Organization of Course

INTRODUCTION

1. Course overview
2. Air Toxics overview
3. HYSPLIT overview

HYSPLIT Theory and Practice

4. Meteorology
5. Back Trajectories
6. Concentrations / Deposition
7. HYSPLIT-SV for semivolatiles (e.g, PCDD/F)
8. **HYSPLIT-HG for mercury**

Overall Project Issues & Examples

9. Emissions Inventories
10. Source-Receptor Post-Processing
11. Source-Attribution for Deposition
12. Model Evaluation
13. Model Intercomparison
14. Collaboration Possibilities

Public Health Context

- Methyl-mercury is a developmental neurotoxin -- risks to fetuses/infants
- Cardiovascular toxicity might be even more significant (CRS, 2005)
- Critical exposure pathway: *methylmercury* from *fish consumption*
- Widespread fish consumption advisories
- Uncertainties, but mercury toxicity *relatively* well understood
  - well-documented tragedies: (a) Minimata (Japan) ~1930 to ~1970; (b) Basra (Iraq), 1971
  - epidemiological studies, e.g., (a) Seychelles; (b) Faroe Islands; (c) New Zealand
  - methylmercury vs. Omega-III Fatty Acids
  - selenium – protective role?
- At current exposures, risk to large numbers of fetuses/infants

+ Wildlife Health Issues
e.g., fish-eating birds

Different "forms" of mercury in the atmosphere

Elemental Mercury -- Hg(0)

- most of total Hg in atmosphere
- *not* very water soluble
- doesn't easily dry or wet deposit
- upward evasion vs. deposition
- atmos. lifetime approx ~ 0.5-1 yr
- globally distributed

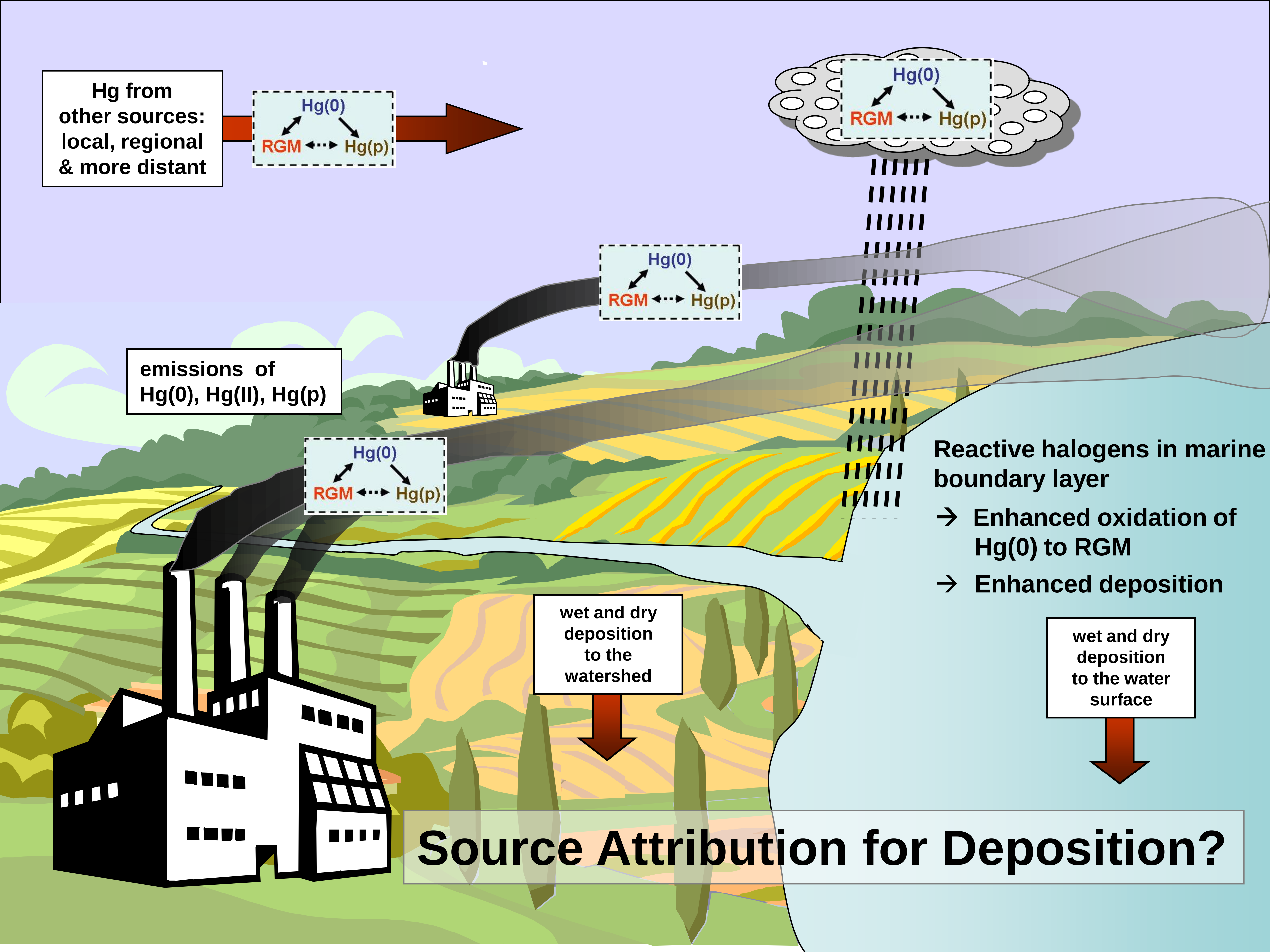
Atmospheric methyl-mercury?

Reactive Gaseous Mercury -- RGM

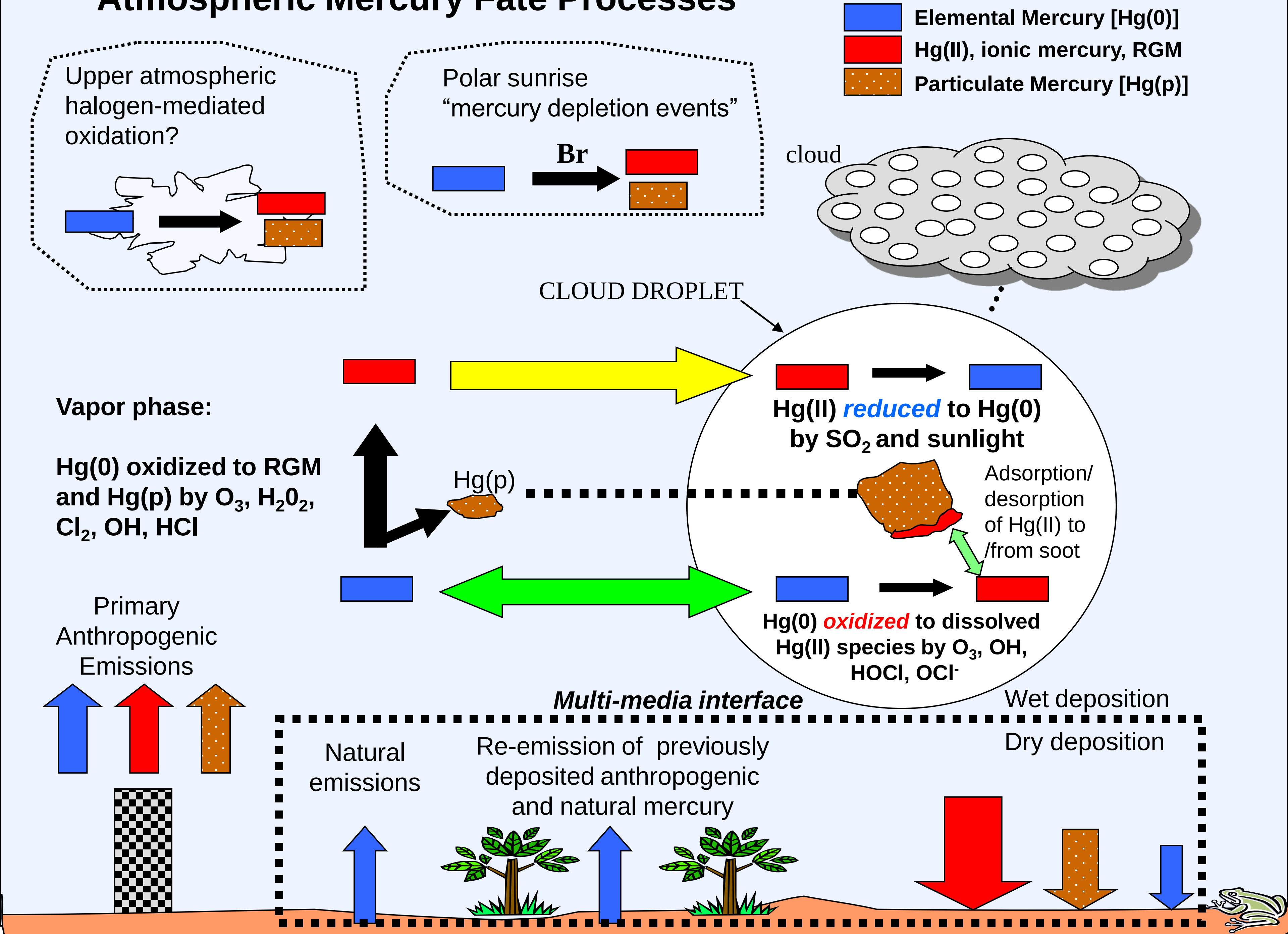
- a few percent of total atmos Hg
- oxidized Hg (HgCl2, others)
- operationally defined
- *very* water soluble and "sticky"
- atmos. lifetime <= 1 week
- local and regional effects
- bioavailable

Particulate Mercury -- Hg(p)

- a few percent of total atmos Hg
- not pure particles of mercury
- Hg compounds in/on atmos particles
- species largely unknown (HgO?)
- atmos. lifetime approx 1~ 2 weeks
- local and regional effects
- bioavailability?


Hg from
other sources:
local, regional
& more distant
Hg(0)
RGM
Hg(p)
Hg(0)
RGM
Hg(p)
Hg(0)
RGM
Hg(p)
emissions of
Hg(0), Hg(II), Hg(p)
Hg(0)
RGM
Hg(p)
Reactive halogens in marine boundary layer
→ Enhanced oxidation of Hg(0) to RGM
→ Enhanced deposition
wet and dry
deposition
to the
watershed
wet and dry
deposition
to the water
surface
Source Attribution for Deposition?

