Detection Limits for Source Emissions Sampling Methods: The Uncertainty of Uncertainty.

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Chester LabNet

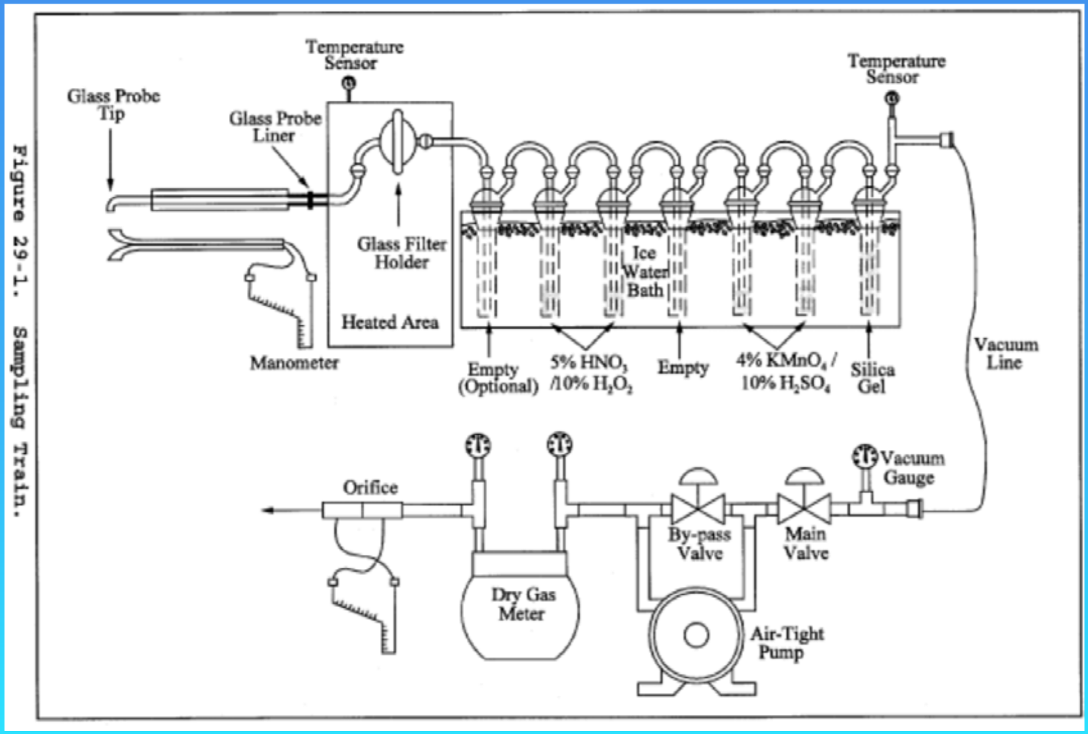
Presented at the 2019 National Environmental Monitoring Conference

