# Odorous Statistics

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# Introduction

- ➔ Odour pollution is a common environmental issue
  - → Industrial sites
- ➔ But difficult to measure
  - → Often subjective (like noise)
  - → Human response complex
- ➔ Statistical questions
  - → Can odours be better measured?
  - → Are there alternatives?

# Outline

→ **Presentation consists of four parts:**
- → Sampling of odours and odorants
- → Review of olfactometry measurement process
- → Statistical analyses of odour/VOC variability in emissions
- → Future directions

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# Sampling

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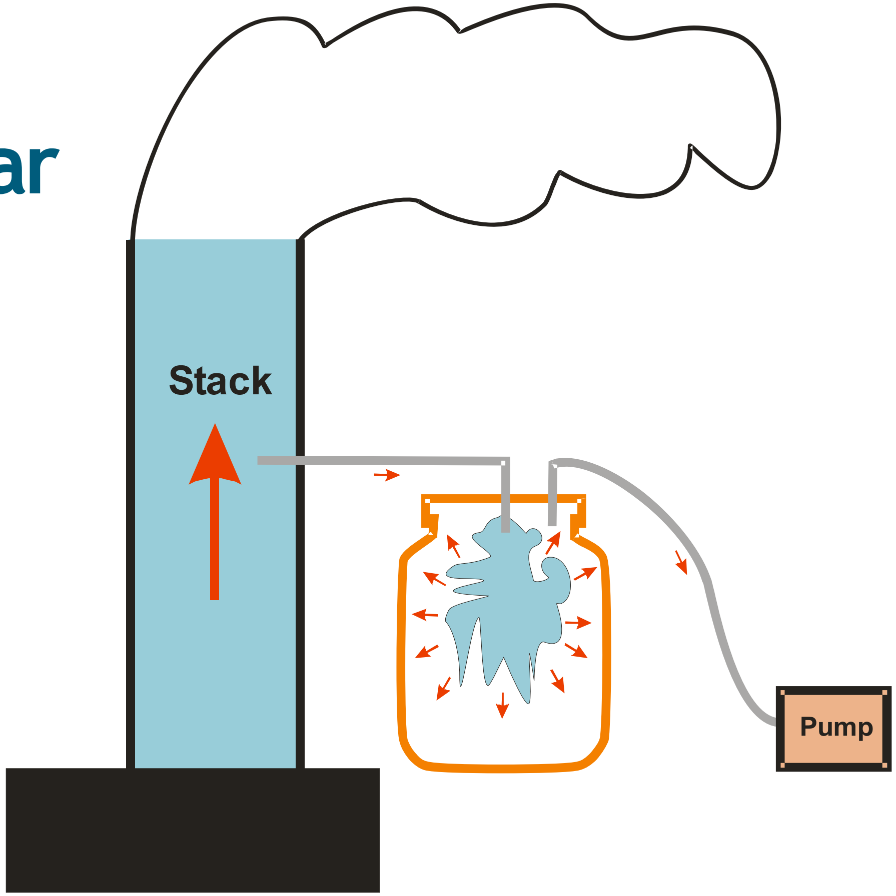
# Sampling Odour

- **Direct from stack**
  - High concentration
  - Sometimes wet
- **Sucked into Mylar bag**
  - Flushed with dry $N_2$
  - Care to avoid contamination
  - Diluted if humid
  - Take bag to olfactometry laboratory

