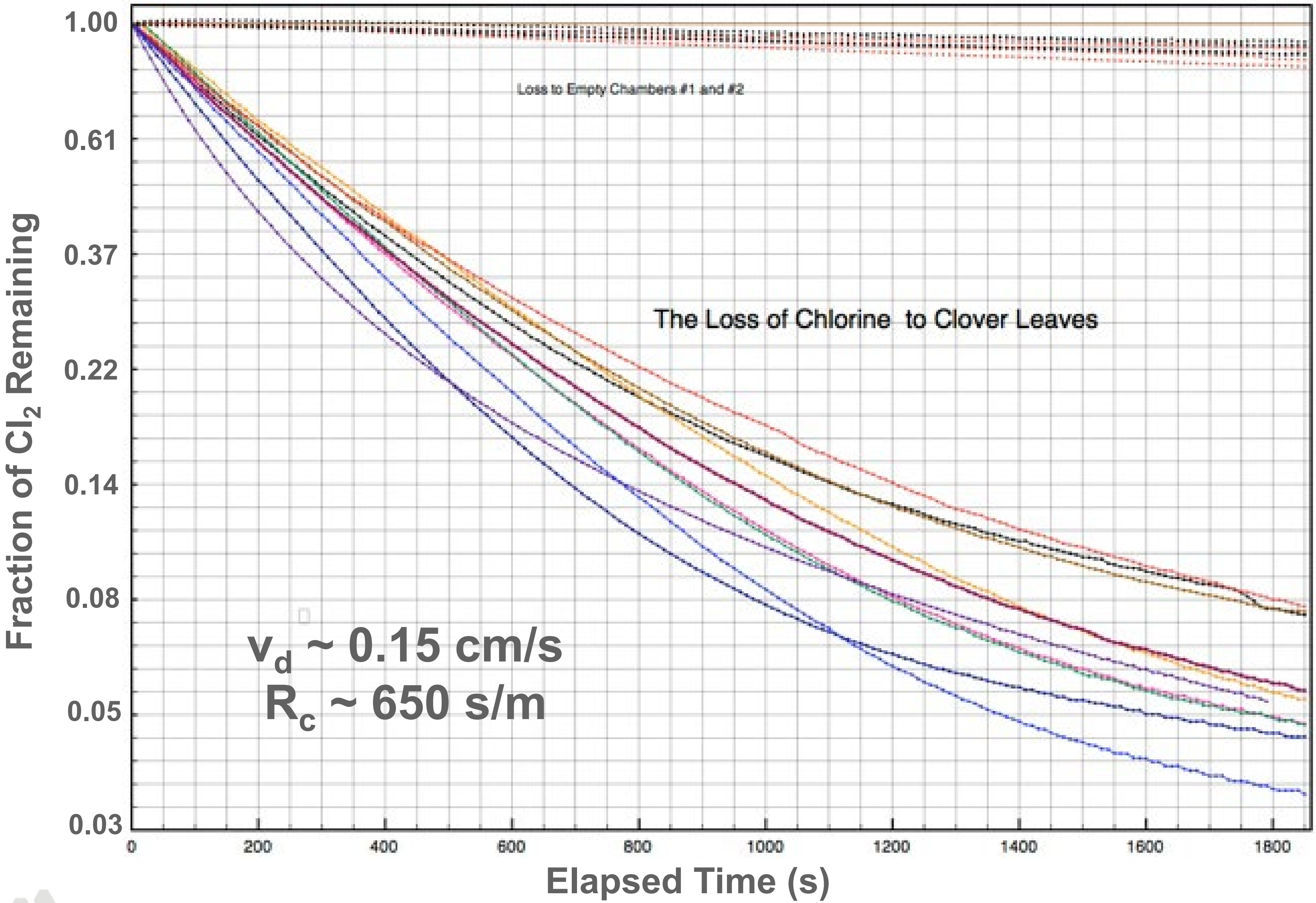
- Leaf Area determined photographically using the image analysis program ImageJ
- Conifer sprigs counted and the surface area estimated based on the number and the surface area of a typical needle
- Grass plugs given a nominal leaf area index of 7