Atmospheric Mercury Fate Processes



(Evolving) Atmospheric Chemical Reaction Scheme for Mercury

	Reaction	Rate	Units	Reference
	GAS PHASE REACTIONS			
?	**$Hg^0 + O_3 \rightarrow Hg(p)$**	3.0E-20	cm^3/molec-sec	Hall (1995)
	$Hg^0 + HCl \rightarrow HgCl_2$	1.0E-19	cm^3/molec-sec	Hall and Bloom (1993)
	$Hg^0 + H_2O_2 \rightarrow Hg(p)$	8.5E-19	cm^3/molec-sec	Tokos et al. (1998) (upper limit based on experiments)
	$Hg^0 + Cl_2 \rightarrow HgCl_2$	4.0E-18	cm^3/molec-sec	Calhoun and Prestbo (2001)
?	**$Hg^0 + OH \rightarrow Hg(p)$**	8.7E-14	cm^3/molec-sec	Sommar et al. (2001)
new	**$Hg^0 + Br \rightarrow HgBr_2$**			
	AQUEOUS PHASE REACTIONS			
	$Hg^0 + O_3 \rightarrow Hg^{+2}$	4.7E+7	$(molar\text{-}sec)^{-1}$	Munthe (1992)
	$Hg^0 + OH \rightarrow Hg^{+2}$	2.0E+9	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1997)
	$HgSO_3 \rightarrow Hg^0$	$T*e^{((31.971*T)-12595.0)/T}$ [T = temperature (K)]	sec^{-1}	Van Loon et al. (2002)
?	**$Hg(II) + HO_2 \rightarrow Hg^0$**	~ 0	$(molar\text{-}sec)^{-1}$	Gardfeldt & Jonnson (2003)
	$Hg^0 + HOCl \rightarrow Hg^{+2}$	2.1E+6	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1998)
	$Hg^0 + OCl^{-1} \rightarrow Hg^{+2}$	2.0E+6	$(molar\text{-}sec)^{-1}$	Lin and Pehkonen(1998)
	$Hg(II) \leftrightarrow Hg(II)_{(soot)}$	9.0E+2	liters/gram; t = 1/hour	eqlbrm: Seigneur et al. (1998) rate: Bullock & Brehme (2002).
	$Hg^{+2} + hv \rightarrow Hg^0$	6.0E-7	$(sec)^{-1}$ (maximum)	Xiao et al. (1994); Bullock and Brehme (2002)

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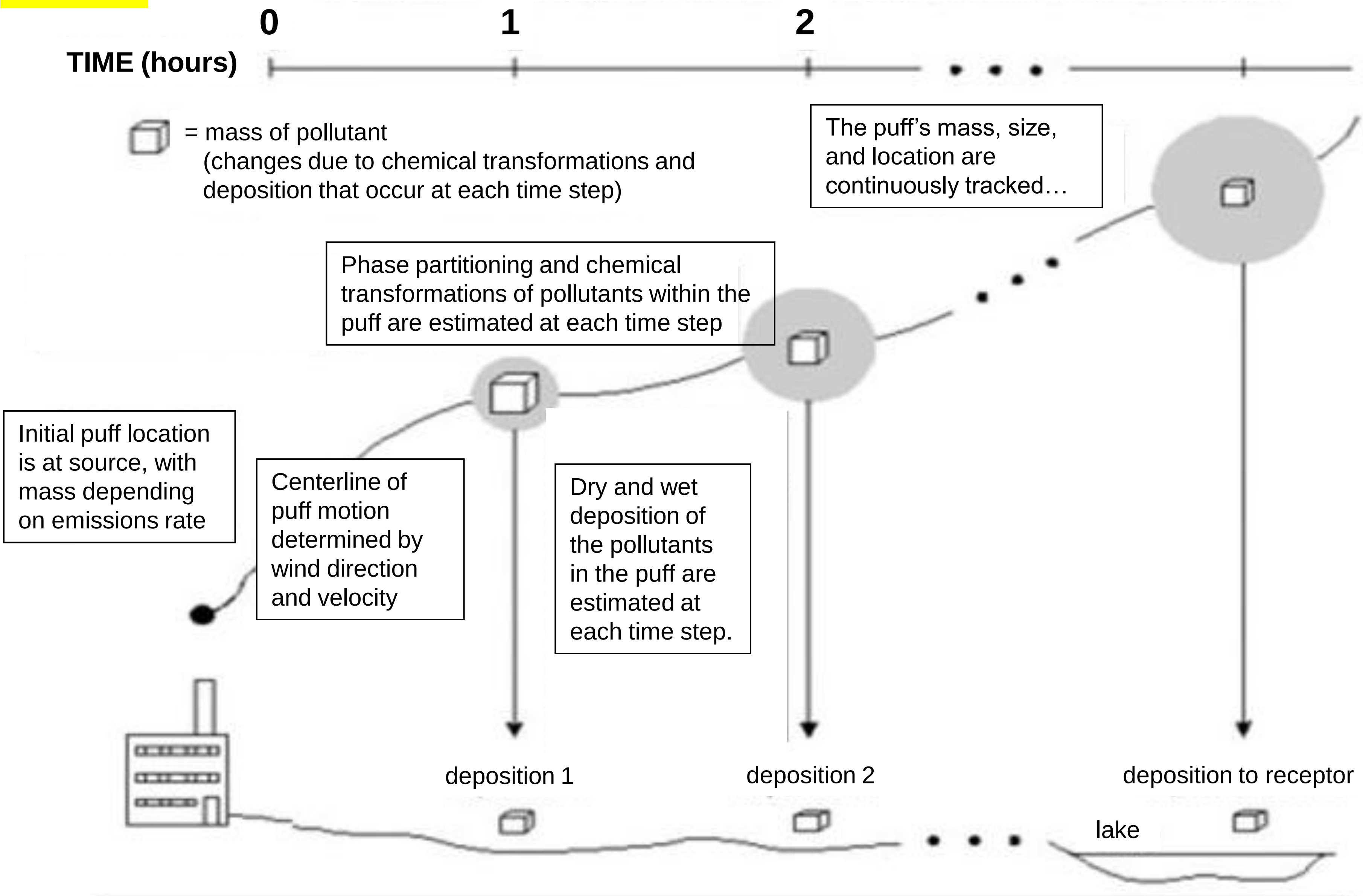
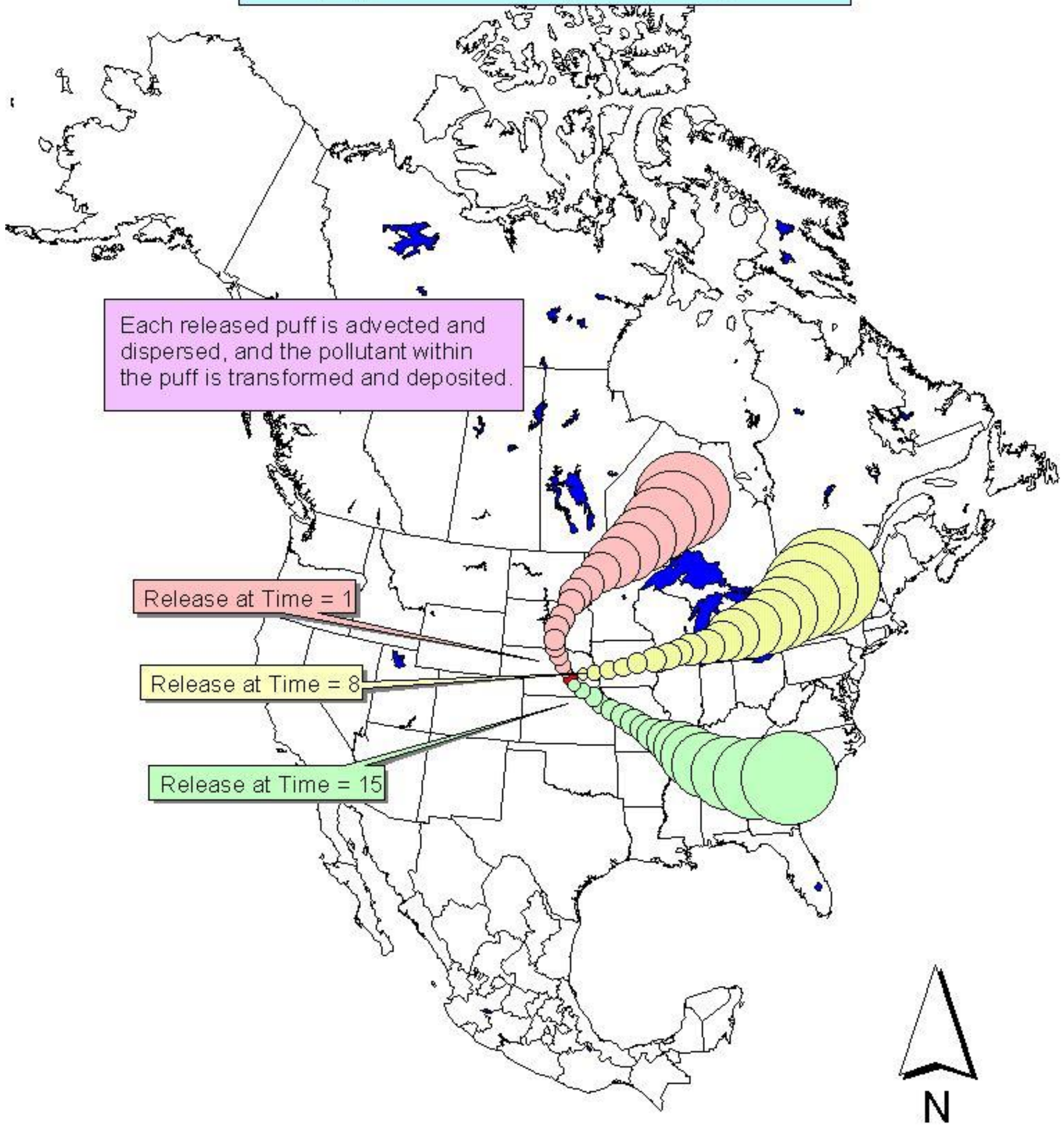
NOAA
HYSPLIT
MODEL

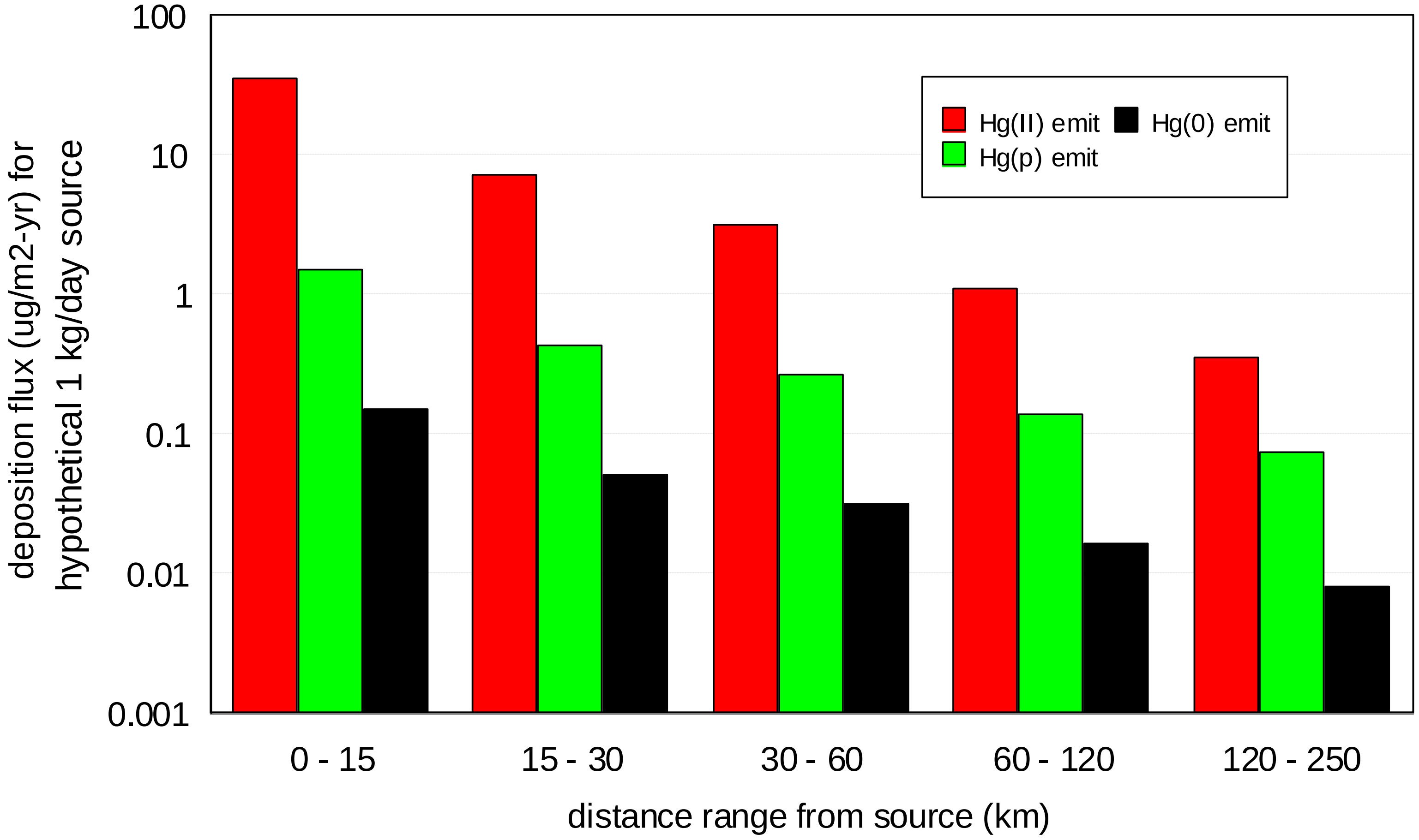
Lagrangian Puff Atmospheric Fate and Transport Model



Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).