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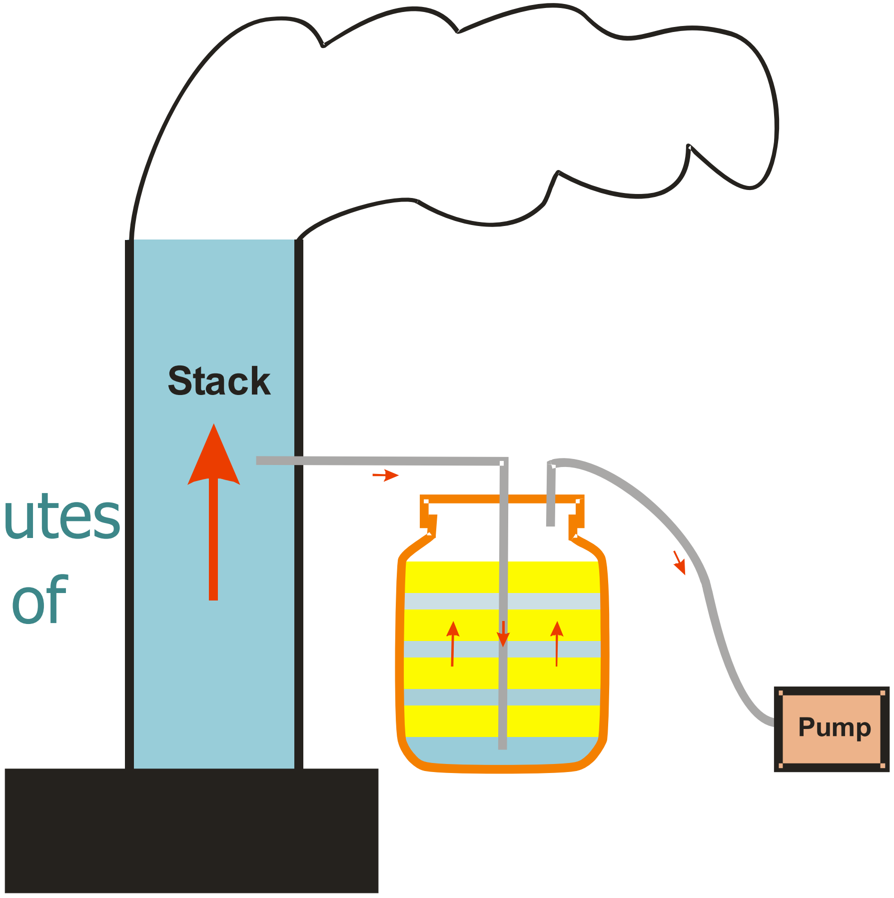
# Sampling odorants

- **Suck air through absorbent material**
  - Known volume via pump
  - Absorbent targets chemical species
  - Sometimes drying required
  - Can take 30-60 minutes
  - Laboratory analysis of odorants
    - Usually chromatography



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# Review of Olfactometry Measurement Process