Water Sample

Air Sample

Collecting Water Samples

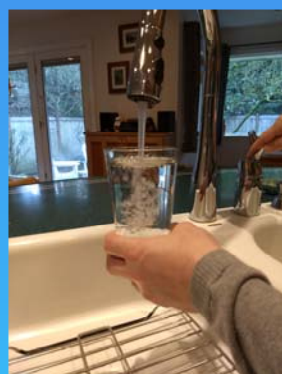
Collecting Source Emission Samples‡



‡ 40 CFR Part 60, Appendix A-8, Method 29

Collecting Source Emission Samples



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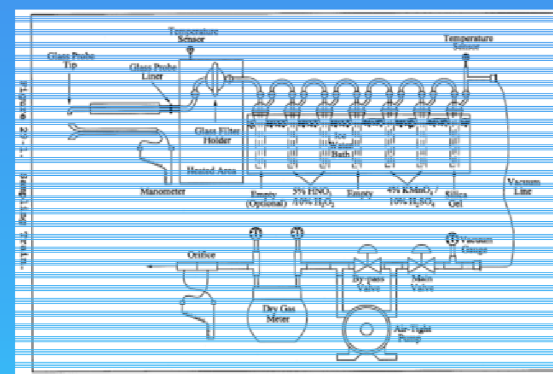
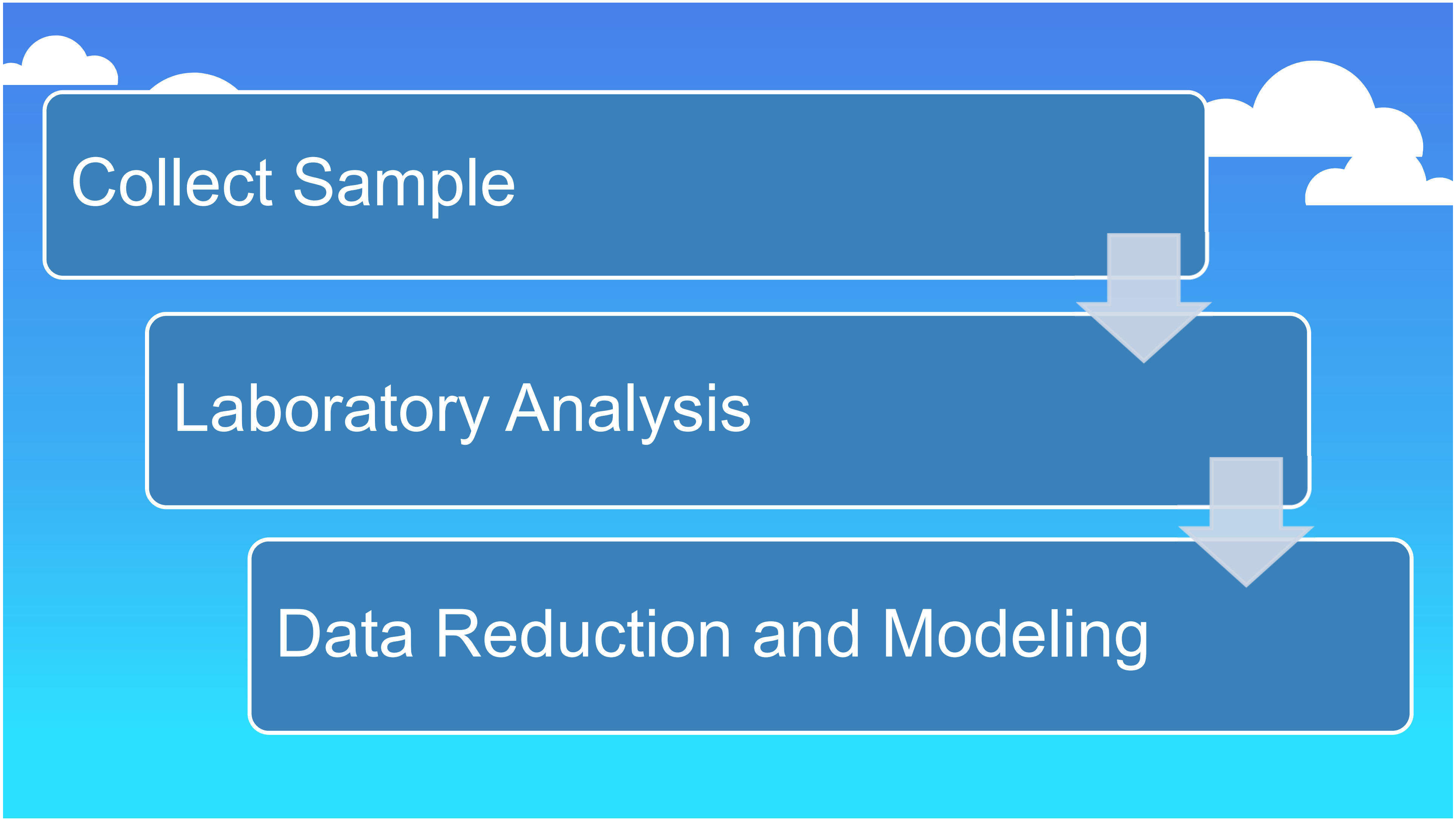
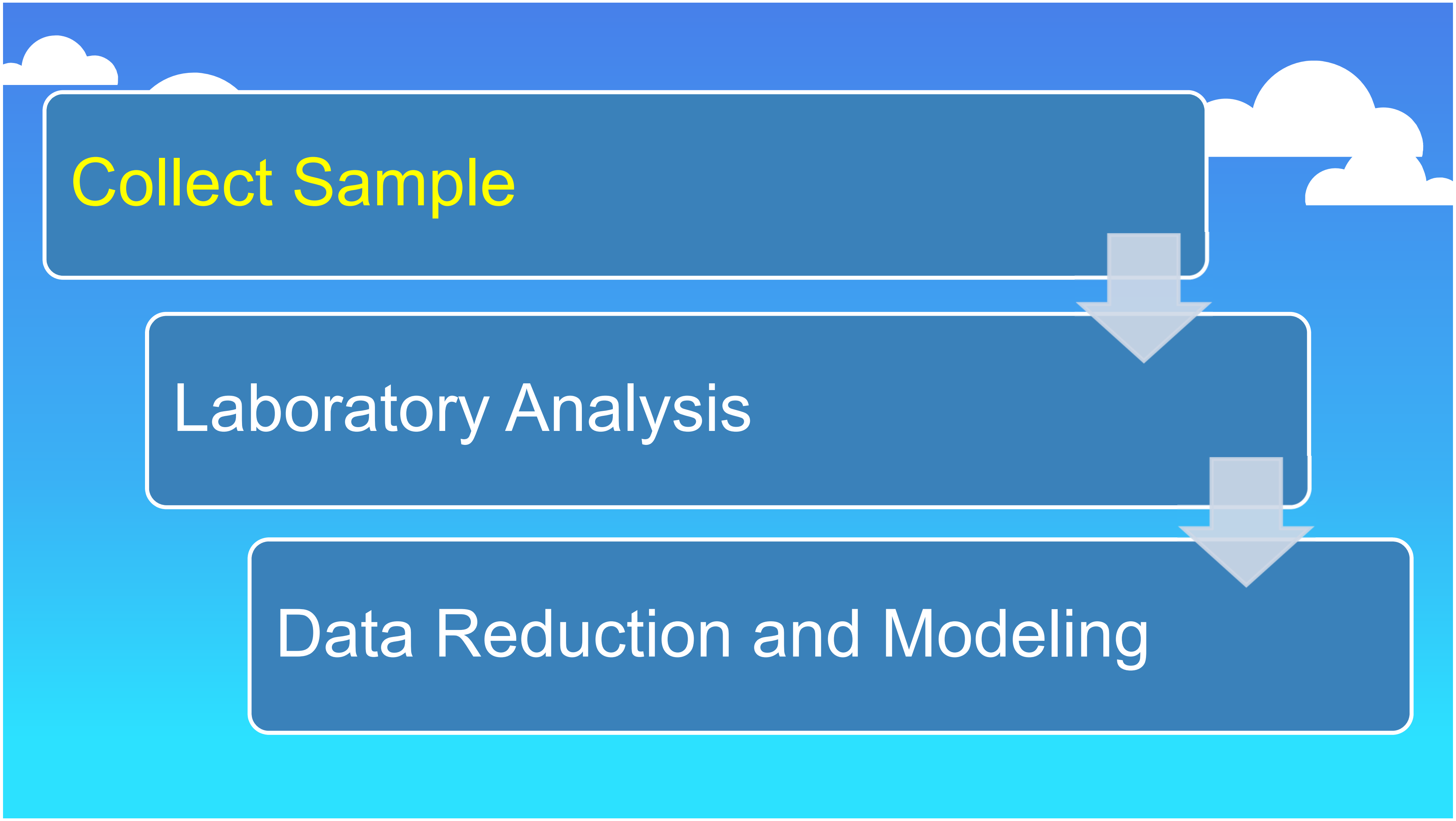


Figure 29-1. Sampling Train.
Temperature Sensor
Glass Probe Tip
Glass Probe Liner
Glass Filter Holder
Heated Area
Manometer
Ice Water Bath
Temperature Sensor
Empty (Optional)
5% HNO_3 /10% H_2O_2
Empty
4% $KMnO_4$ / 10% H_2SO_4
Silica Gel
Vacuum Line
Orifice
Vacuum Gauge
By-pass Valve
Main Valve
Dry Gas Meter
Air-Tight Pump