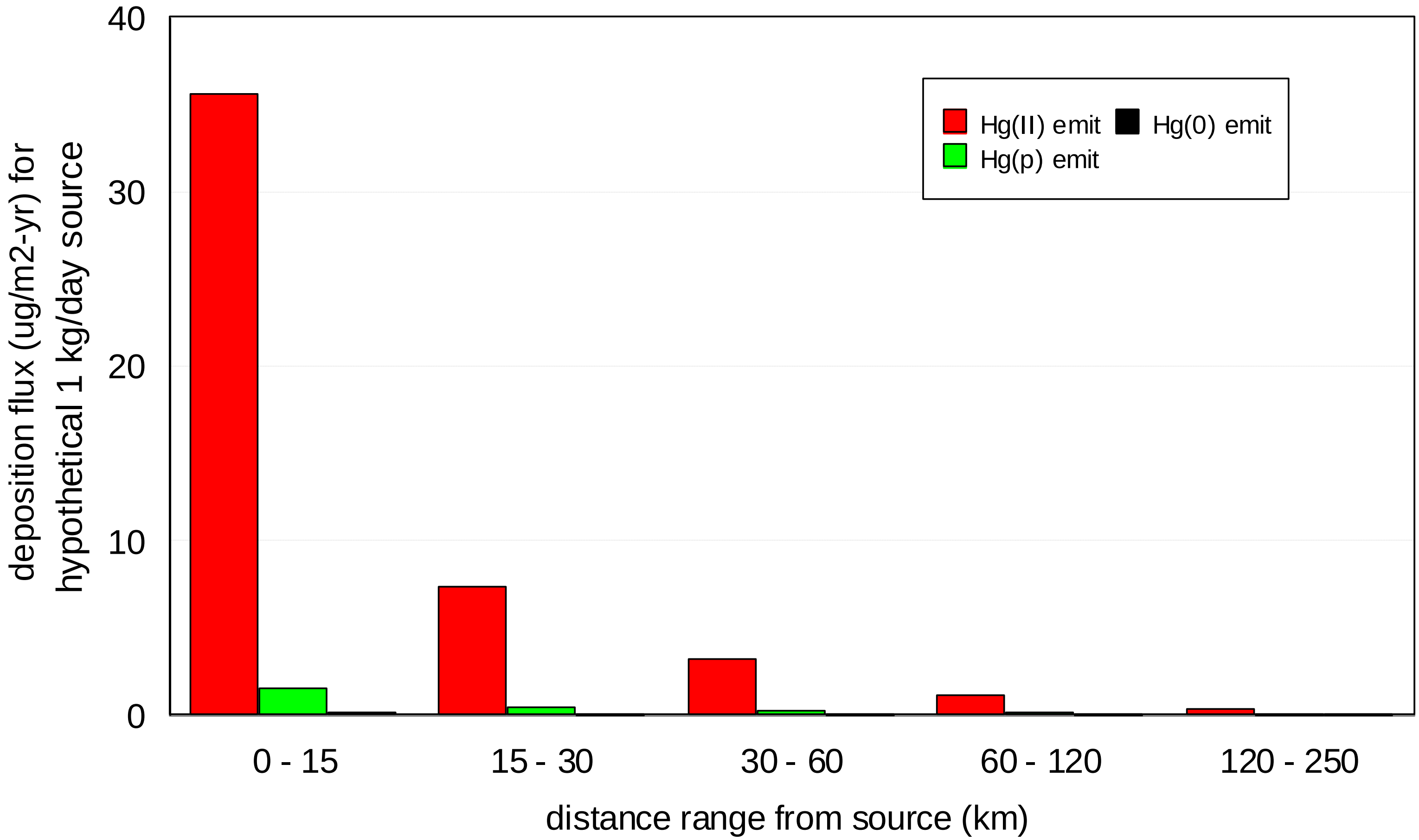
Why are emissions speciation data - and potential plume transformations -- critical?



Logarithmic

NOTE: distance results averaged over all directions –
Some directions will have higher fluxes, some will have lower

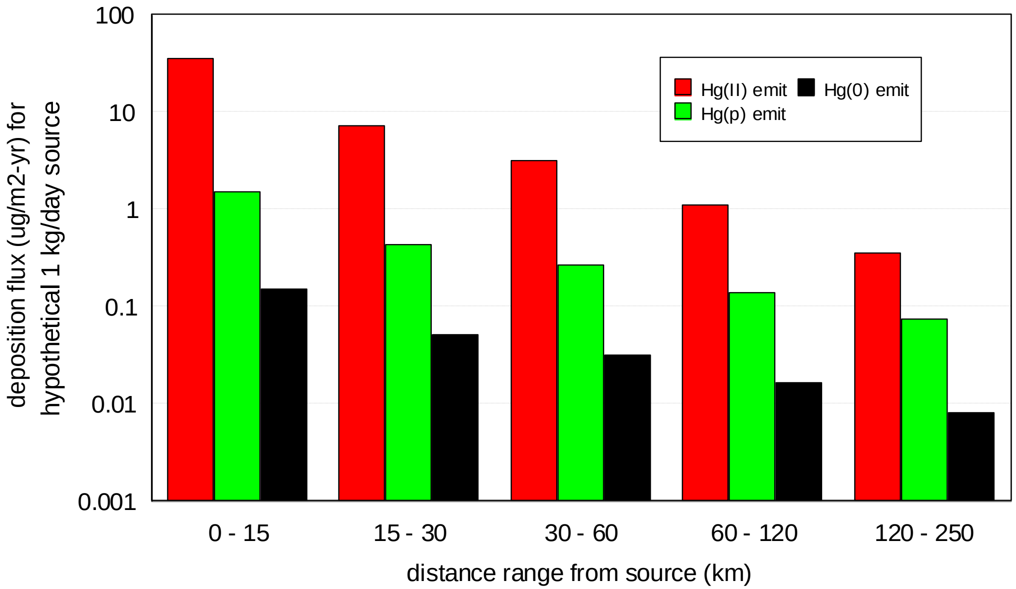
Why is emissions speciation information critical?



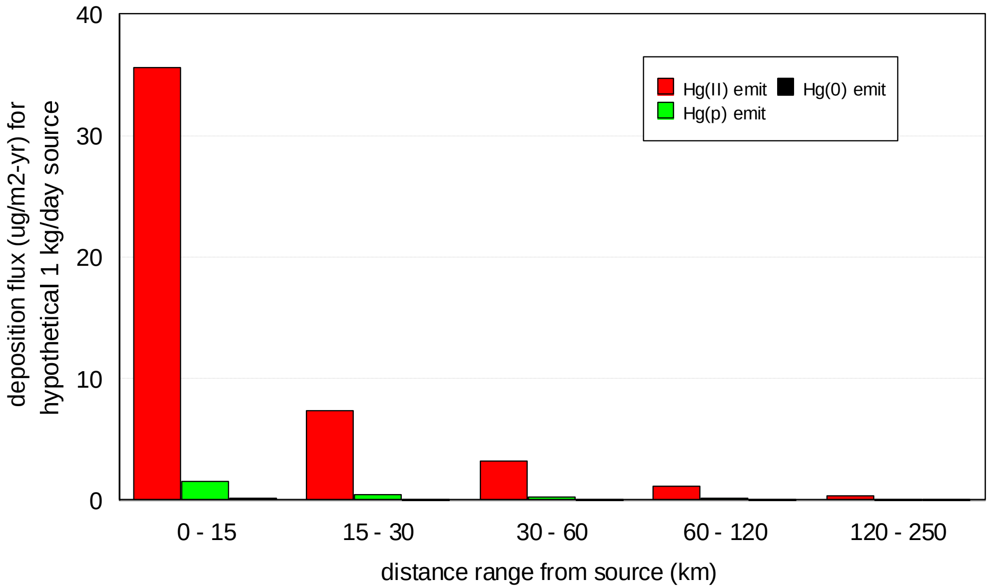
Linear

Why is emissions speciation information critical?

