

**Time Variability in Hazardous Gas Deposition  
(Adsorption) and Re-Evaporation (Desorption) as  
a Cloud from a One-Minute Accidental Release  
Passes By**

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# Conceptual Model

- The hazardous release from pressurized liquefied storage can take place in a minute or less if the hole is large enough (diameter > about 5 or 10 cm)
- Field measurements such as at Jack Rabbit II (chlorine) show that the emission rate decreases rapidly with time. Depending on orientation, the rate of decrease varies from linear to exponential.
- With wind speeds > about 1 m/s, downwind concentrations and deposition at distances of 100 -1000 m therefore ramp up and drop to nearly zero within a few minutes
- Some of the deposited gas and liquid can re-evaporate (desorption); some can react with other chemicals and the products may stay in the ground
- Fast response instruments are needed to detect the concentration and deposition patterns in the air and in the substrate

## Are there any observations of the above phenomena?

- The following three slides show the sampler set up and observed instantaneous puff time series measured during the Joint Urban 2007 field study in Oklahoma City. The tracer was SF<sub>6</sub>. Note the rapid ramp up and slower decrease as the puff moves away. This is because the puff size ( $\sigma_x$ ) keeps increasing as it moves downwind.
- At JR II, the in-situ samplers (Jaz, Canaries, Raes) produced time series of 2-3 sec averages over the period of exposure (see the slides after the JU2007 slides). Stand-off remote sensors also had rapid response but could not “see” far into the edge of the plume (and needed calibration using nearby in situ samplers).