Collect Sample
Laboratory Analysis
Data Reduction and Modeling

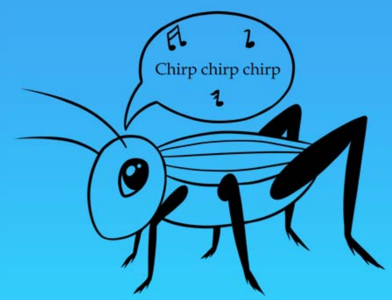

Collect Sample
Laboratory Analysis
Data Reduction and Modeling

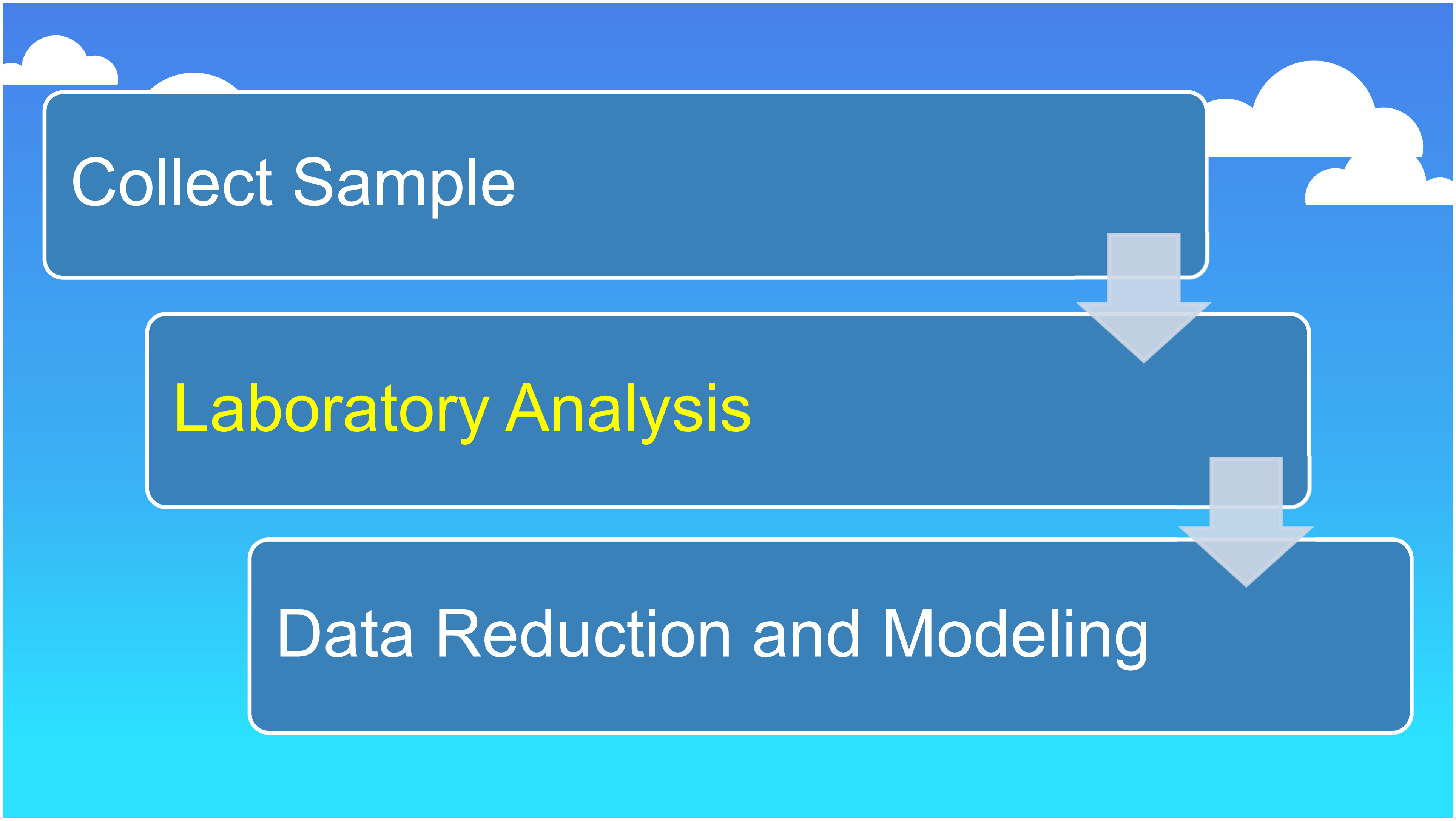
Source Sampling Collection Uncertainties

- Glassware preparation
- Analyzer drift
- Accuracy of O2/CO2 measurements (in turn affects your calculation of molecular weight, sample volume, flow, etc.)
- Experience/skill of testers/Human error
- Quality of reagents
- Environmental conditions
- Source stream homogeneity
- Sample loss due to leaks
- Measurements of pressure and temperature
- Thermocouples
- Number of points/port used
- Size/alignment of the nozzle during sampling (straight into the flow?)
- Flow meter uncertainty
- Leak during run (2+ hours continuous)
- Sample bottle type and cleanliness
- Interfering gases
- Field balances and other standards (field balance, field caliper, field barometer, etc.)
- Flow measurements (many factors go into this alone)
- Quality of gas standards
- Measurements of pressure and temperature
- Length of sample run(s) (what snapshot of the process are you capturing?)
- Number of runs (gives you some sense of repeatability)
- Pitot specifications
- Sampling location
- Moisture content of gasses (impinger pH)
- Meter volume
- Recovery of sample in the field (cleanliness?)
- Post-analysis calculations to lbs/year or…

Source Sample Collection Uncertainties

Where are these accounted for in the Detection Limit?