Logarithmic

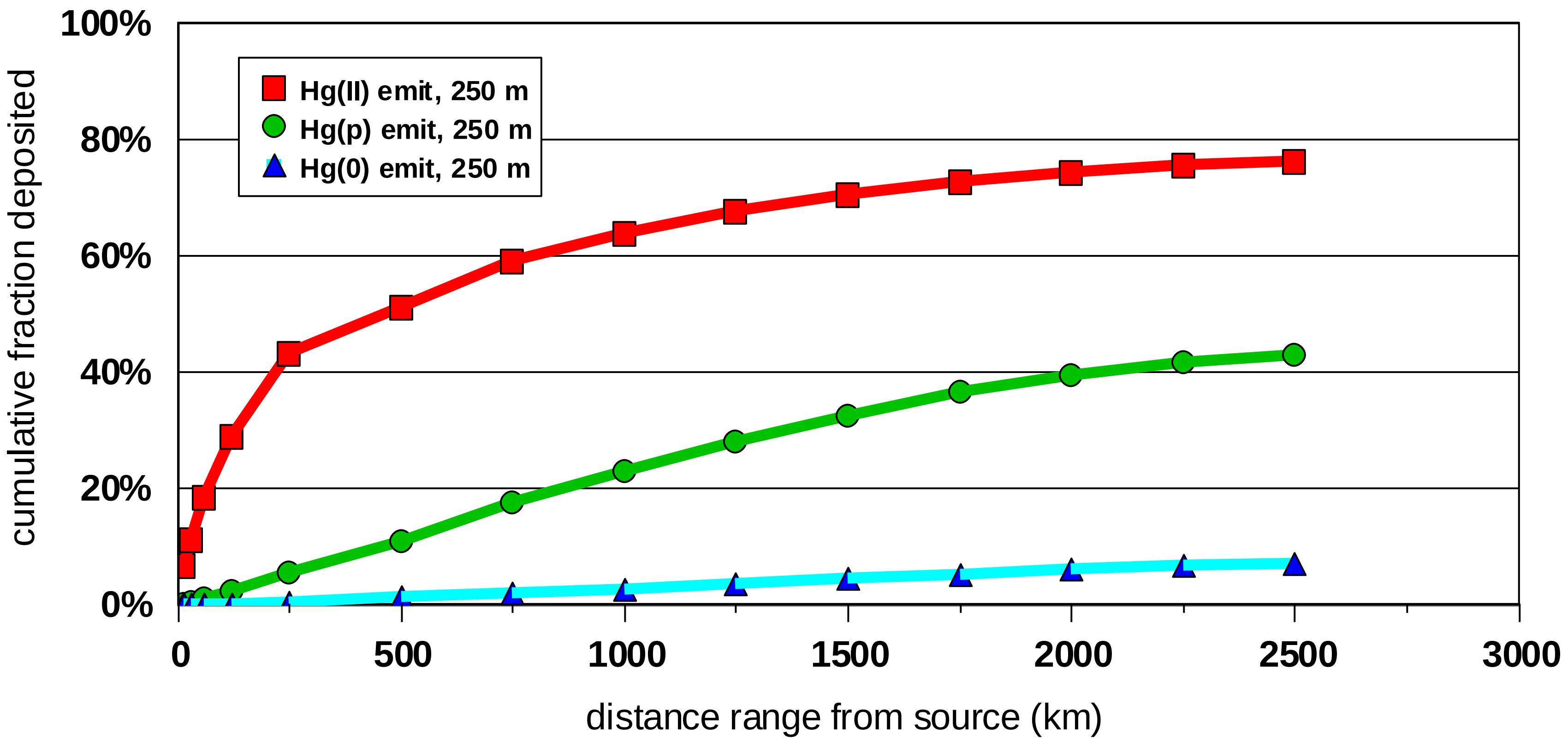


Linear

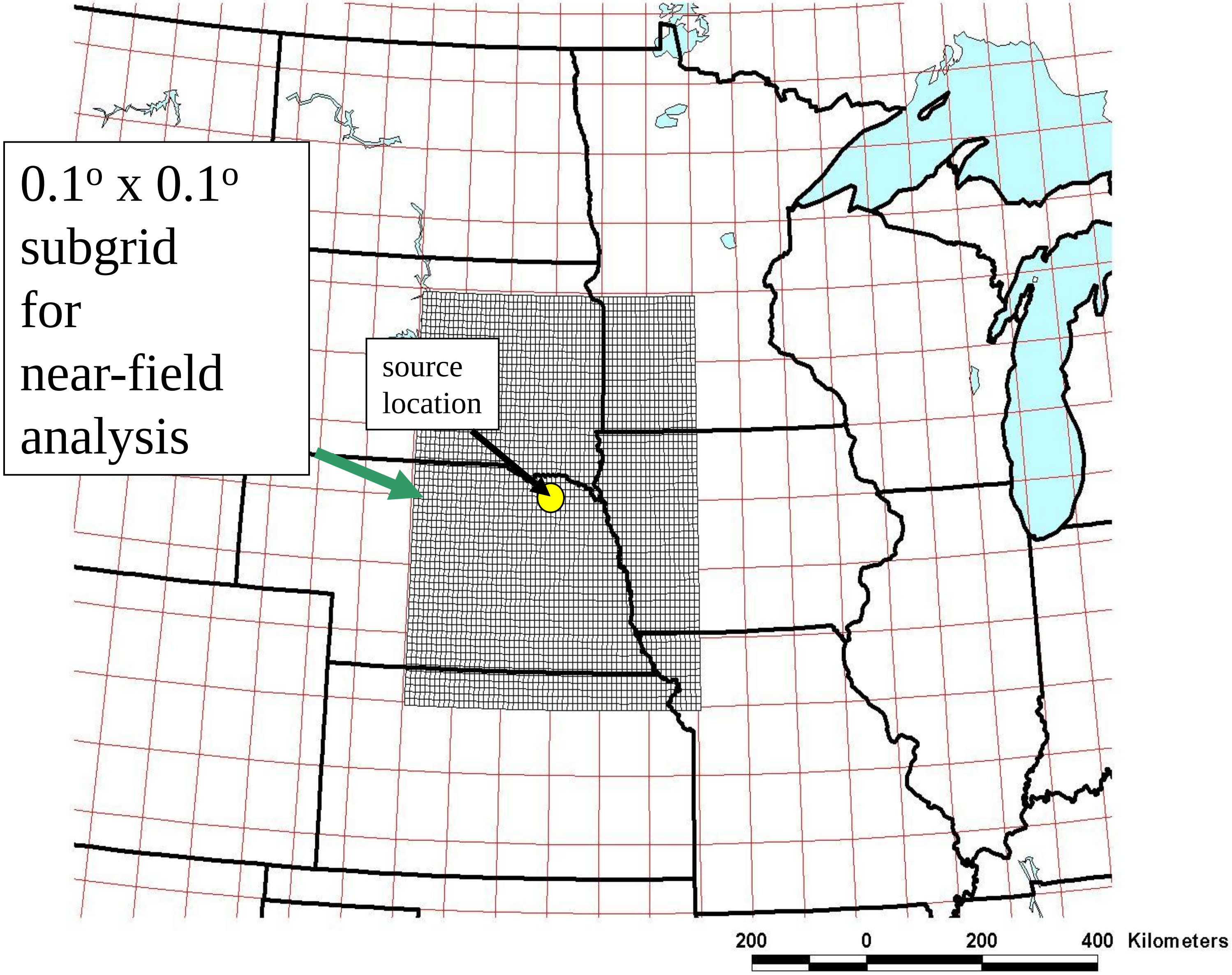


The <u>fraction deposited</u> and the <u>deposition flux</u> are both important, but they have very different meanings…
The fraction deposited nearby can be relatively "small", But the area is also small, and the relative deposition flux can be very large…

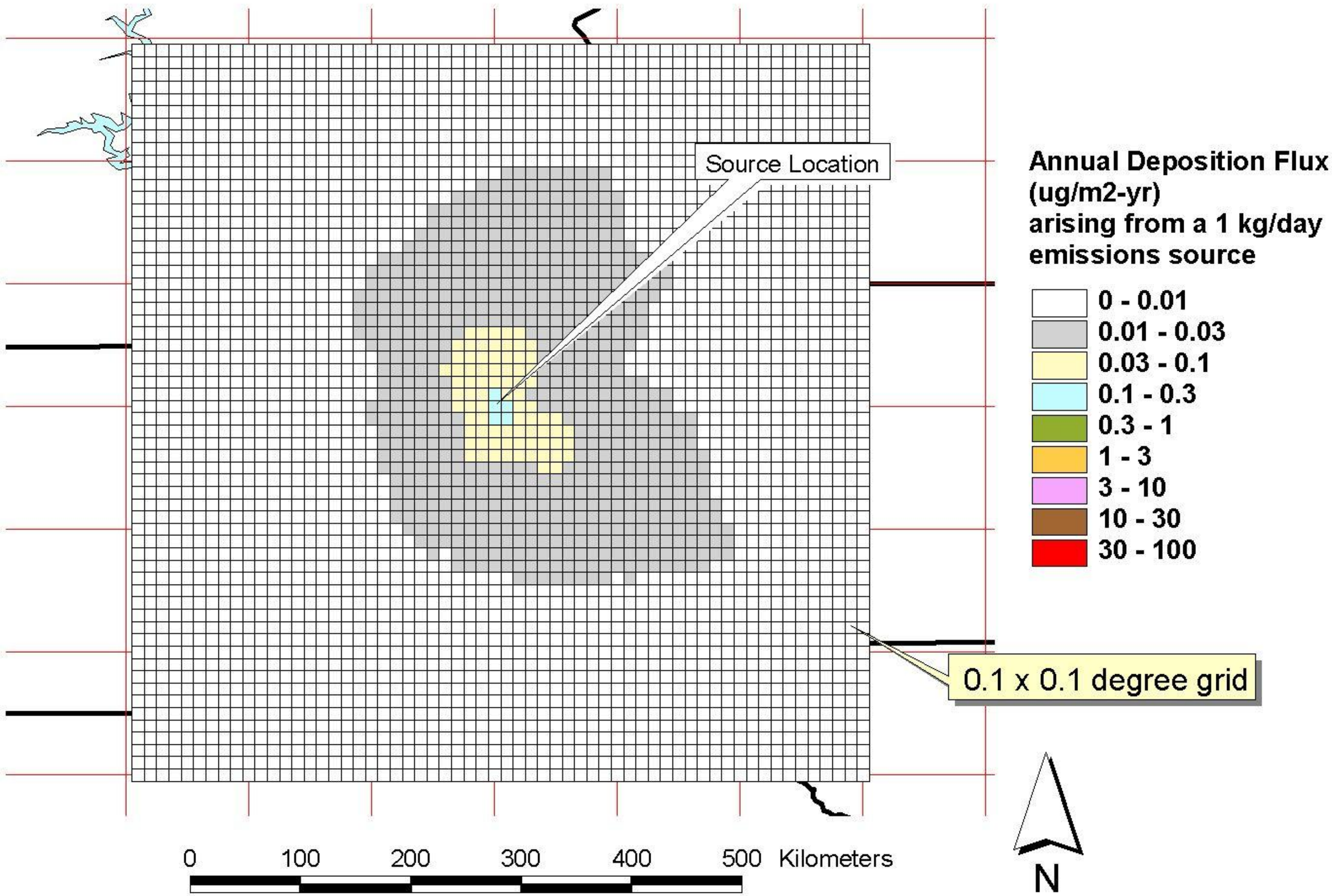
Cumulative Fraction Deposited Out to Different Distance Ranges from a Hypothetical Source



Source at Lat = 42.5, Long = -97.5; simulation for entire year 1996 using archived NGM meteorological data

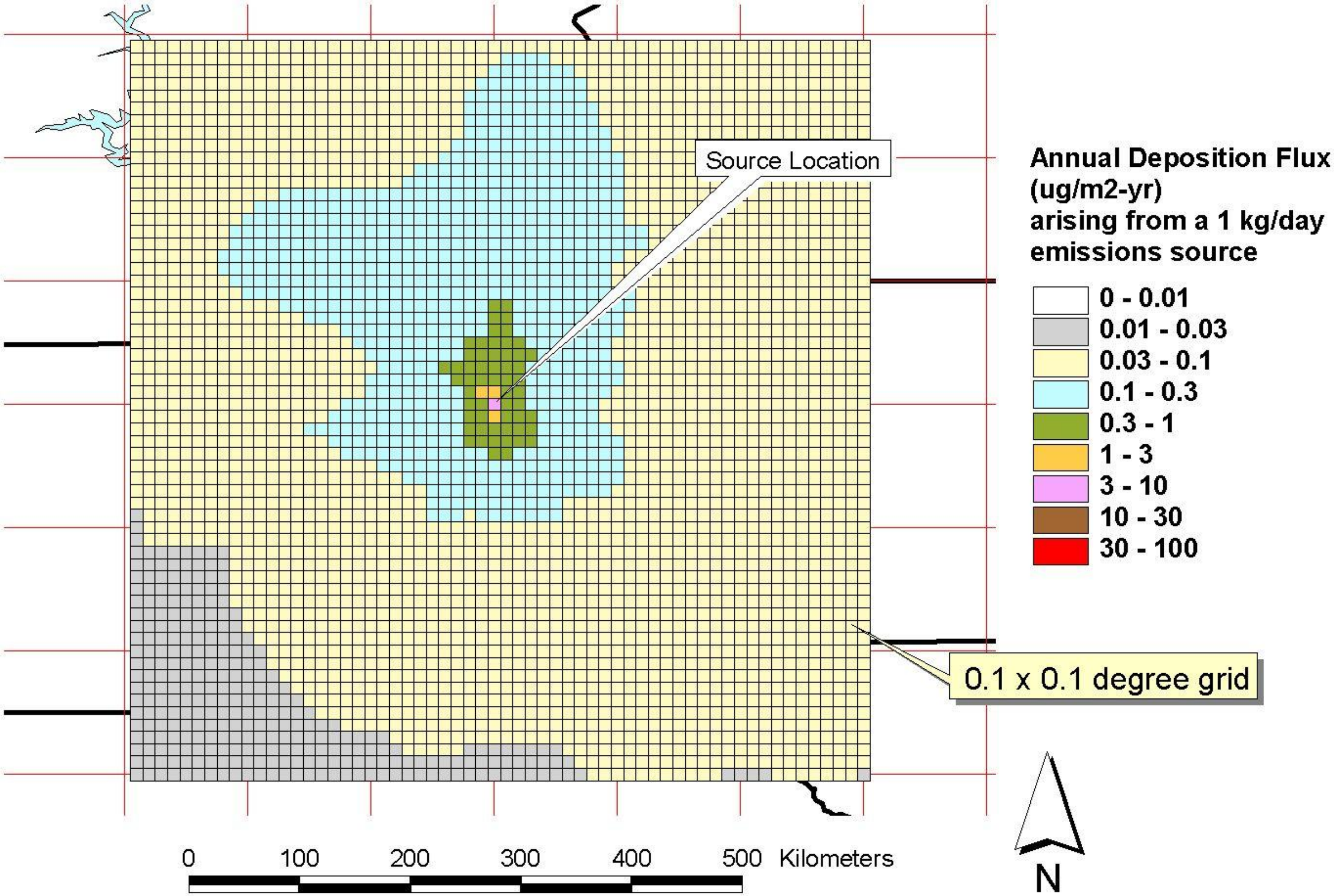

0.1° x 0.1°
subgrid
for
near-field
analysis
source
location
200
0
200
400 Kilometers

Annual deposition summary for emissions of elemental Hg from a 250 meter high source



Hypothetical emissions source at lat = 42.5, long = -97.5;
simulation for entire year 1996 using archived NGM meteorology (180 km resolution)

Annual deposition summary for emissions of particulate Hg from a 250 meter high source