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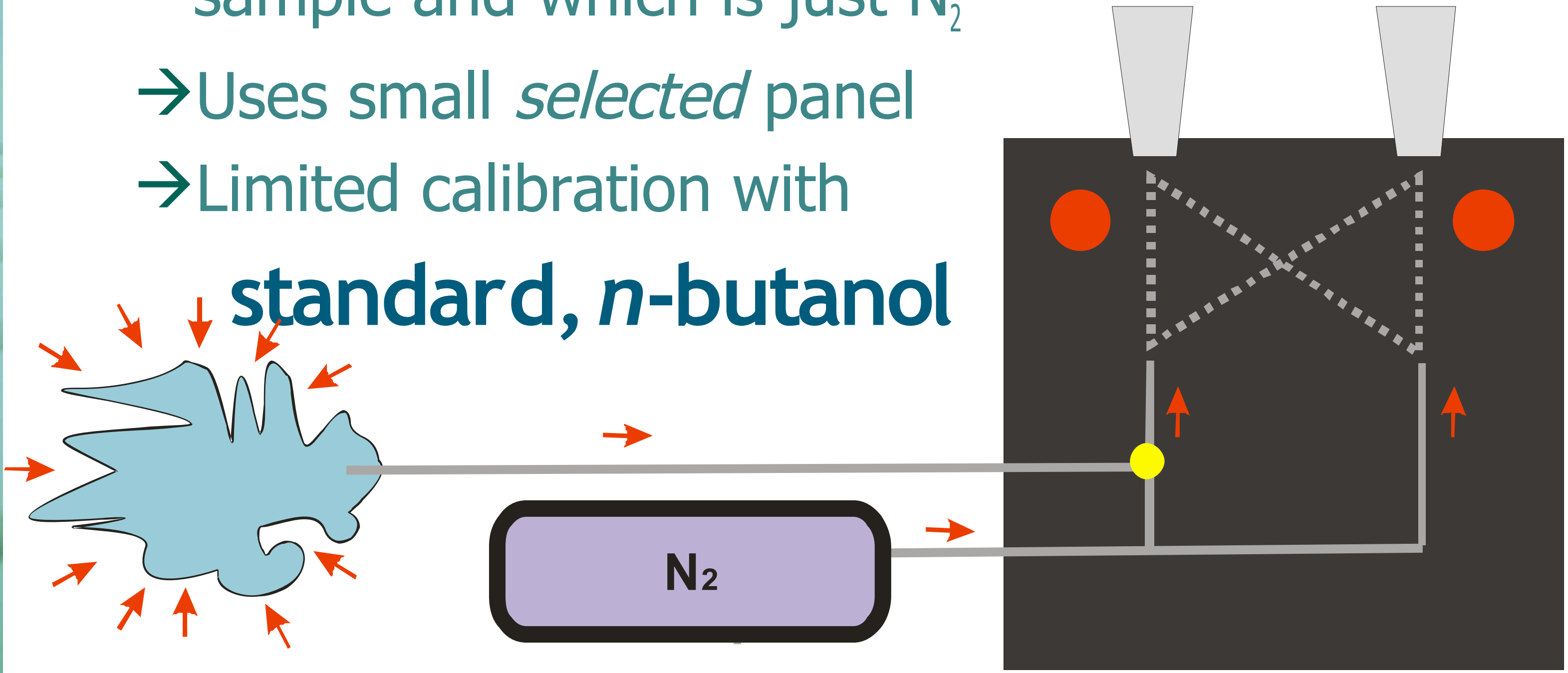
# Dynamic Olfactometry

- **Follows AS 4323.3**
  - Based on serial dilution with dry $N_2$
  - Concentration increased until *just* detected
  - Person must correctly identify which outlet has sample and which is just $N_2$
  - Uses small *selected* panel
  - Limited calibration with **standard, *n*-butanol**



# The detail

- Panel member reports one of three levels of surety
  - Guess
  - Inkling
  - Certain
- Always deceasing dilution
  - Technical reason – easier to purge between stages
  - Panelists work in parallel – reduces purging
- Stops when reporting
  - "Certain" and Correct
  - For that level and the next

# "Analysis"

- Average dilution on a log scale
- Standard error using standard formulae
- Accuracy limited
  - Small panels – typically 3 or 4
  - Same relative accuracy when levels high or low
- Delete "bad" data
- Good accuracy claimed
  - Better than 25%

# Errors that are ignored

- Large dilution steps
  - Hardware set factor of two
  - Induces $\sigma$ of $1/\sqrt{12}$ on $\log_2$ scale
- Definition of certain
  - Highly subjective
  - Difficult to quantify
- Calibration one dimensional
  - Standard uses just one odour
  - Not necessarily like the target odour
- Standard incomplete
  - Does not eliminate interactions between panel members

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# With the Result

- Uncertainty much larger than standard suggests
  - More like –60% to +150% or worse
  - Really need panel size of 30-100
- Highly dependent on procedures
  - Particularly training/selection of panelists
  - Not useful for longitudinal studies unless panel kept constant
- AND statistically inefficient
  - Ignores most results

# On the Plus Side

- → **Odour data can be useful**
  - → Real odour as measured by real people
  - → Includes *all* potential odour sources
  - → Measurement follows an Australian Standard
- → **Can study relationships**
  - → Even though individual measurements poor
- → **Calibrate odorant to odour data**
  - → Allows odorant data to measure changes over time