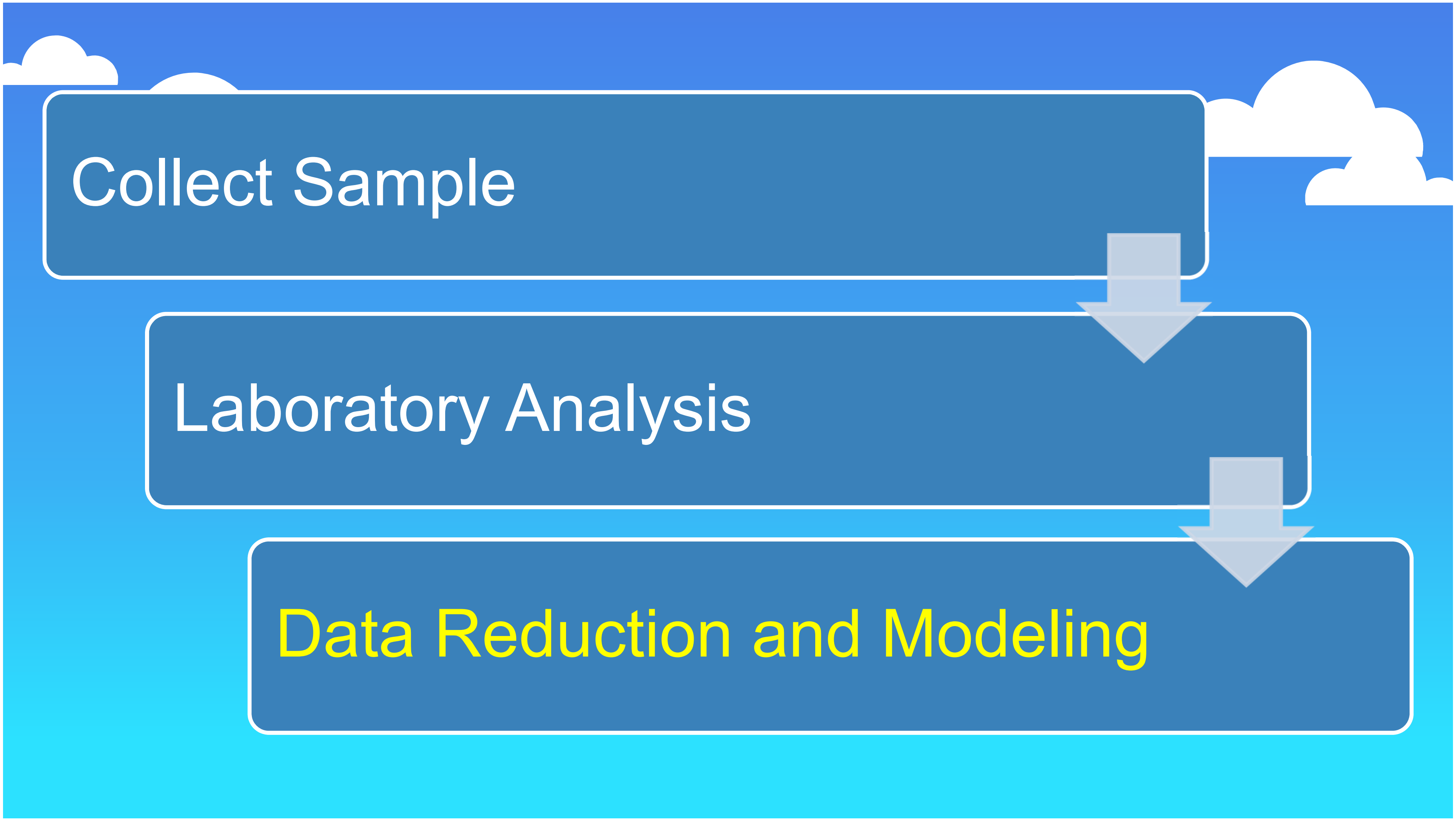

Collect Sample
Laboratory Analysis
Data Reduction and Modeling

Laboratory Detection Limits

NELAC accredited labs follow “Definition and Procedure for the Determination of the Method Detection Limit, Revision 2” (aka “MUR method”)

- Standard deviation of low concentration standards.
- Standard deviation of, and concentration of, blank samples.
- Taken through entire process, including all preparatory steps.

Does not take into account sampling activities.


Collect Sample
Laboratory Analysis
Data Reduction and Modeling

Modeling Math!!

Uncertainty from:

Sampling? No.

Lab? Yes.

Uncertainty from other measurements?

No.

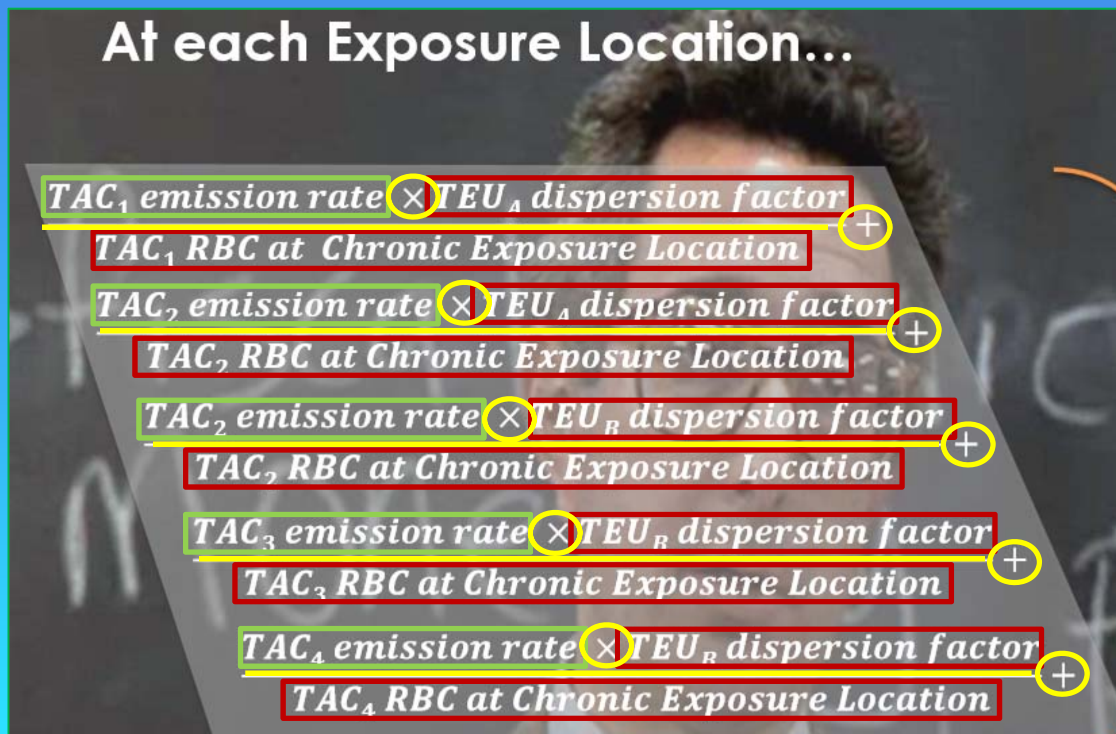
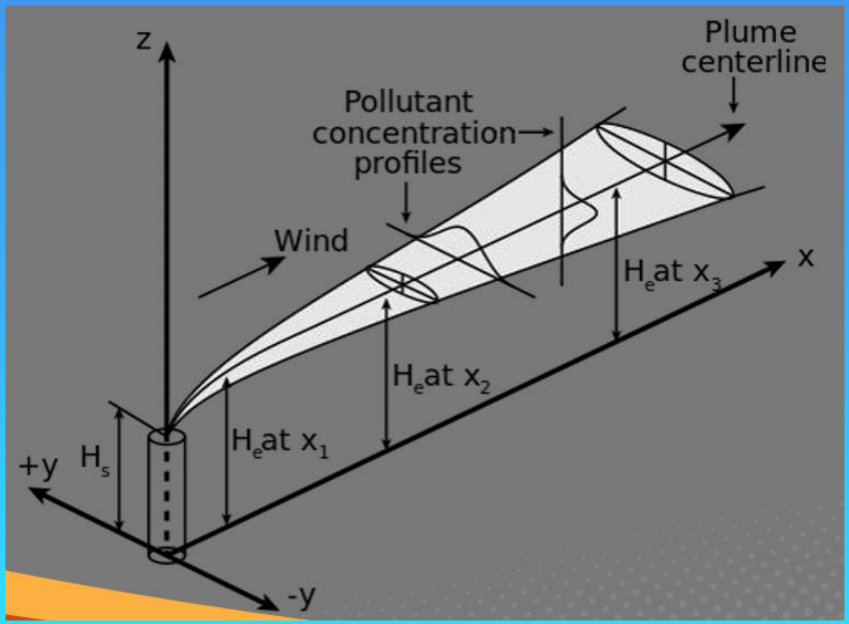
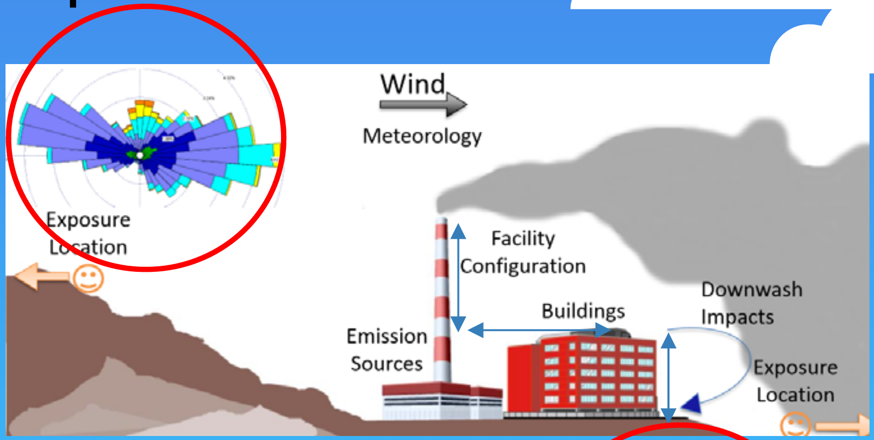