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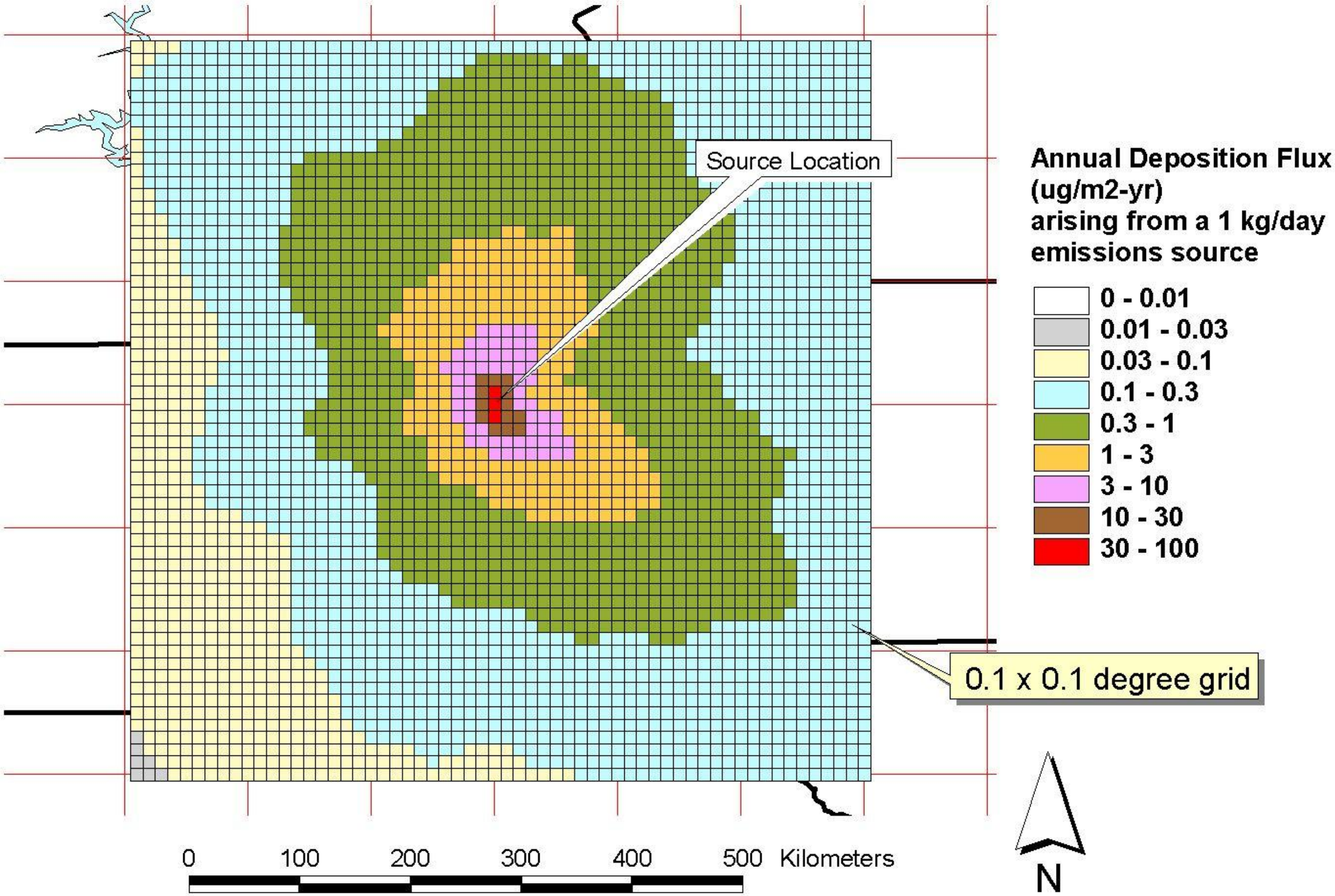

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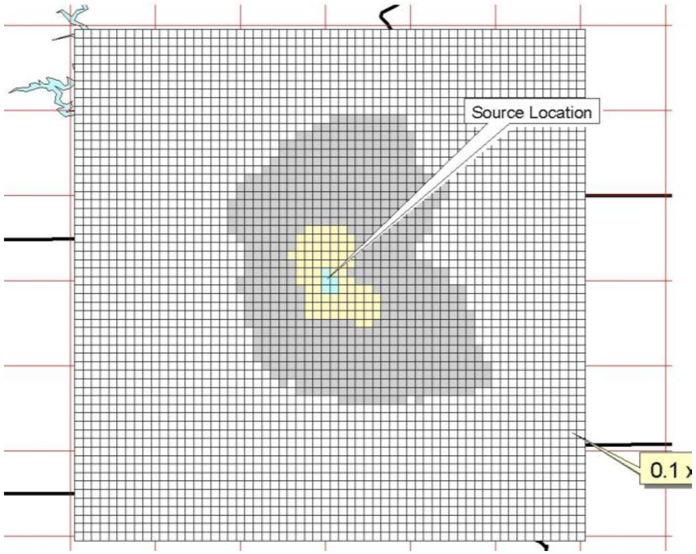
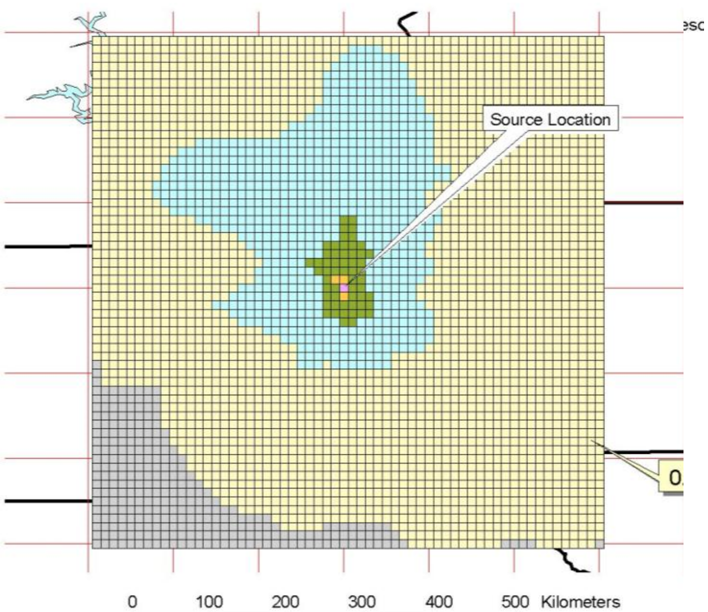


Annual Deposition Flux (ug/m2-yr) arising from a 1 kg/day emissions source

- 0 - 0.01
- 0.01 - 0.03
- 0.03 - 0.1
- 0.1 - 0.3
- 0.3 - 1
- 1 - 3
- 3 - 10
- 10 - 30
- 30 - 100

Annual deposition summary for emissions of particulate Hg from a 250 meter high source



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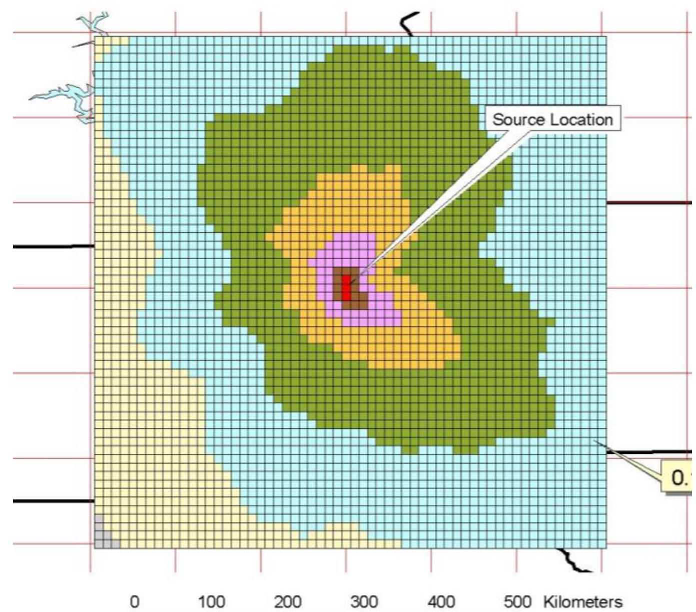

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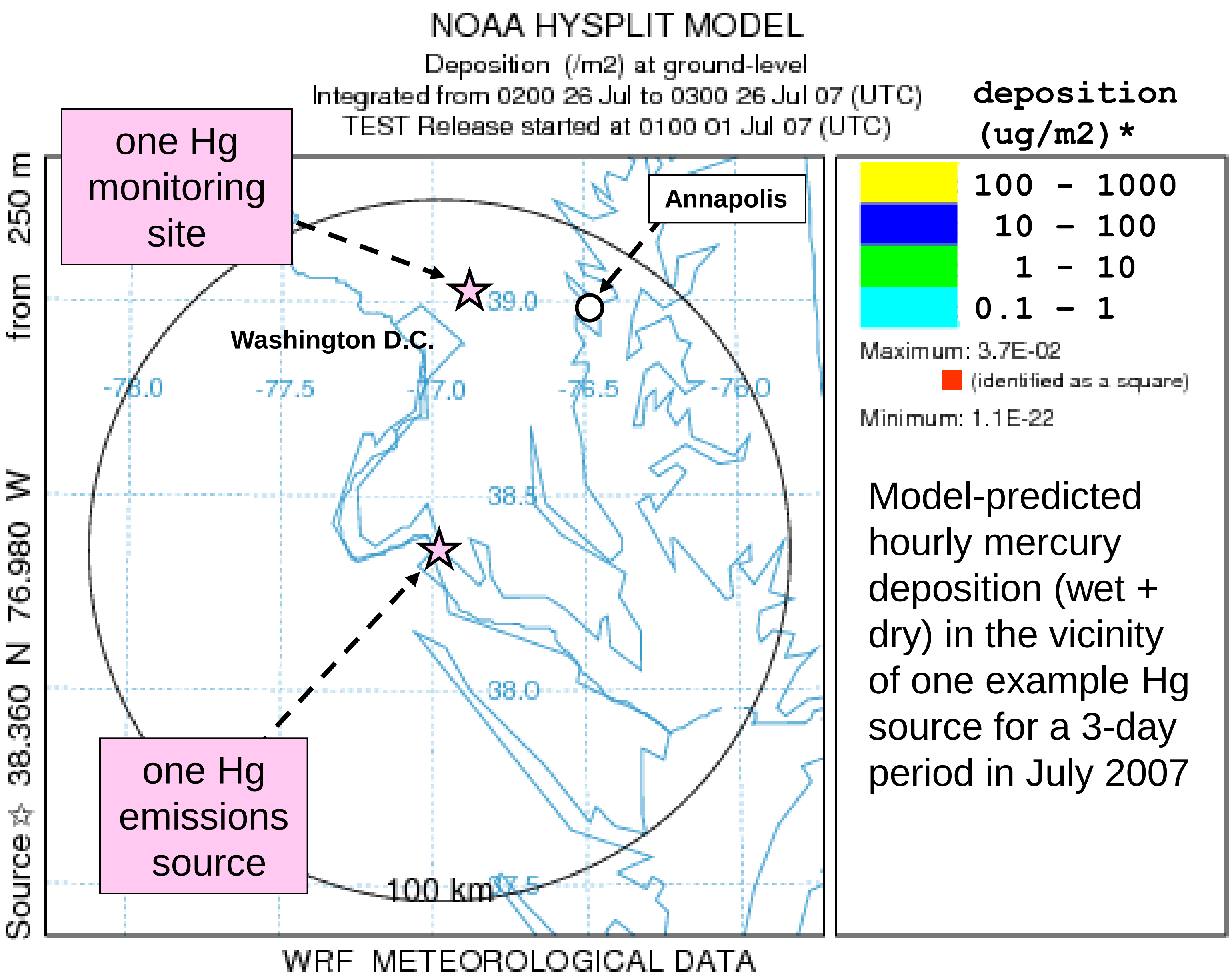
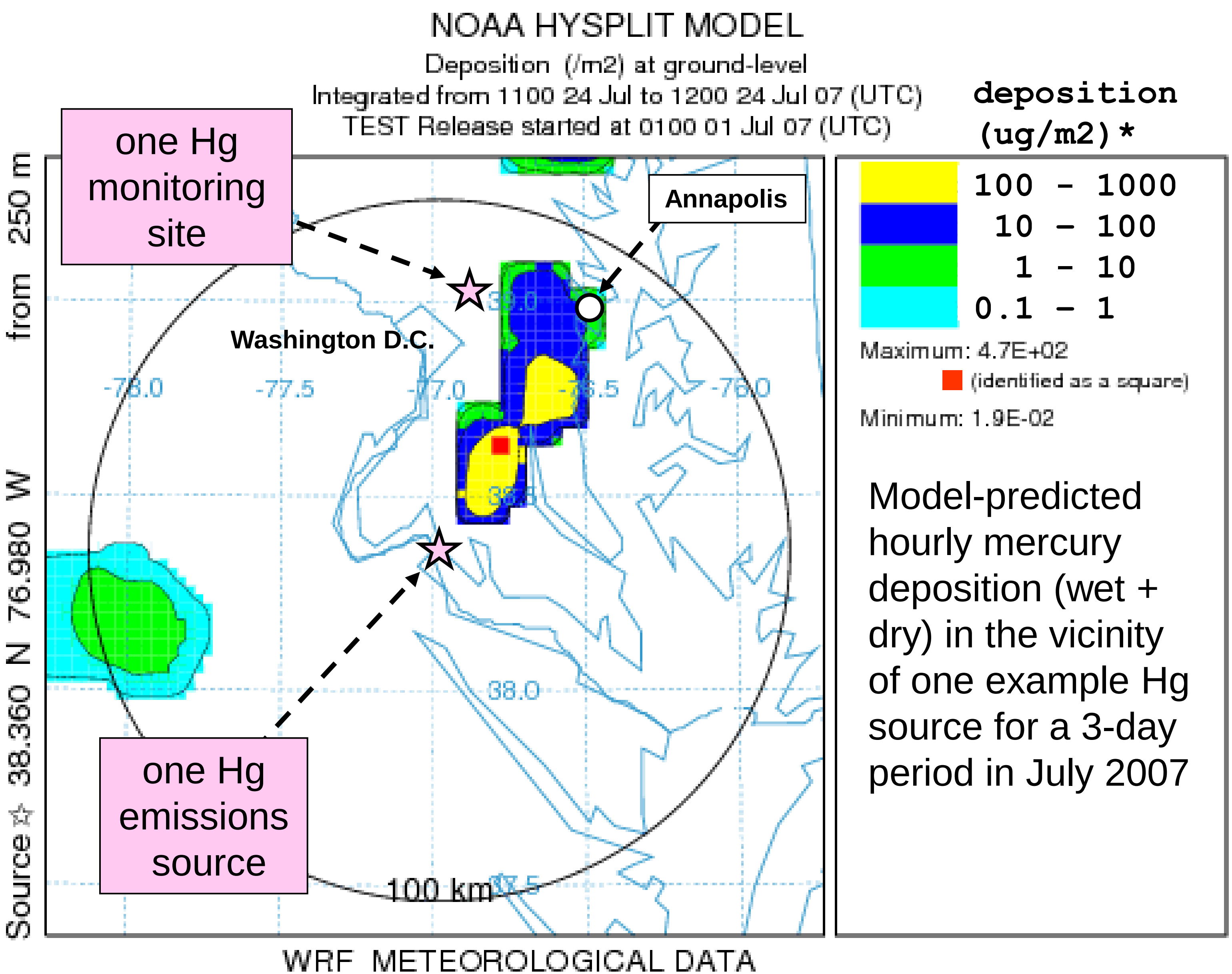