# Better Statistical Model

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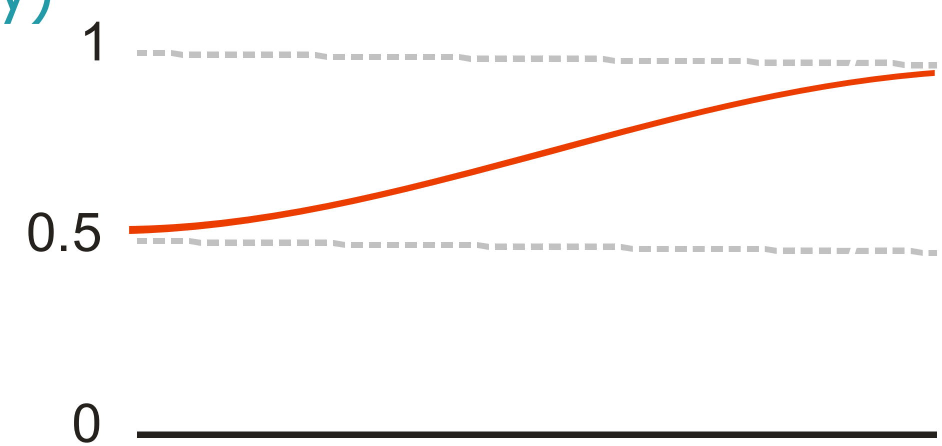
# Simpler is better

- Simply record whether selection of outlet correct or not
  - Binomial response – known error structure
  - Natural link function is modified logistic
    - In log of dilution
    - Readily programmed in R (with effort) or Glim (trivially)

$$p = \frac{1/2 + e^{x}}{1 + e^{x}}$$



# Details of "Simple"

- → **Panelist effects**
  - → Probably major source of final estimation error
  - → Ideally need a mixed GLM
  - → Hierarchical
    - Between panelists
    - And a panelist over time

# Pros and Cons

- **Pro**
  - Completely removes subjective rating of certainty
  - Uses all the data from each panelist
  - Has good statistical base and hence errors on estimates
- **Con**
  - Fails to use the information from certainty
  - Still problem of large dilution steps
  - Panelist remembers their previous certainty
  - Calculation no longer simple

# Ideal Changes to Procedures

- Dilution steps
  - Each panelist has different starting dilution
  - Intermediate steps
- Non-sequential dilutions
  - Obtain better independence
- BUT these may be limited by hardware

# Relationships to Odorants

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# Two Issues

- Odour and odorants sampled differently
  - Different times
  - Different interval lengths

- Relationship itself
  - Modeling

# Data

- **Historic data**
  - Collected during 2001 – 2006
  - Used for earlier analyses
- **New data from two sampling regimes**
  - Bimonthly sampling
    - Collected during October 2006 – April 2007
    - Two or three data points per operating unit
      - Approximately every two months
  - Intensive sampling
    - Collected during November 2006 - July 2007
    - Samples collected
      - Hourly
      - Daily
      - Weekly

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# Analysis of Variability of Odour and Odorant Data