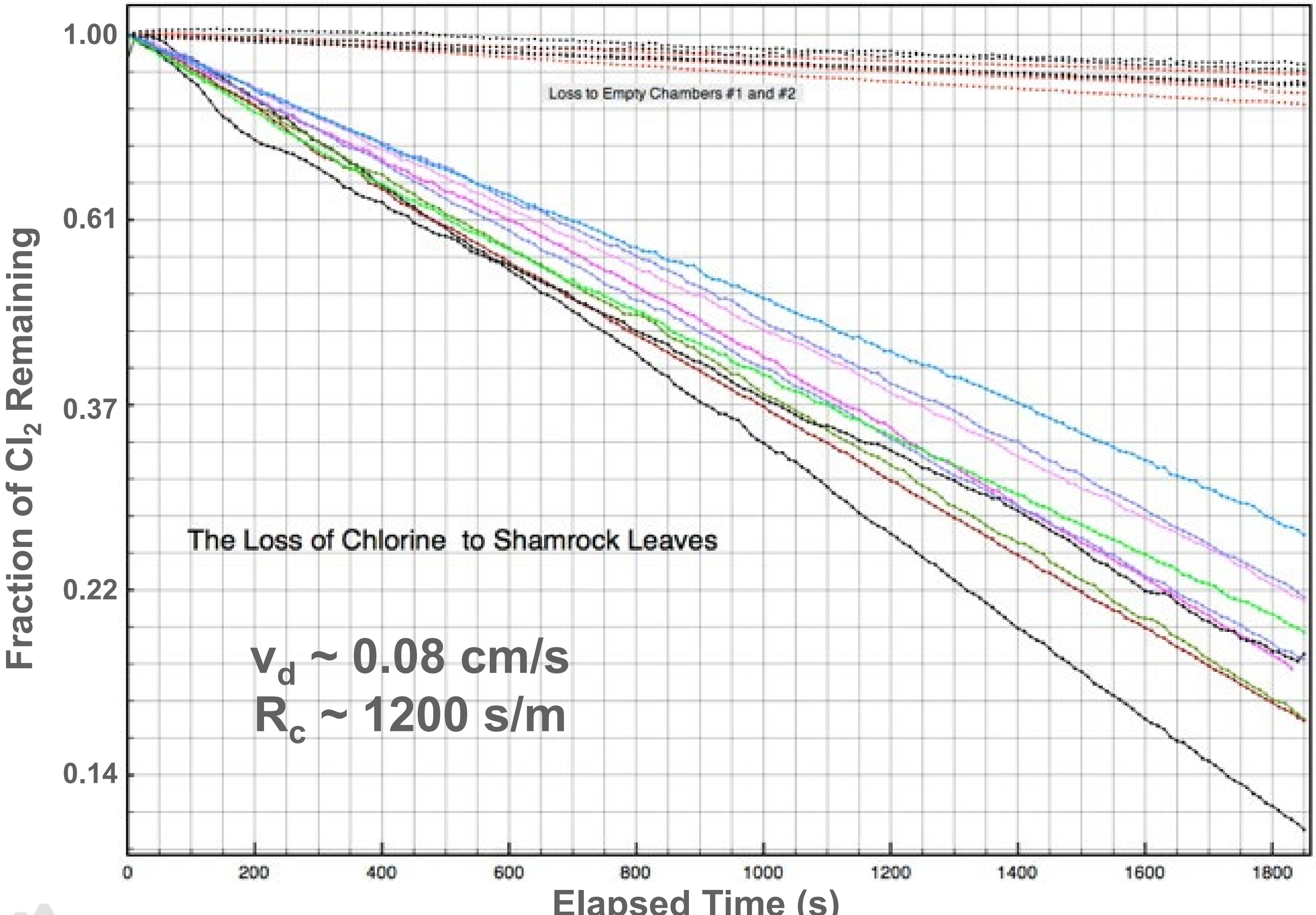
Additional Challenges

- **Measuring chemical concentrations over time within the vessel must be done carefully; need to use different sensors or dilution to cover the desired range of 2 – 1000 ppm (for Cl_2)**
- Need to "condition" the vessels with the chemicals before testing
- **Need to translate the observed depletion rates into the *surface depletion resistance* R_c**
  - Requires estimation of a "leaf area index" or an equivalent surface-to-surface area ratio
  - At high concentration, destruction of plant material may limit depletion (have not observed that yet)