Model-predicted hourly mercury deposition (wet + dry) in the vicinity of one example Hg source for a 3-day period in July 2007

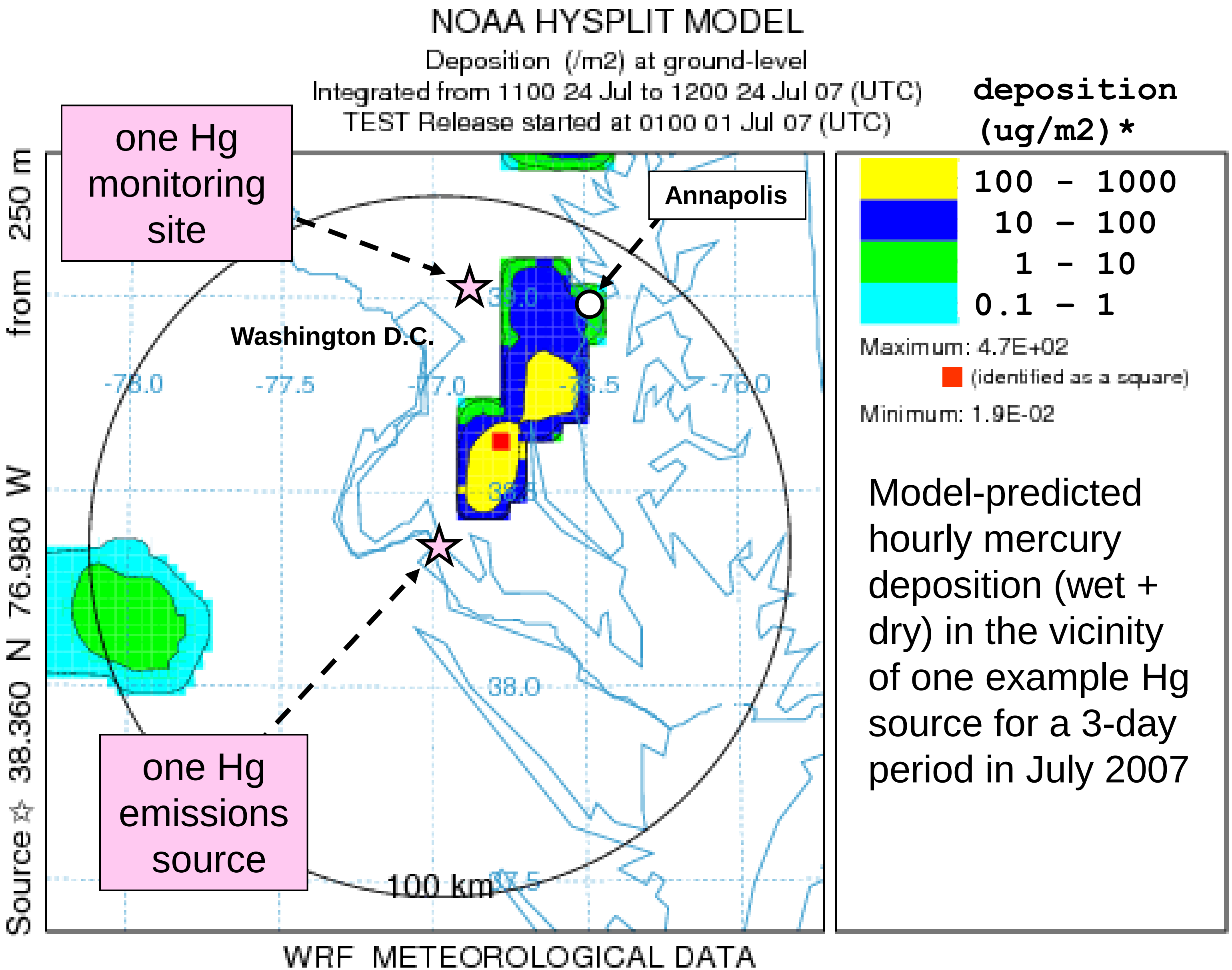
** hourly deposition converted to annual equivalent*



Model-predicted hourly mercury deposition (wet + dry) in the vicinity of one example Hg source for a 3-day period in July 2007

** hourly deposition converted to annual equivalent*

Large, time-varying spatial gradients in deposition & source-receptor relationships



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* hourly deposition converted to annual equivalent

Exercise 8:

- open up command prompt
- navigate to c:\hysplit4\working_08

```
cd c:\hysplit4\working_08 [enter]
```

- run conc_run_08.bat

```
conc_run_08 [enter]
```

Note – conc_run_08.bat CALLS conc_set_08.bat

conc_set_08.bat is very complex

If there is time, we can examine this batch file

Imported into Excel

Exercise_08_DEPOSITION.txt

Deposition To Each Receptor During Simulation
time course for sum of all mercury forms (mass units)

						Lake Chapala			Whole Domain		
nt	year	month	day	hour	minute	total deposition	dry deposition	wet deposition	total deposition	dry deposition	wet deposition
1	8	8	2	0	0	0.0E+00	0.0E+00	0.0E+00	1.6E+00	1.2E+00	4.6E-01
2	8	8	3	0	0	0.0E+00	0.0E+00	0.0E+00	1.9E+00	1.3E+00	6.4E-01
3	8	8	4	0	0	7.0E-02	3.7E-02	3.3E-02	2.2E+00	1.2E+00	9.6E-01
4	8	8	5	0	0	2.5E-02	4.9E-03	2.0E-02	2.6E+00	1.3E+00	1.3E+00
5	8	8	6	0	0	3.9E-03	1.1E-03	2.7E-03	2.0E+00	1.4E+00	6.7E-01
6	8	8	7	0	0	0.0E+00	0.0E+00	0.0E+00	2.0E+00	8.4E-01	1.2E+00
7	8	8	8	0	0	4.6E-07	1.5E-07	3.2E-07	2.6E+00	8.6E-01	1.8E+00
8	8	8	9	0	0	9.7E-05	4.5E-05	5.3E-05	2.5E+00	1.9E+00	5.8E-01
9	8	8	10	0	0	3.2E-02	1.7E-02	1.5E-02	1.9E+00	1.4E+00	5.8E-01
10	8	8	11	0	0	5.5E-03	4.1E-03	1.4E-03	2.2E+00	1.8E+00	3.7E-01
11	8	8	12	0	0	2.1E-06	1.8E-06	2.9E-07	2.0E+00	1.7E+00	2.8E-01
12	8	8	13	0	0	1.9E-03	0.0E+00	1.9E-03	1.9E+00	1.3E+00	6.3E-01
13	8	8	14	0	0	0.0E+00	0.0E+00	0.0E+00	2.4E+00	2.1E+00	3.1E-01
14	8	8	15	0	0	0.0E+00	0.0E+00	0.0E+00	2.1E+00	1.4E+00	6.9E-01
15	8	8	16	0	0	0.0E+00	0.0E+00	0.0E+00	4.8E-01	1.5E-01	3.2E-01
16	8	8	17	0	0	0.0E+00	0.0E+00	0.0E+00	1.3E+00	1.2E+00	1.4E-01
17	8	8	18	0	0	0.0E+00	0.0E+00	0.0E+00	2.4E+00	1.5E+00	8.8E-01
18	8	8	19	0	0	1.5E-04	0.0E+00	1.5E-04	2.7E+00	1.8E+00	9.2E-01
19	8	8	20	0	0	5.5E-03	3.6E-03	1.9E-03	2.2E+00	1.6E+00	5.9E-01
20	8	8	21	0	0	9.6E-04	1.1E-04	8.5E-04	2.6E+00	7.5E-01	1.9E+00
21	8	8	22	0	0	1.4E-02	6.7E-03	7.4E-03	2.4E+00	1.2E+00	1.2E+00
22	8	8	23	0	0	7.7E-03	5.7E-03	2.0E-03	2.2E+00	1.6E+00	6.1E-01
23	8	8	24	0	0	0.0E+00	0.0E+00	0.0E+00	2.0E+00	1.8E+00	1.9E-01
24	8	8	25	0	0	0.0E+00	0.0E+00	0.0E+00	2.4E+00	1.8E+00	6.2E-01
25	8	8	26	0	0	0.0E+00	0.0E+00	0.0E+00	2.3E+00	1.0E+00	1.2E+00
26	8	8	27	0	0	1.4E-05	0.0E+00	1.4E-05	2.3E+00	1.4E+00	9.2E-01
27	8	8	28	0	0	4.3E-05	7.0E-06	3.6E-05	2.9E+00	1.5E+00	1.4E+00
28	8	8	29	0	0	1.6E-06	0.0E+00	1.6E-06	2.1E+00	1.1E+00	1.1E+00
total for 4wk long simulation						**1.7E-01**	**8.1E-02**	**8.7E-02**	**6.0E+01**	**3.8E+01**	**2.2E+01**