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# Variation Within Data

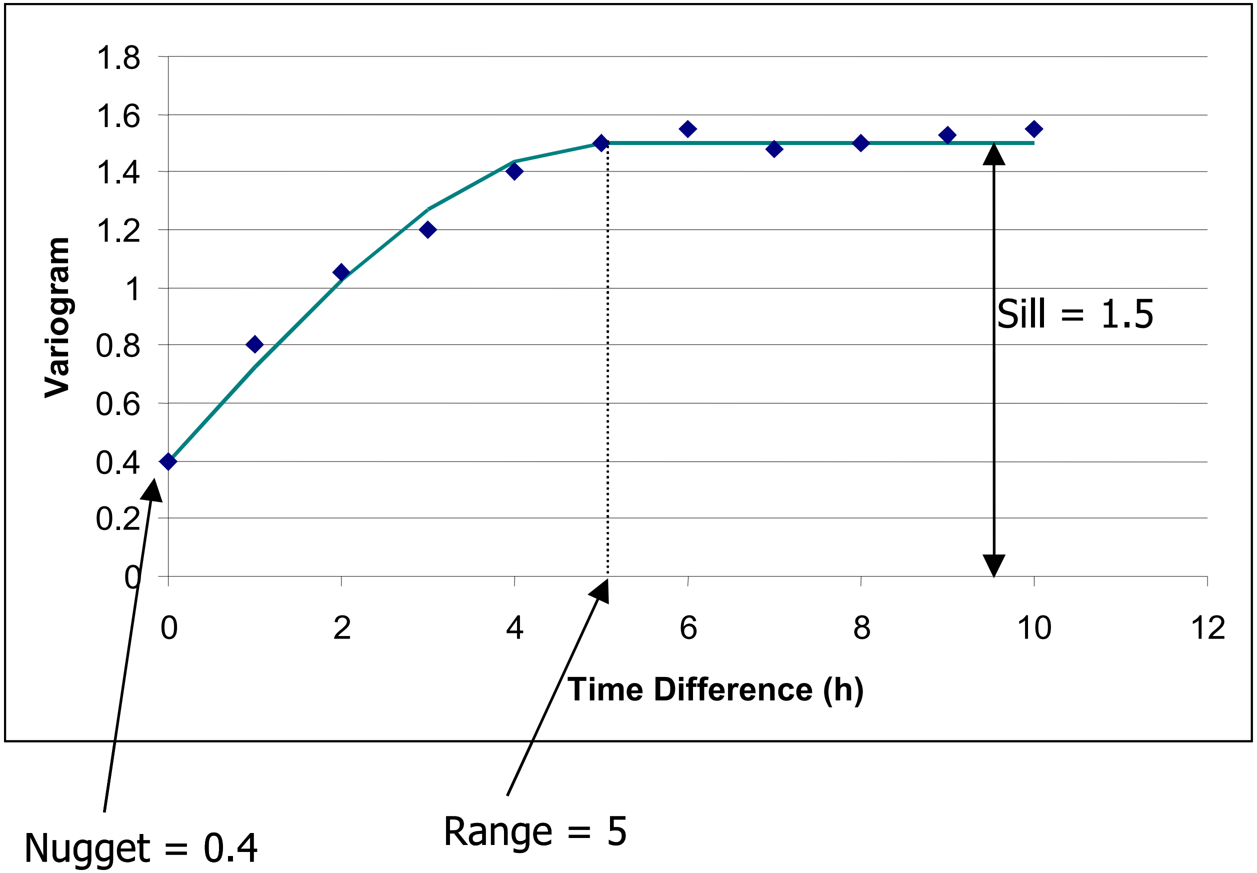
- Geostatistical approach
  - Typically used for spatially dependent data
  - Used here for temporally dependent data
- Confidence intervals for overall variance
- Four variables investigated
  - Acetaldehyde
  - Acetone
  - Total aldehydes and ketones
  - Measured odour
- Five operating units
- All variables standardised
  - Direct comparisons

# Variogram

- Variance as a function of time *between* samples
  - Samples collected at time *t* and *t+h*
  - Function of *h*, not *t*
- Model attributes
  - Nugget
    - Measure of repeatability for samples collected at or very close to the same time
    - High values mean less repeatable
  - Range
    - Extent of dependence
  - Sill
    - Maximum value for the model
    - Difference between sill and nugget called the Partial Sill
    - Overall variability of the data

# Example Variogram

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{\alpha=1}^{N(h)} \left[ z(t_\alpha) - z(t_\alpha + h) \right]^2$$



# Variogram Fitting

- Often done manually
  - Allows expert knowledge to be incorporated
  - Can ignore effect of outliers
- Automated process
  - Small dataset, needed statistically more efficient procedure – maximum likelihood
  - Wanted to avoid incorporating preconceptions
  - GeoR add-on component of R statistical package