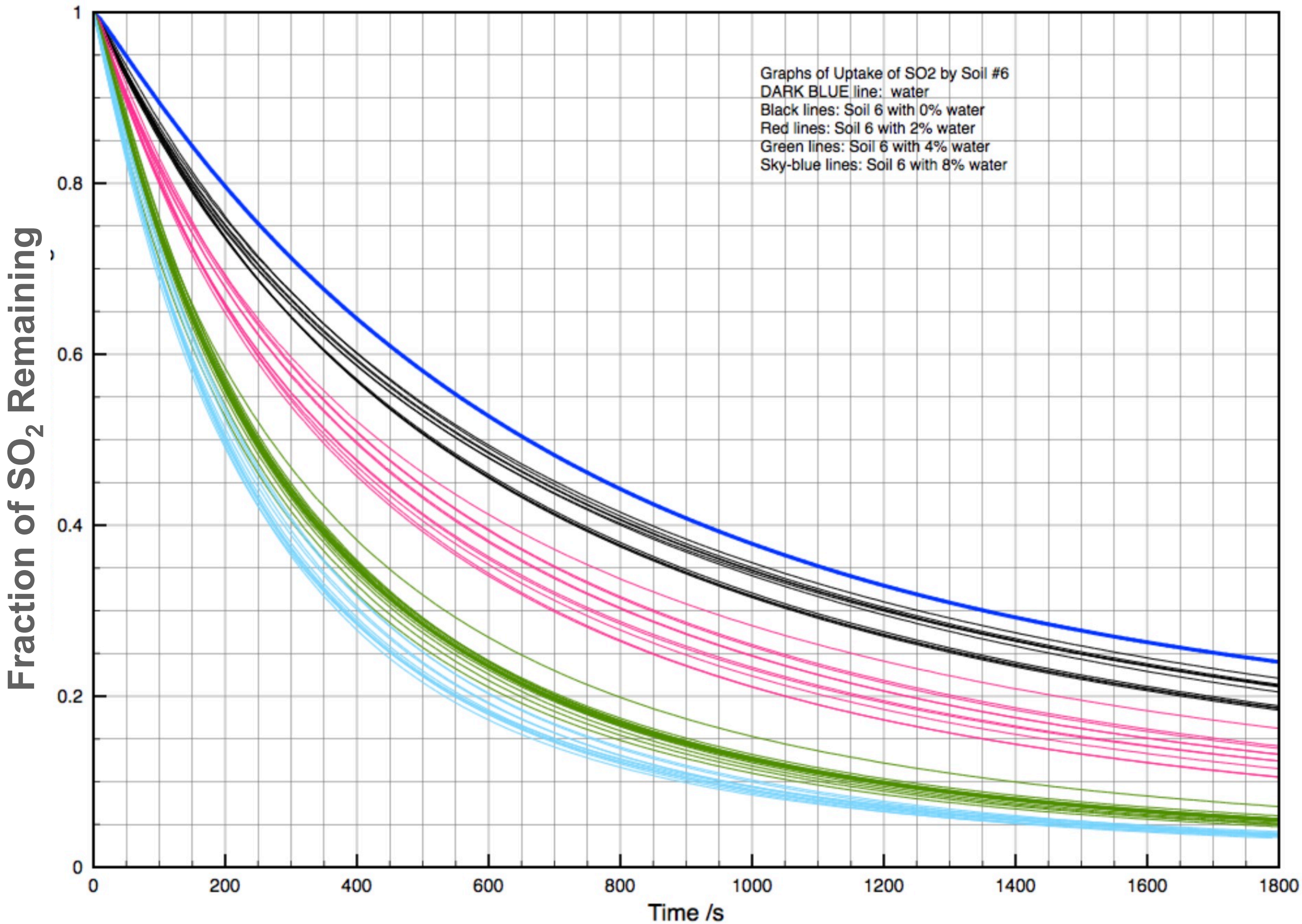
Data Summary Chlorine - Clover



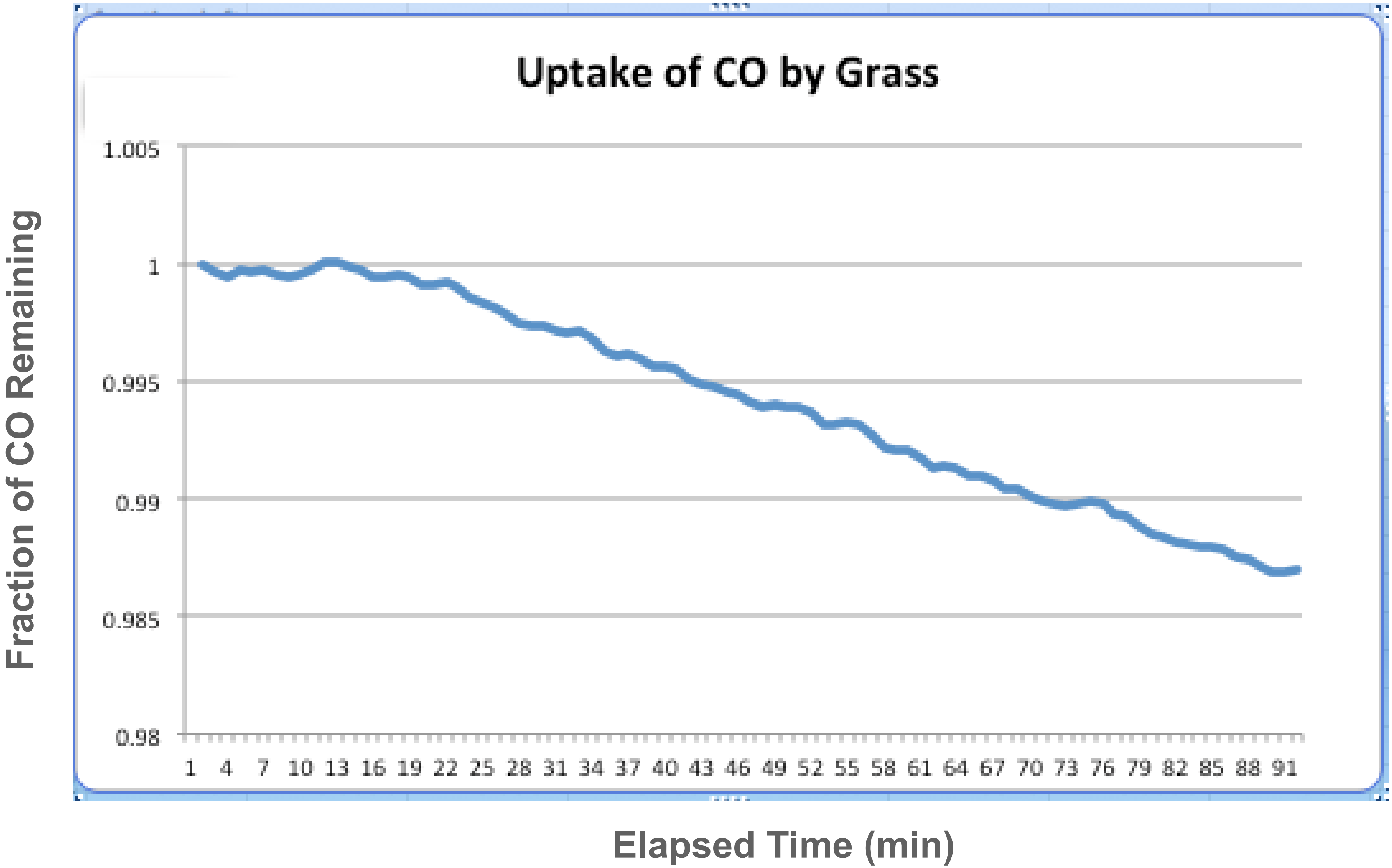
Data Summary Chlorine - Shamrock



Data Examples for SO_2 (Soil)



Data example for CO



Final Results from Experimental Program

Surface depletion resistance R_c (s/m)

Vegetation/soil type	Chlorine	SO2	HCl	Ammonia	CO	H2S
Broadleaf evergreen forest	1023	9208	1592	8801	114942	49650
Broadleaf deciduous forest	1023	9208	1592	8801	114940	49650
Broadleaf and needleleafed mixed	869	9164	1378	4992	72400	28566
Needleleaf deciduous forest	1023	9208	1592	8801	114940	49650
Needleleaf evergreen forest	930	8887	1392	1985	56883	29431
Tundra	220	490	147	166	75000	19753
Broadleaf shrubs	1266	10929	1989	11038	93670	39108
Grassland/Prairie	295	4045	401	2089	73500	37878
Field crops	618	6333	929	5067	88567	18765
Surburban areas	618	6339	930	5072	88567	18765
Urban areas	618	6339	930	5072	88567	18765
Bare areas	174	354	106	135	75187	20661
Water	821	660	102	297	75230	25864
soil low moisture	128	217	66	104	77562	27633
soil high moisture	220	490	147	166	75000	19753

Conclusions

- Chlorine generally the most reactive material of chemicals considered – this resulted in reductions of Protective Action Distances of ~25%
- CO and H2S very weakly reactive – will not significantly change results
- Awaiting results from University of Arkansas chlorine deposition wind tunnel study – should be available late summer/early fall