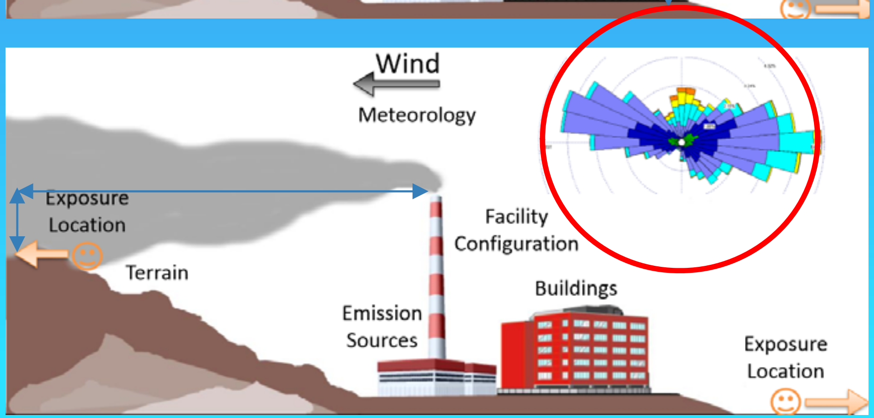
Diagram Used with permission of Maul Foster & Alongi, Inc.

Modeling Step 1: Math!!

Don't worry, this won't be on the test.







Diagrams used with permission of Maul Foster & Alongi, Inc.

Remember This Math?

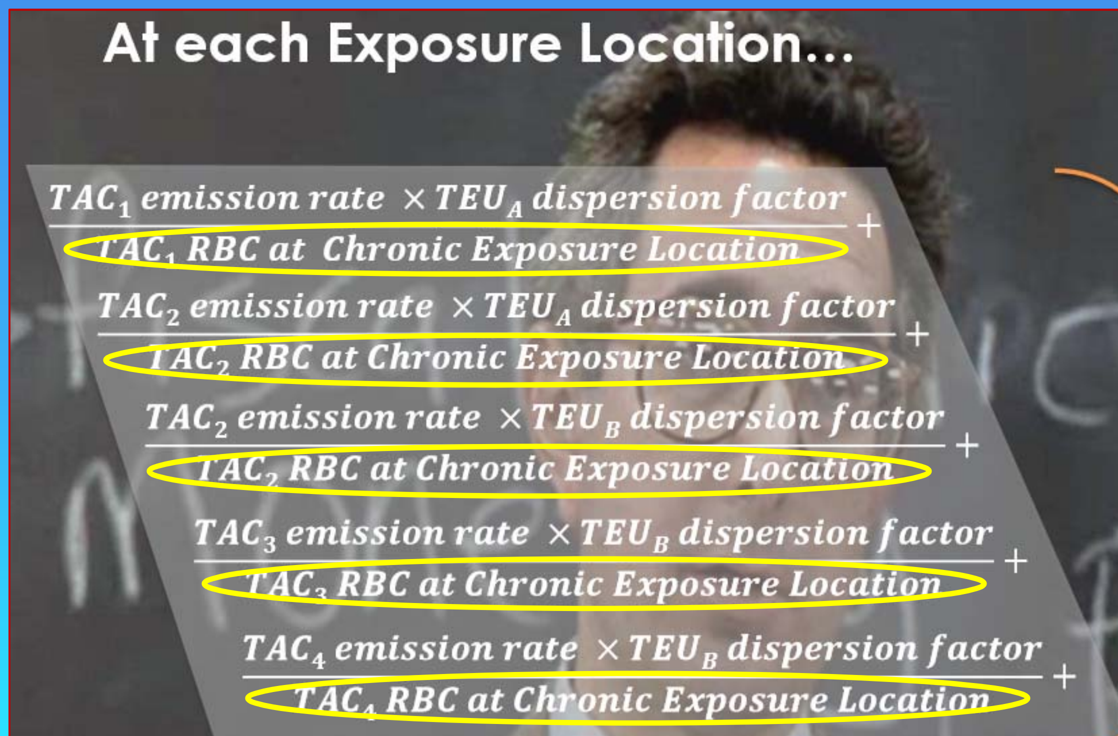
Diagram Used with permission of Maul Foster & Alongi, Inc.

Modeling Step 2: Determination of Exposure Locations

- Distances measured by Google Earth. Uncertainty?
- Even if using a laser distance meter, uncertainty is still there (and many other problems).
- May be measured using USGS or other gov't maps, still have uncertainty.

Distance measurements contribute to modeling uncertainty, because…

Remember This Math?



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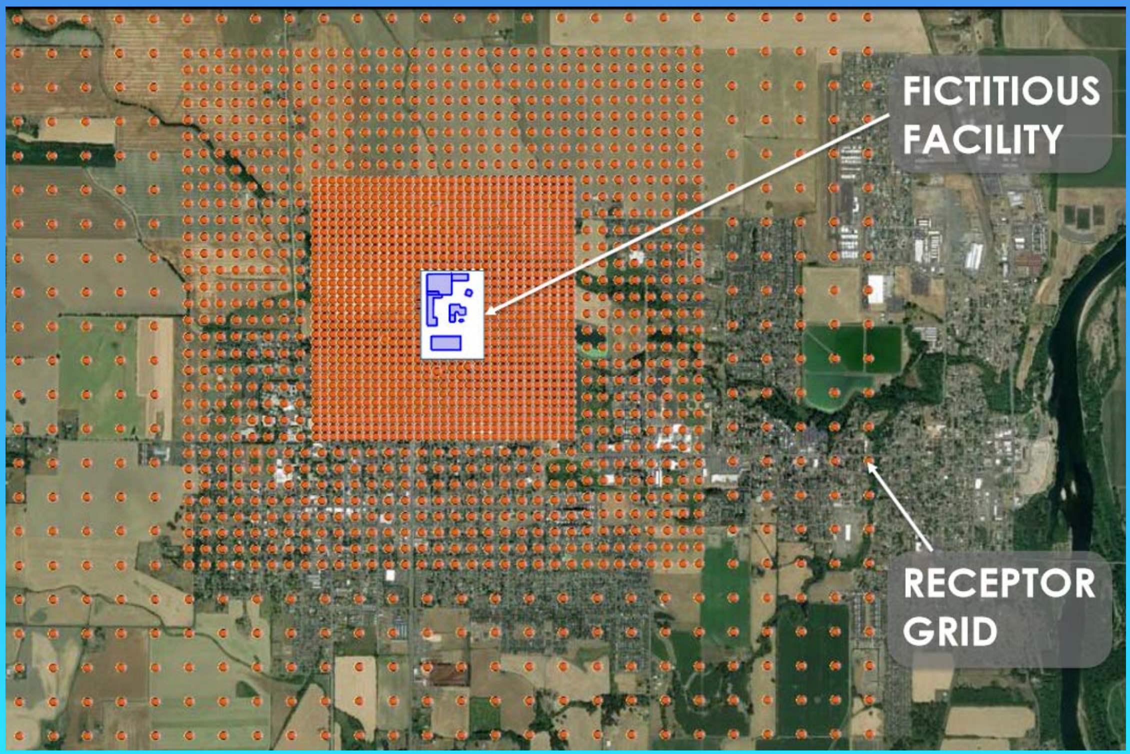
Modeling Step 3: More Math!!