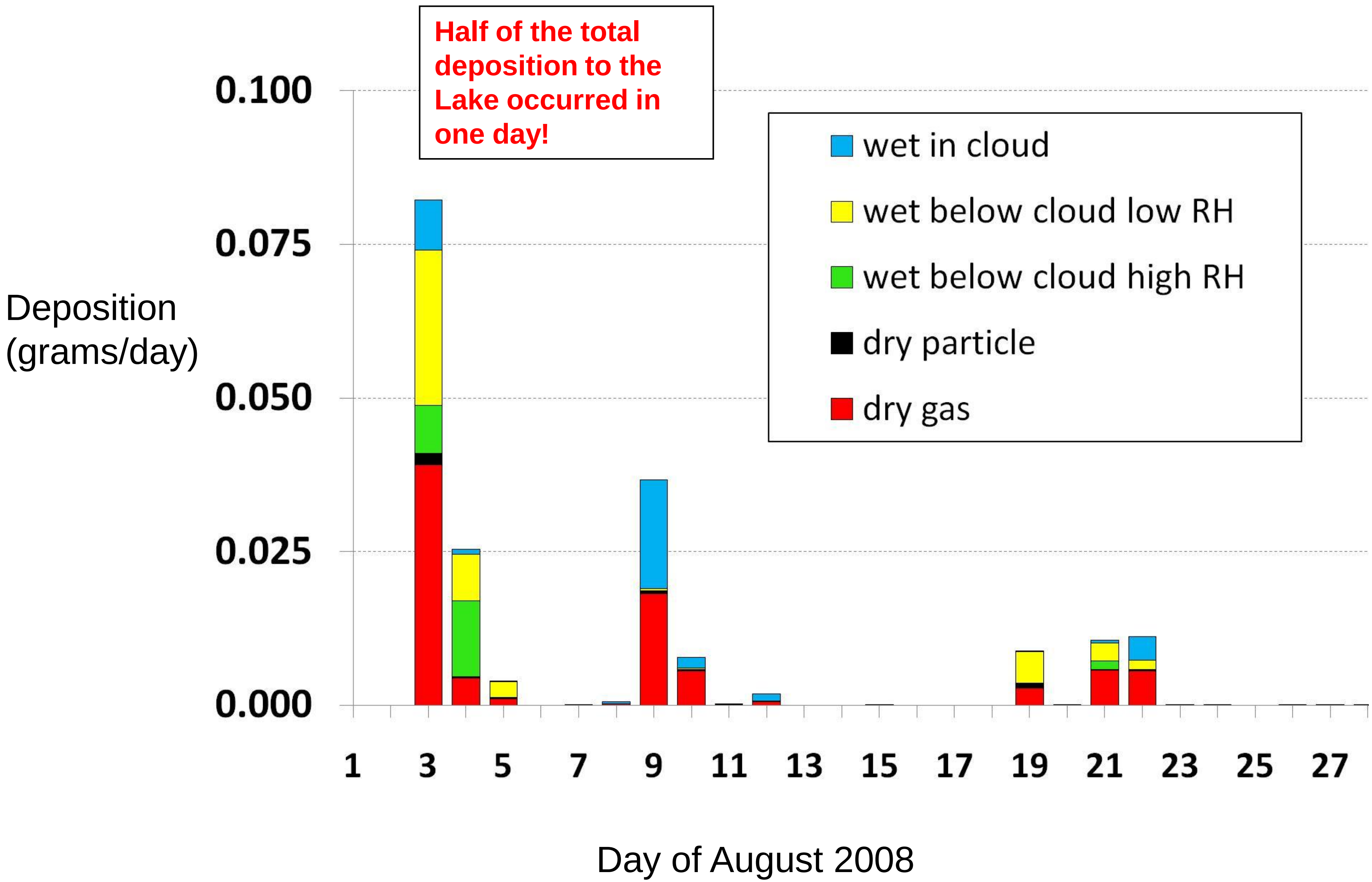
During the simulation,
1 gram/ hr was emitted,
over 672 hours…

A total of 672 grams of RGM were emitted

The fraction of these emissions deposited in Lake Chapala was
0.17 / 672
= 0.00025
= 0.025%

A total of 9% of the emissions were deposited during the simulation:
60 / 672 = 0.09 = 9%

Mercury Deposition (grams/day) to Lake Chapala arising from emissions of 1 gram/hr of Reactive Gaseous Mercury (RGM) from a source 40 km Northwest of the Lake



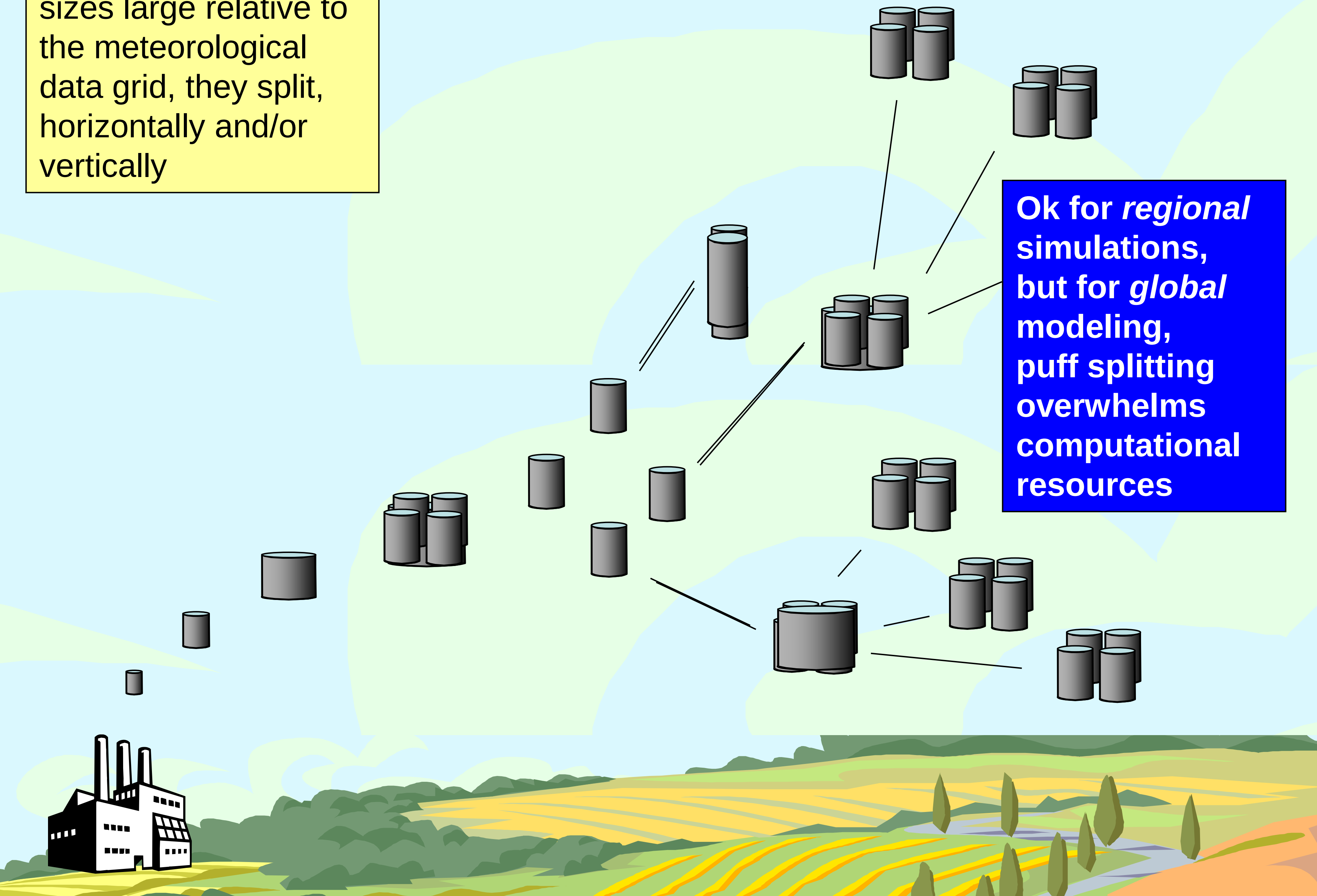
In order to estimate the actual impact of a source, we multiply this unit-emissions result by the actual emissions

For example, if the actual source emitted 1000 grams per day of RGM, then this simulation would imply that for Aug 2008, the source would contribute:

0.17 grams deposited per gram emitted
*** 1000 grams emitted**
= 170 grams to Lake Chapala

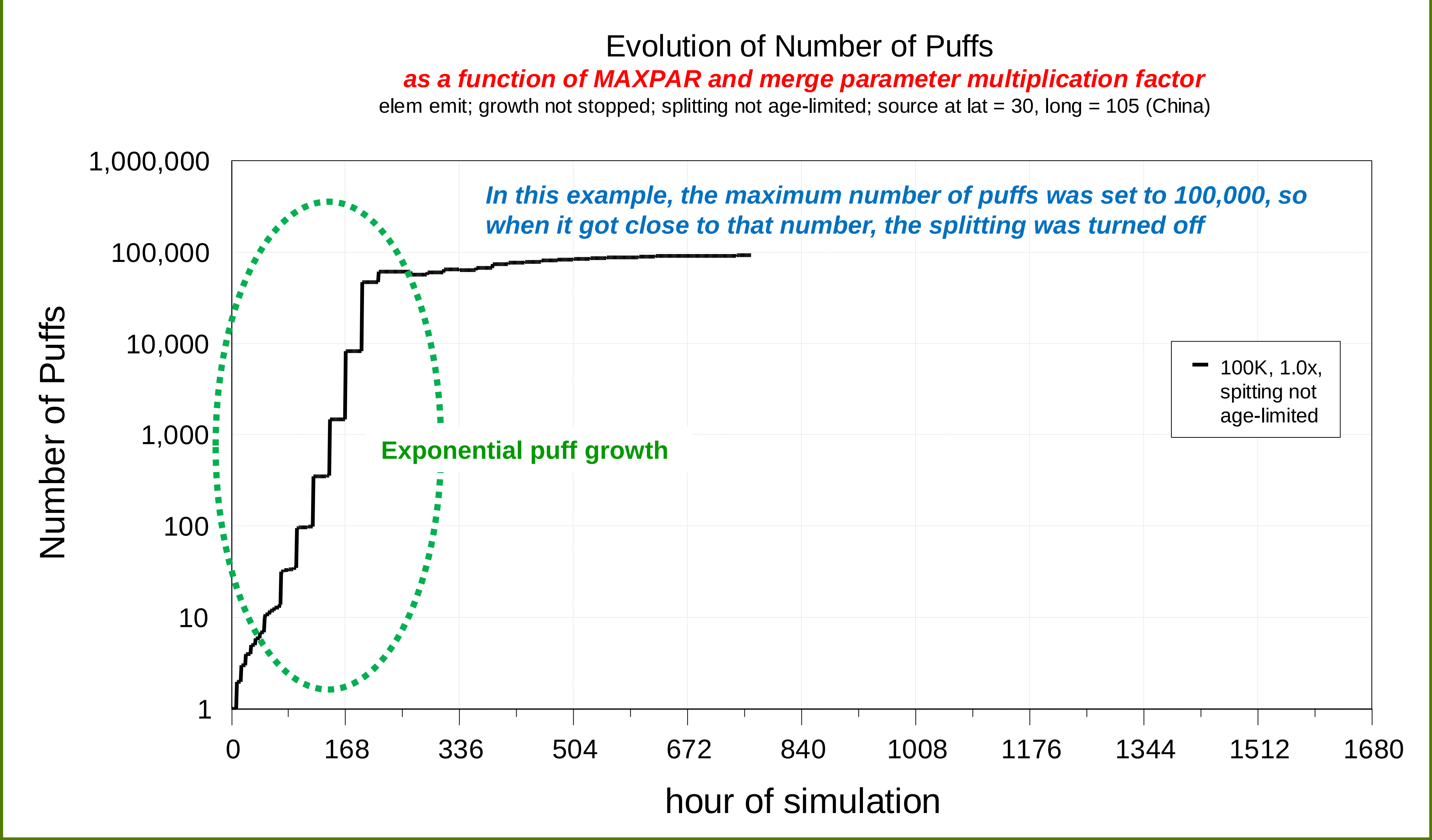
We have tried to extend the mercury modeling to a global basis, but have encountered problems

When puffs grow to sizes large relative to the meteorological data grid, they split, horizontally and/or vertically