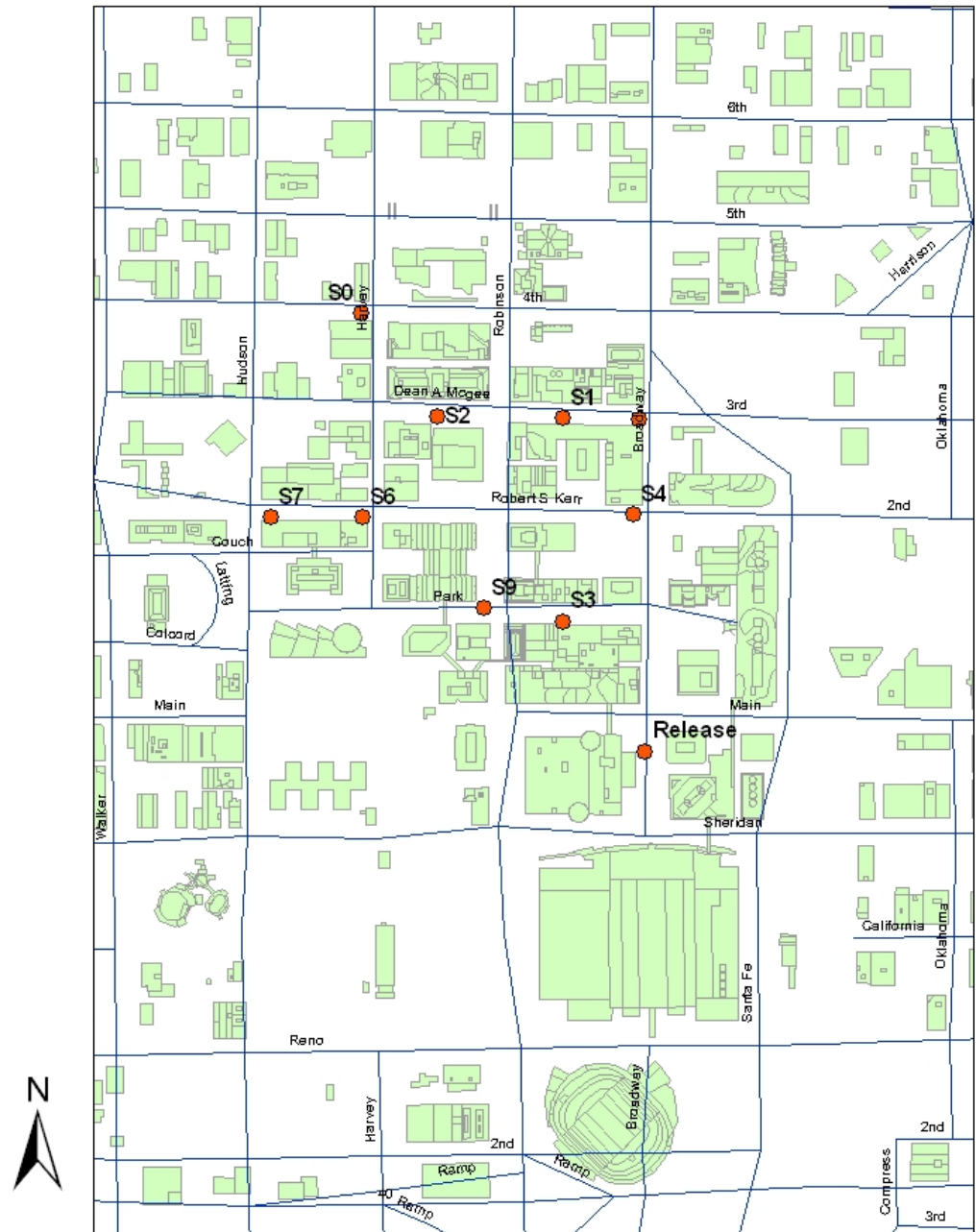
# Simple Puff T&D Model

- Gaussian shape, therefore max C is proportional to  $Q/(\sigma_x \sigma_y \sigma_z)$ , where Q is instantaneous mass released
- $\sigma_t = 0.1t$  (Hanna and Franzese 2000; based on analyzing many field and laboratory data)
- $t = x/u$  and  $\sigma_x = \sigma_t u$ . Therefore  $\sigma_x = 0.1x$
- Assume that the sampler is at distance x. Data files usually have the format of concentrations C versus time after release.