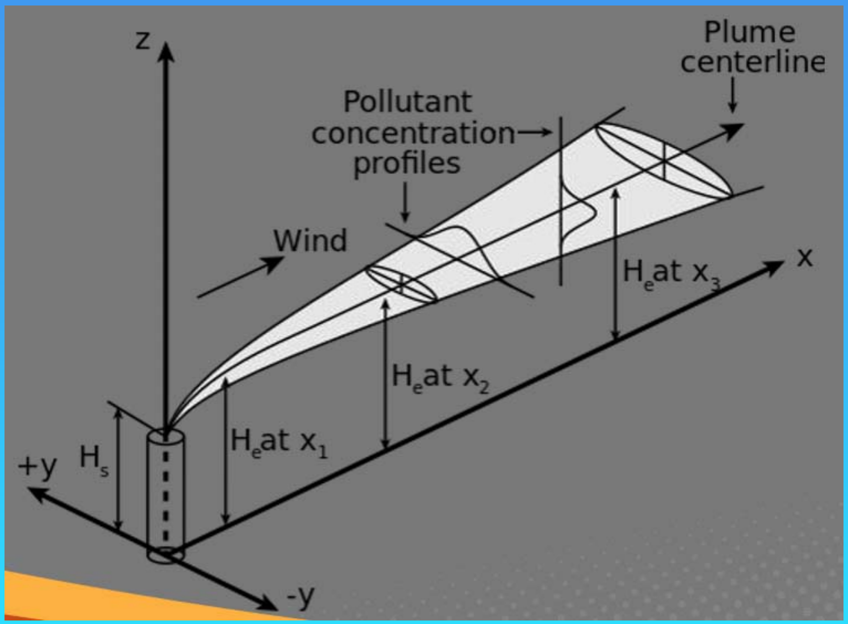


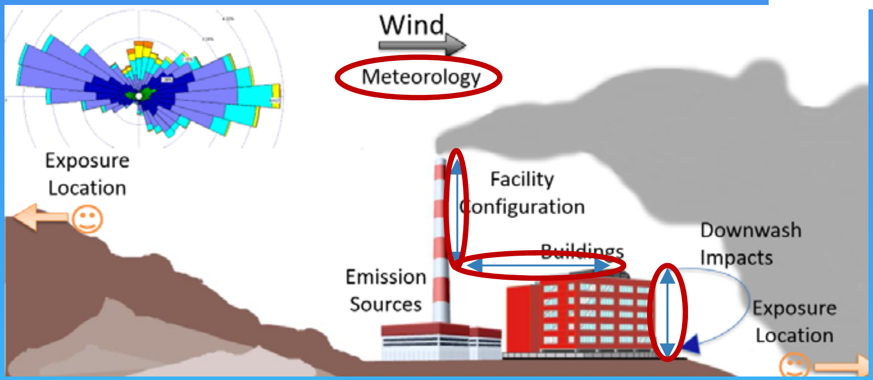
2,149 receptor points requiring data reduction using plume concentrations.

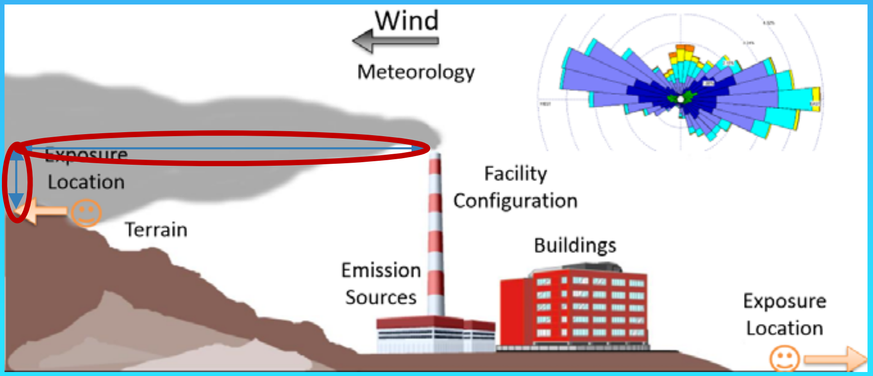
Diagram used with permission of Maul Foster & Alongi, Inc.

Remember This??

Plume concentrations







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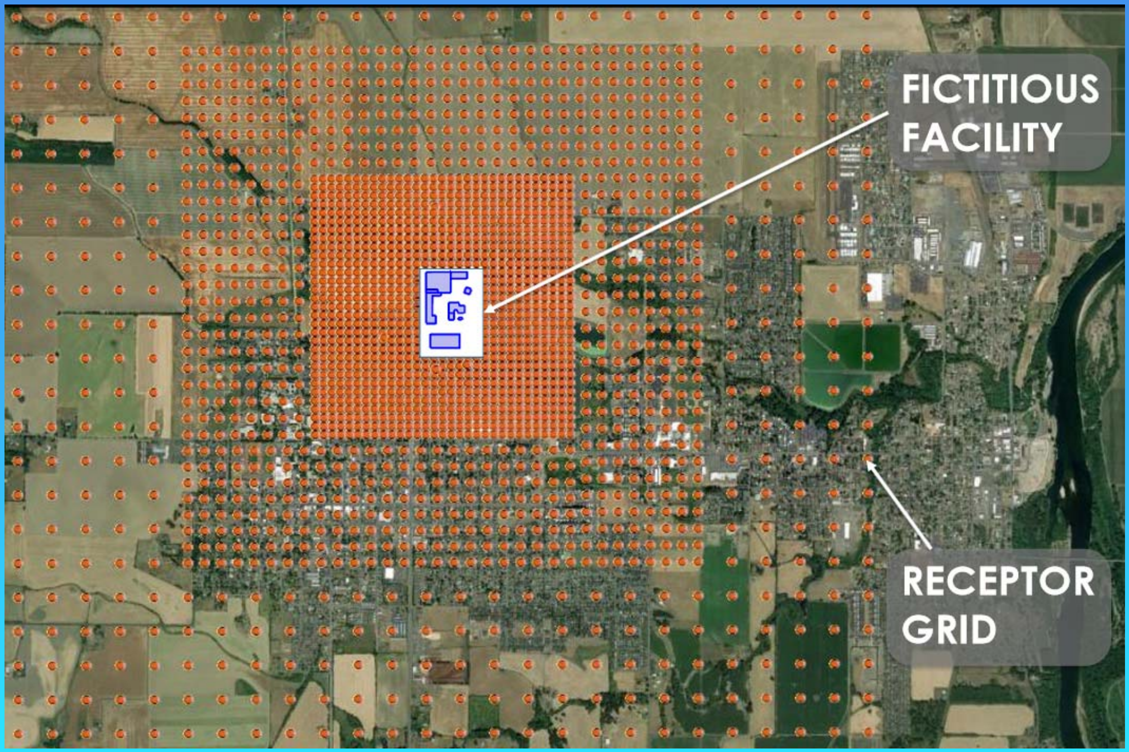
Modeling Step 3: More Math!!