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# Summary

- ➔ **Odour measures clearly more variable than odorant measures**
  - → Some of the increased variability may be due to shorter collection times for odour samples
- ➔ **Similar level of accuracy for odour would need**
  - → ~20 times as much data *and*
  - → A consistent panel
- ➔ **Measured odour not suitable for detecting changes over time**
  - → The Standard not designed for this purpose
  - → However, there is a relationship between variability of odour and odorants, providing way forward

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# Development of the Odour/ Odorant Model

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# Overview

- →**Previous research**
  - →Looked at total volatile organic compounds (VOCs)
- →**Current research**
  - →Chemical odour units using odour thresholds
  - →Much larger dataset
    - More operating units
    - Extra odorants
  - →Fitted new model that potentially takes into account unmeasured odorants and synergies between odorants

# Compounds Used

- Models fitted using different selections of odorous compounds
- Final model included
  - Acetaldehyde
  - Acetone
  - Ammonia
  - Butanal
  - Benzaldehyde
  - Benzene
  - Formaldehyde
  - Propanal
  - Toluene
  - 2-Butanone
  - 2-Pentanone

# Definitions

## → Odour threshold concentration

- → Minimum concentration at which a compound can be detected by the sense of smell
- → Experimentally determined by olfactory lab

| Operating Unit | Odour Threshold Concentration (mg/OU) |
|---|---|
| Acetaldehyde | 0.0019 |
| Acetone | 13 |
| Ammonia | 11.6 |
| Butanal | 0.0057 |
| Benzaldehyde | 0.0121 |
| Benzene | 195 |
| Formaldehyde | 0.043 |
| Propanal | 0.0317 |
| Toluene | 0.325 |
| 2-Butanone | 2 |
| 2-Pentanone | 27 |

# Definitions

- → **Measured odour (OU)**
  - → Determined by panel members at olfactory lab
- → **Chemical odour units (COU)**
  - → Calculated from odorant samples
  - → Ratio that reflects amount by which concentration of odorous compounds that have been detected in the sample exceed their respective odour threshold concentrations
  - → COU obtained for each compound and summed to form overall COU for the sample
  - → COU calculation accounts for typical moisture content of samples coming from different operating units

# Calculation of COU

- **Example:**
  - Acetaldehyde concentration = 5.20 $mg/m^3$
  - Odour threshold = 0.0019 mg/OU
  - COU for acetaldehyde:

    **= 5.20/0.0019**

    **= 2736.84**
  - Calculate COUs for remaining compounds
  - Sum of COU = 3432.22
  - Account for moisture content - typically 42%
  - Total COU for dry component:

    **= 3432.22 * 0.58**

    **= 1990.69**

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# Model Fitting

- → Used $\log_{10}$ of chemical odour units and measured odour
- → Single model - not one per operating unit
  - → More data required to develop stable model for each operating unit
- → First pass examination
  - → Modelled $\log_{10}OU = \log_{10}COU + error$
  - → Avoids regression "errors in variables" problem
    - Odorant measurement

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# Second Pass Model

- Added operating unit component
  - Accounted for discrepancy between the chemical odour units and measured odour for a particular operating unit
  - Incorporated unmeasured odorants and synergistic effects
  - Weighted by number of data points
- Weighted individual offsets were averaged to obtain an overall offset

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# Mixed Result

- →AS 4323.3 flawed
  - →Does directly measure human perception
  - →But does not deliver usable accuracy
  - →Particularly poor statistical treatment
    - In part due to a reluctance to use anything more than elementary methods to solve a non-elementary problem
    - Why doesn't a standard say "use a GLM"
- →Some some better methods
  - →Measuring specific odorants
  - →But still problems
    - Missing odorants

# Where were the Statisticians?

- Why does a standard get drafted where:
  - Fails to meet good sampling practice
  - Fails to achieve independence between panelists
  - Fails to acknowledge all errors
  - Fails to acknowledge existence of computers to do statistics
  - Overstates accuracy