**Joint Urban 2003  
Locations of puff  
release site and  
fast-response  
samplers during  
IOP 8.**

**Streets and  
buildings are  
shown**

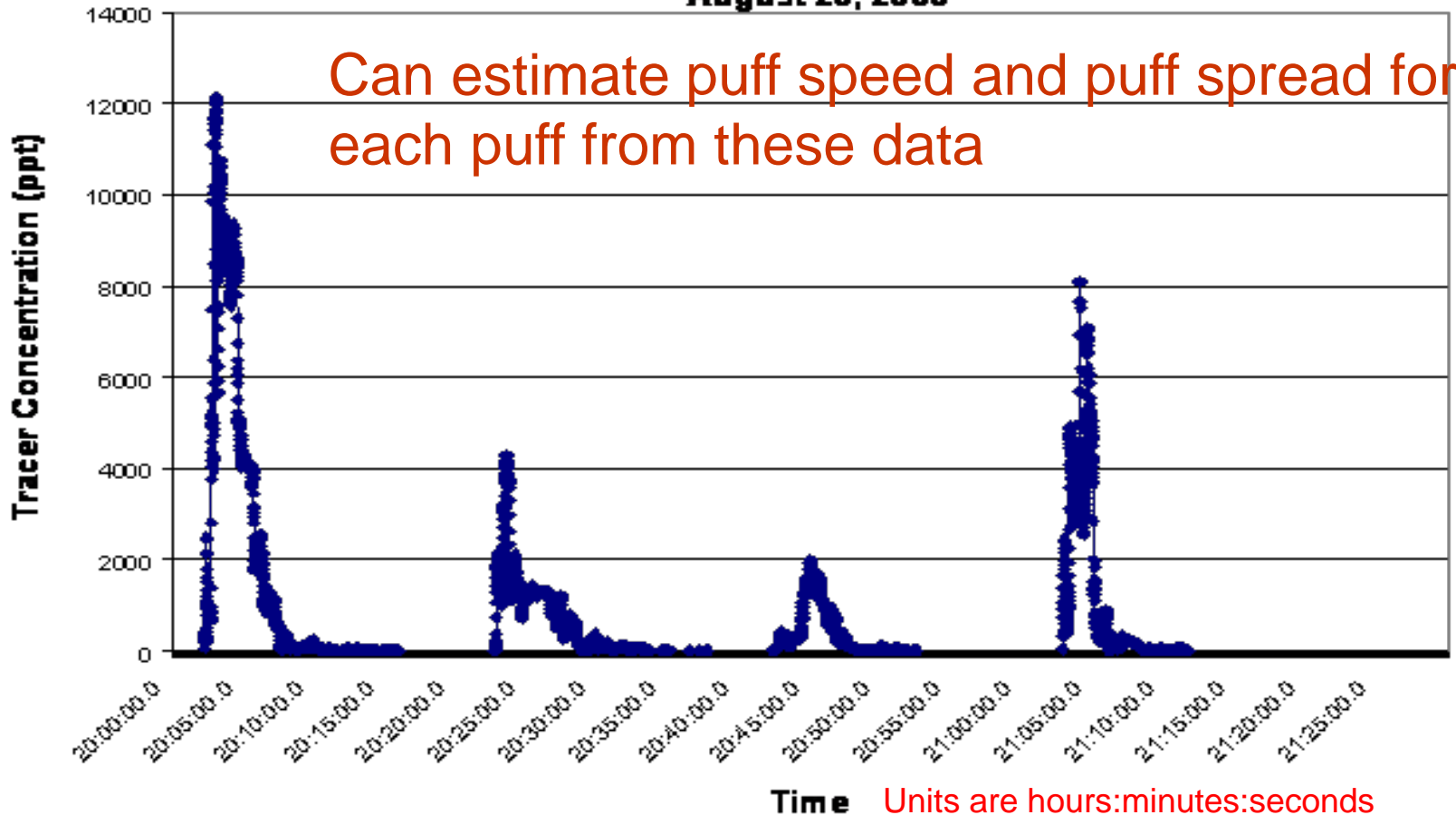
**Domain is about 1  
by 1.5 km**



0 45 90 180 Meters

# Fast Response SF<sub>6</sub> Obs at JU2003 [C(t) for Four Puff Releases, 20 min apart]

JU-2003  
IOP 5, Sampler 8  
August 25, 2003

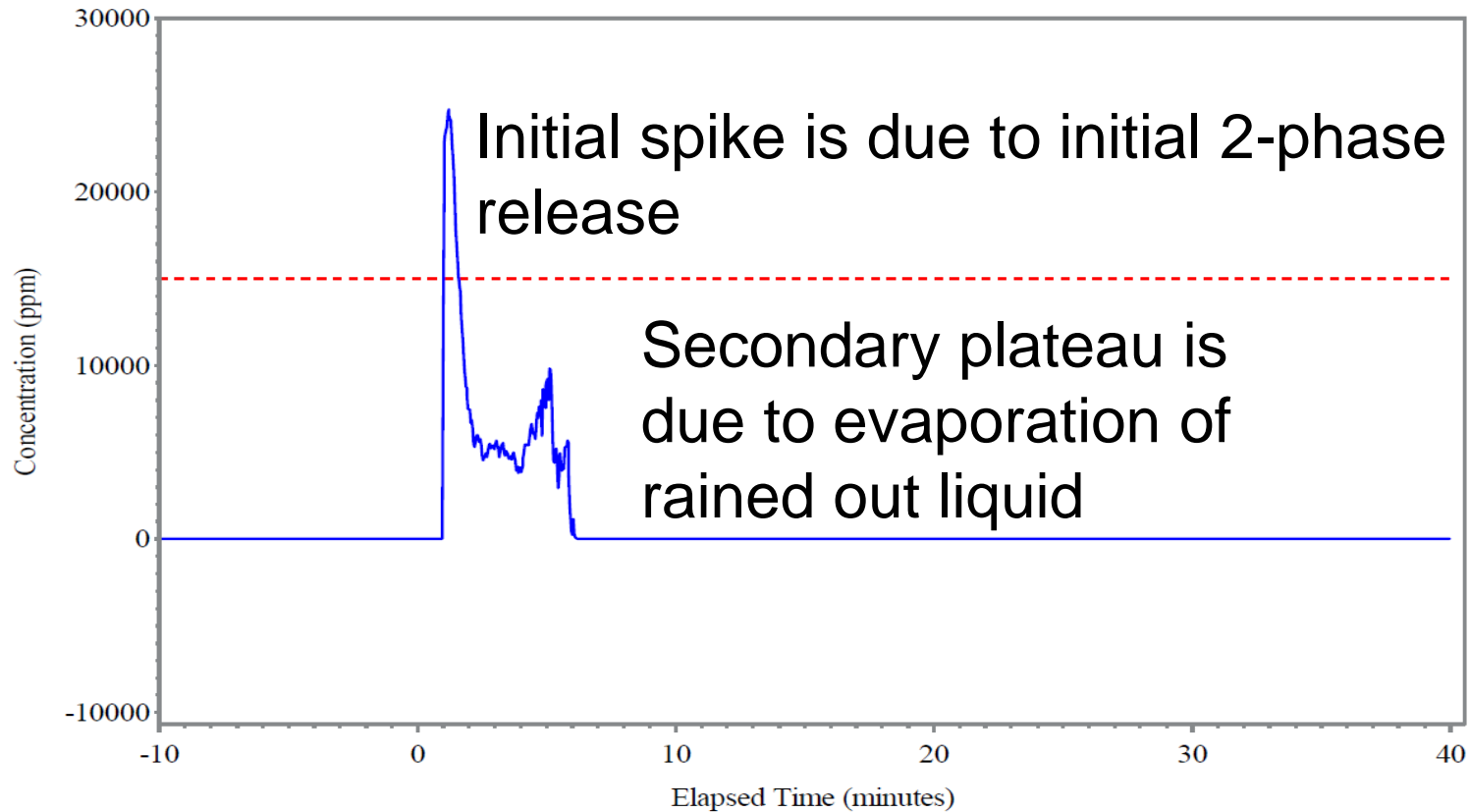


## Chlorine C time series in JR II

- The next slide shows 2-3 sec averaged chlorine concentration C time series for one sampler in Trial 6 of JR II.
- This “Canary” sampler is at  $x = 200$  m. The initial two-phase release (hole at bottom of tank) lasted about a minute. But about 30% of the release mass rained out around the source and subsequently evaporated over the next 5 or so min.
- The time series indicates the initial spike due to the two-phase jet, followed by a lower C plateau, due to the evaporating rained out pool, that lasted about 5 min

# Fast response chlorine obs at JR II Trial 6 [C(t) for release duration of about 1 min] (courtesy of Simon Gant)

FINAL Trial 6, Location 200-05-0.3, Unit 20 Canary Concentrations



Distance= 200 m, Azimuth= 355 degrees.  
If present, dashed red line indicates upper calibration limit.



# Model comparisons and analyses of JR chlorine and ammonia C time series

- In the various JR I and JR II publications containing model comparisons with observations, nearly all the emphasis is on the arc-maximum short-term concentrations resulting from the initial two-phase jet.
- At JR I, there were limited observations of deposition. In an unpublished document, Hicks et al. presented analyses of rained-out ammonia penetrating into the underlying substrate. Most of the penetration below the ground surface was via cracks and “worm-holes”.
- In both JR I and II, after a release trial ended, the area wasn't “opened up” to researchers until concentrations dropped below a certain level. I have not seen a detailed analysis of the time delays, although they were in the range of 20 or 30 min.

**How do we best meld knowledge from 1) the extensive research done with ammonia deposition and desorption at air pollution levels (e.g., 1 to 100 ppb), and from 2) similar studies but at chemical accident levels (e.g., 10 to 100,000 ppm)**

- Many groups have measured ammonia deposition and desorption for soils and for vegetated surfaces. They generally only have a small number of samplers, which cannot measure above about 1 ppm.
- Mass spectroscopy appears to be a promising method for expanding observations at higher concentrations.
- However, research is needed to allow production of, say, 100 sampler systems at a reasonable price and can be operated by technicians.