2,149 receptor points requiring data reduction using plume concentrations.

Each point on grid used for further mathematical modeling.

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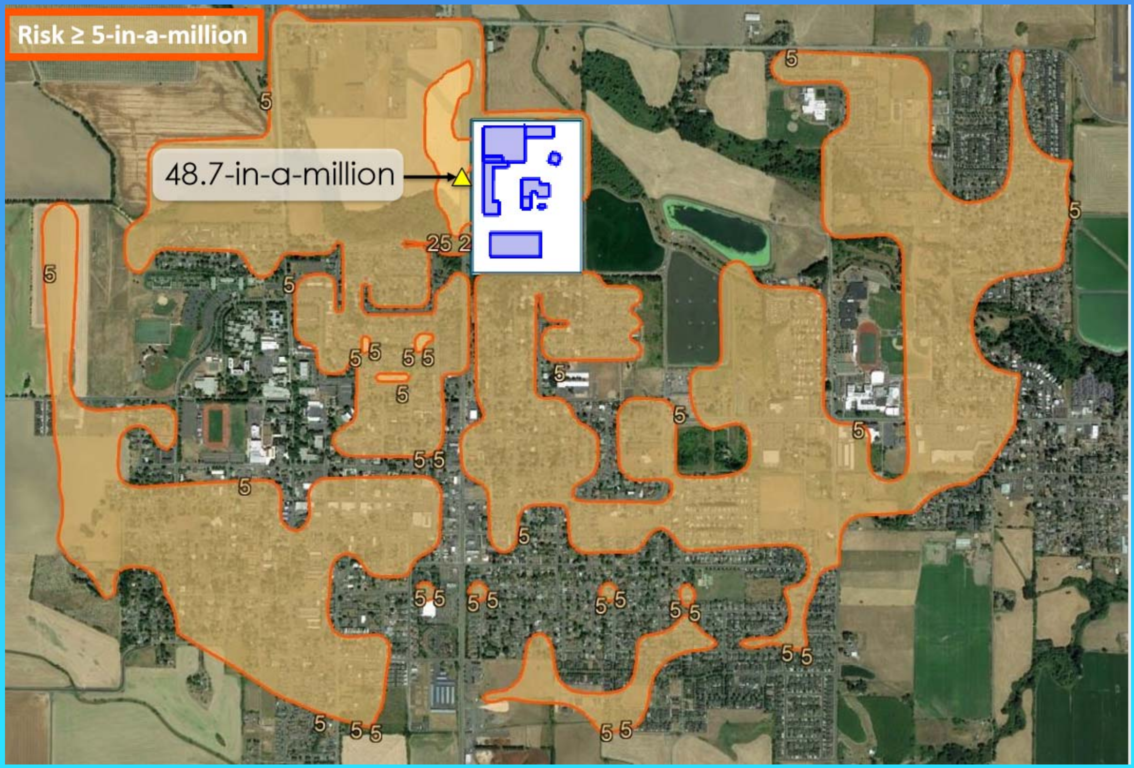
Modeling Step 4: Yet More Math!!



2,149 receptor points in conjunction with terrain modeling used to mathematically model isopleths.

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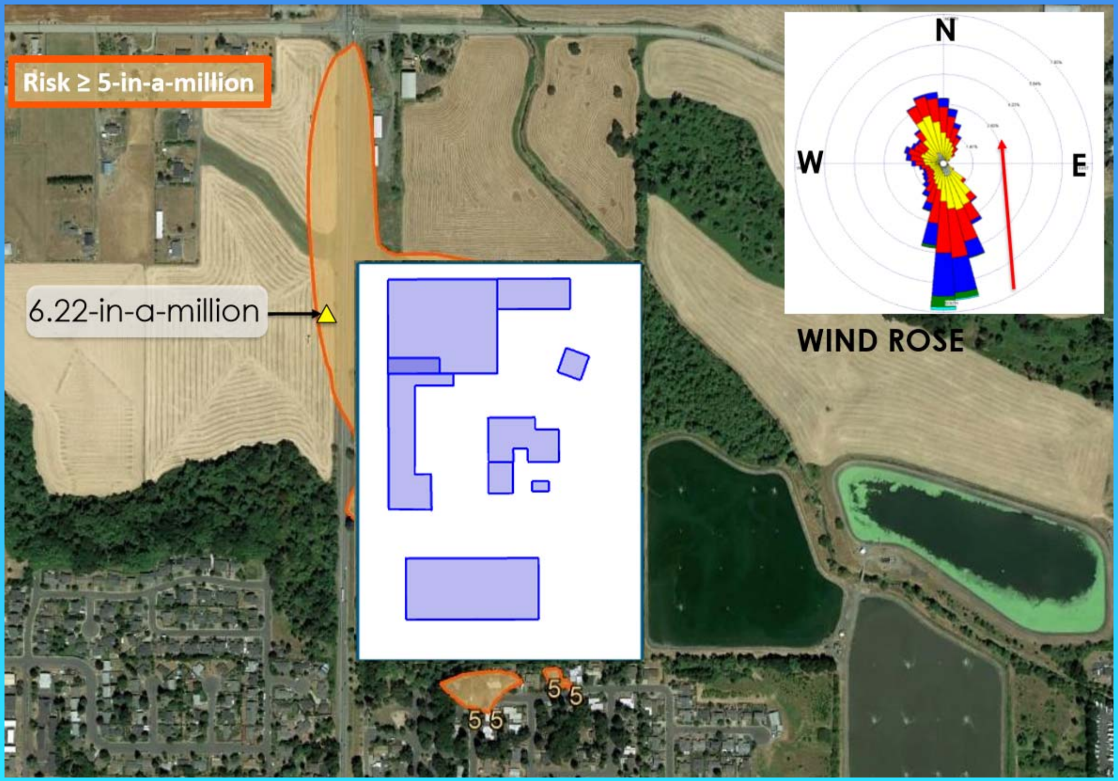
Modeling Step 5: Math with Met Data!!



[stage whisper]:

What's the uncertainty of the meteorological data?