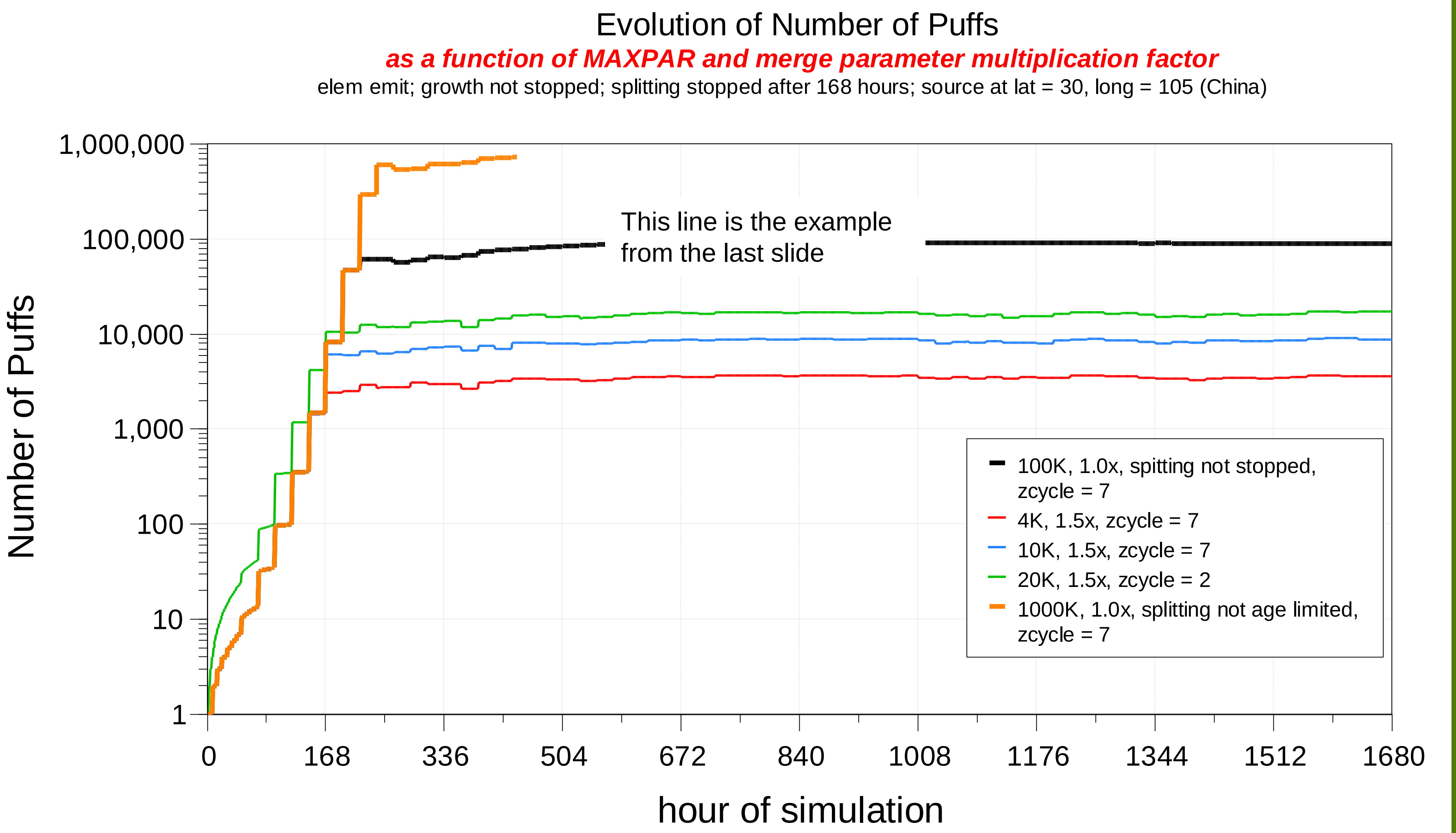


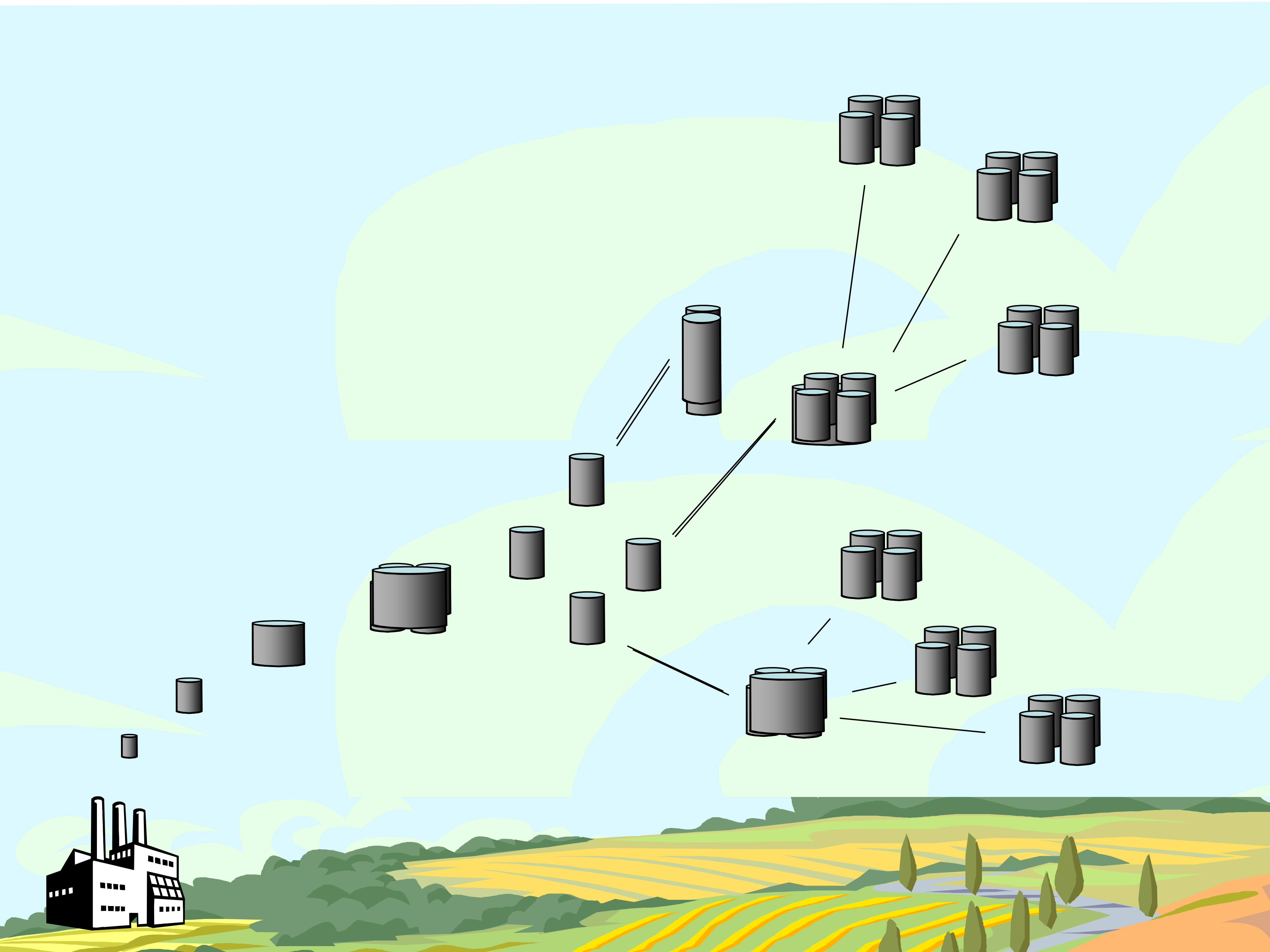
Ok for *regional* simulations, but for *global* modeling, puff splitting overwhelms computational resources

Due to puff splitting, the number of puffs quickly overwhelms numerical resources

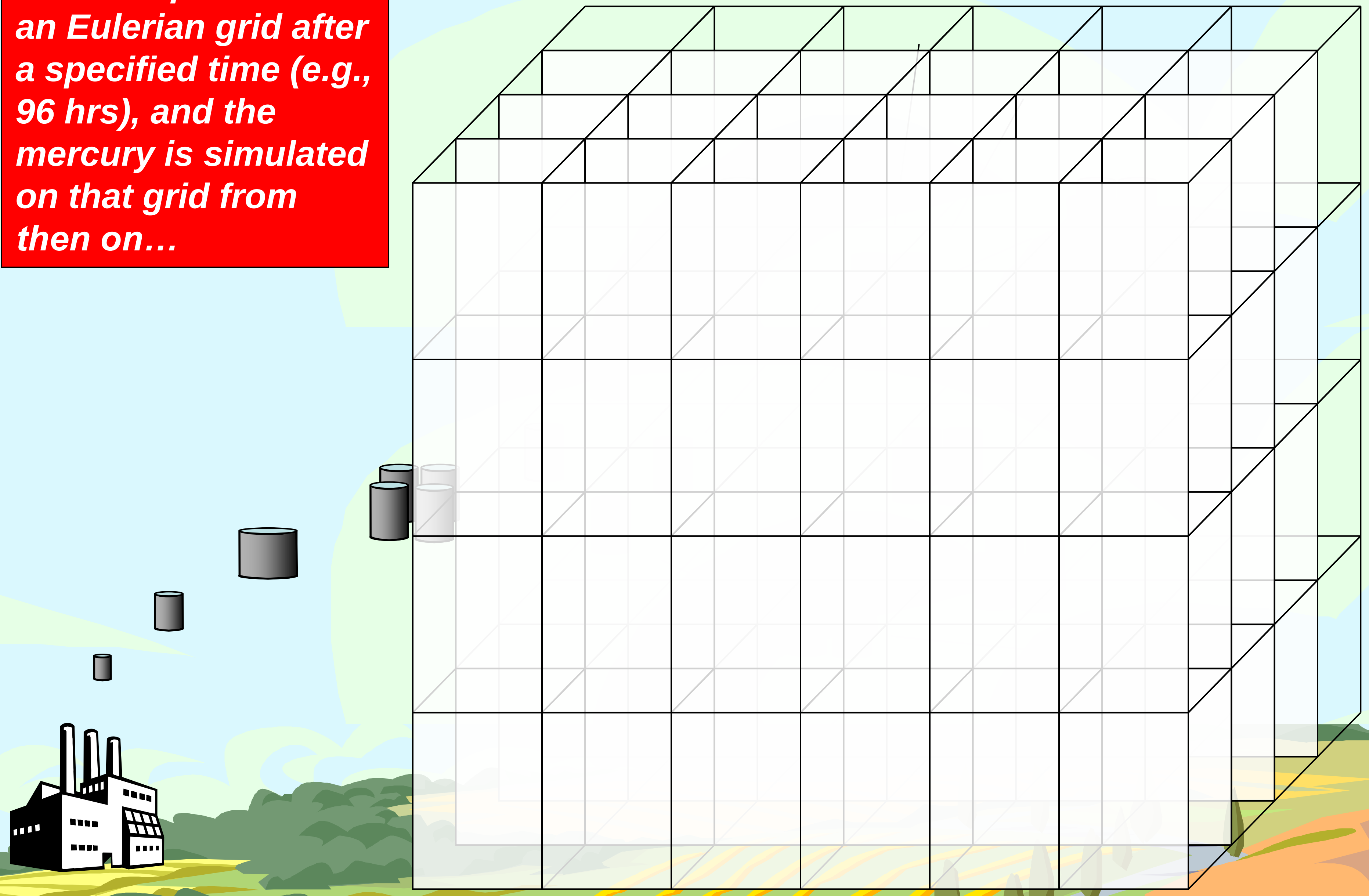


In each test, the number of puffs rises to the maximum allowable within ~ one week





In the new version of HYSPLIT (4.9), puffs are "dumped" into an Eulerian grid after a specified time (e.g., 96 hrs), and the mercury is simulated on that grid from then on…



The version of HYSPLIT that we are running in this workshop has the Global Eulerian Model (GEM) integrated with the puff/particle model

And a new version of the HYSPLIT-Hg model now includes this GEM integration

We could run HYSPLIT-Hg / GEM at this workshop, but, it takes a little too long…