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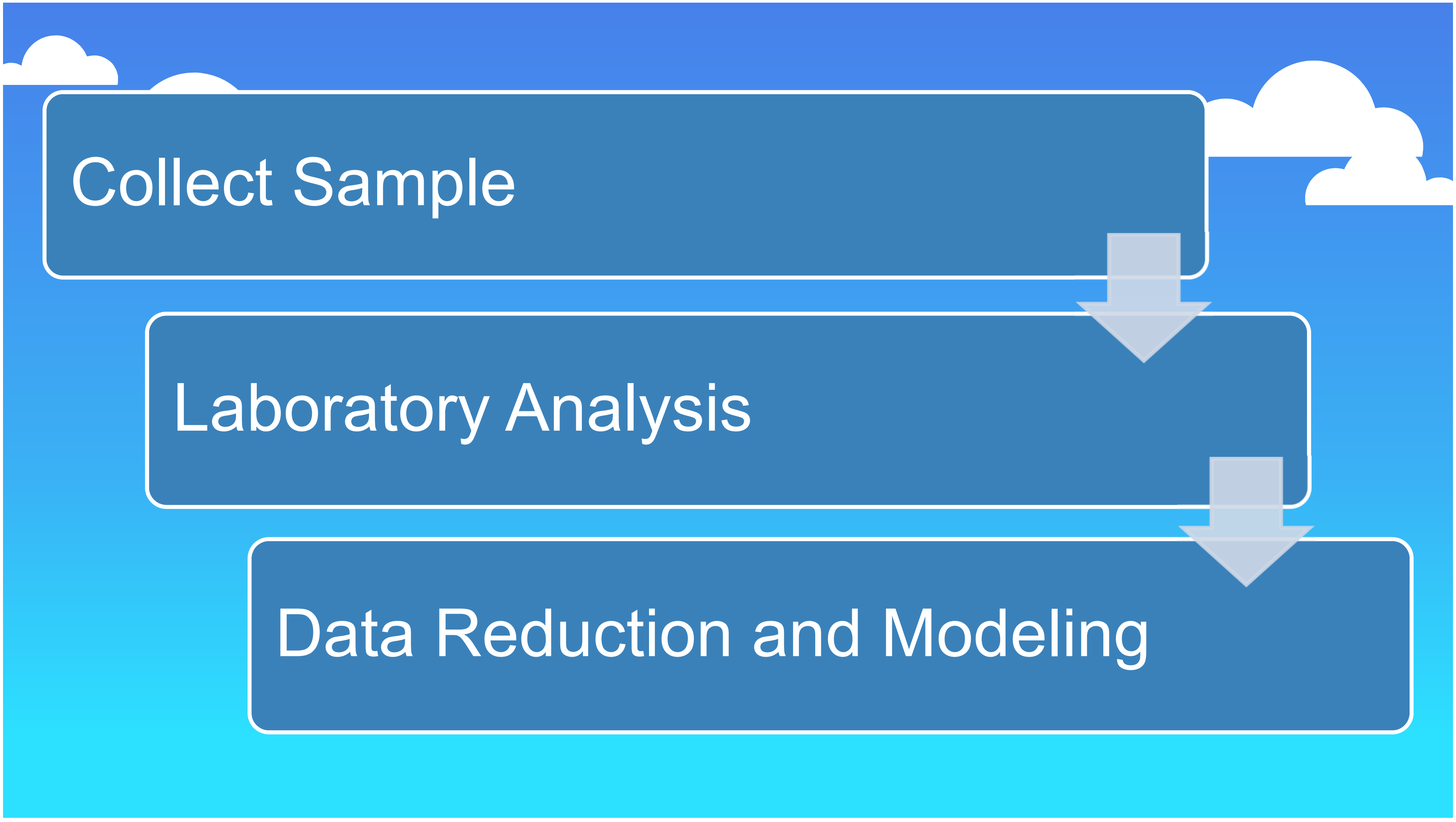

Collect Sample
Laboratory Analysis
Data Reduction and Modeling

Sources of Uncertainty

Sampling‡

- Length of sample run(s)
- Number of runs
- Scale and quality of instrument calibrations
- Sample loss due to leaks
- Analyzer drift
- Interfering gases
- Accuracy of O2/CO2 measurements
- Measurements of pressure and temperature
- Pitot specifications
- Non-uniform distribution of pollutants in stack
- Experience/skill of testers
- Flow measurements
- Quality of reagents
- Quality of gas standards
- Sample bottle type and cleanliness
- Glassware preparation
- Environmental conditions
- Moisture
- Field balances and other standards
- Reference balance and other reference standards
- Thermocouples
- Sampling location
- Number of points/port used
- Meter volume
- Filter efficiency and material
- Size and alignment of the nozzle during sampling
  Sample hold time and handling
- Instrument precision and accuracy
- Human error

Analysis (Laboratory)

- Preparation
- Analysis

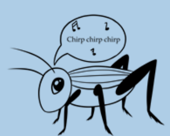
Data Modeling

- Meteorological data
- Distance/Height measurements
- Compounding uncertainties during data reduction

‡Contributed by Kelly Dorsi, Bison Engineering

Sources of Uncertainty Contained in Final Reported Detection Limit

Sampling



Analysis (Laboratory)

- Preparation
- Analysis

Data Modeling

Sources of Uncertainty

Sampling‡

- Length of sample run(s)
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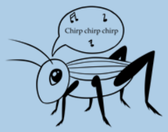
Sources of Uncertainty Contained in Final Reported Detection Limit

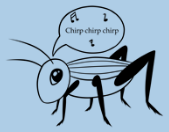
<u>Sampling</u>



<u>Analysis (Laboratory)</u>

- Preparation
- Analysis

<u>Data Modeling</u>



BUT WAIT! THERE'S MORE!!

Do my detectable results indicate a human health hazard?

Depending on sample collection and laboratory preparation technique, results may indicate total analyte, not bio-available analyte.

Human health hazard levels often determined by World Health Organization (WHO) – what is their uncertainty?

Is it possible to address this issue using current Source Test Methods? (hint: probably not, at least not with current technology)

Pop Quiz

Q: Where does most of the uncertainty lie in Source Sampling final results?

A: Not with the lab.

Q: At what stage in the process are the detection limits determined that are used in reporting final results?

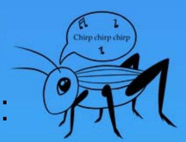
A: At the lab.

Q: Is ignoring the uncertainty from field sampling and data modeling going to bias the "detection limit" high or low?

A: Low – if other uncertainties were taken into account to create a true Method Detection Limit, the reported detection limit would be higher.

<u>Conclusion (Points to Ponder)</u>

Q: How does this low bias in Method Detection Limit affect the regulatory decision making process?

A: 

Q: Is it reasonably possible to take into consideration *all* uncertainty contributions in a Source Sampling Method?

A: Yes. Some aspects of uncertainty that are currently not considered during field testing or modeling could be considered.

AND

A: No. Technology would need to change to include <u>all</u> contributions.

How Certain Are You?

Hint: one of these is not being sampled, and at least one is using an incorrectly sized probe.†

†With thanks to Bill Guyton, ERM

QUESTIONS?

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With great appreciation to:

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