Odour Management – Sulfurous Compounds

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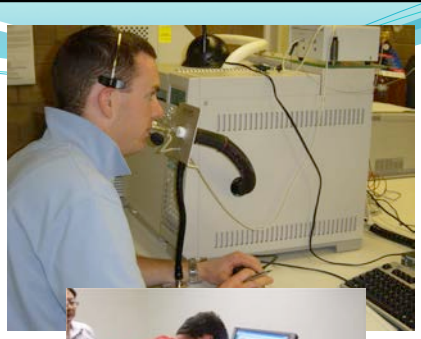

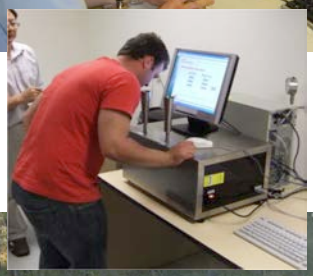

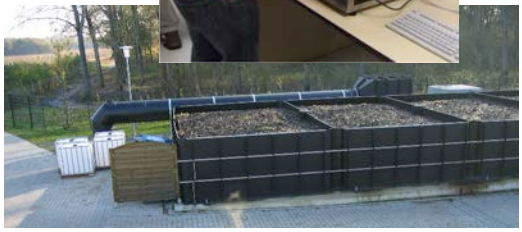

UNSW Odour Laboratory (est. 1999)

- Chemical analysis
  - VOC & S analysis - GC-MS/FPD
  - VSC & VNCO analysis - GC-SCD/NCD
  - GHG & PG analysis - FTIR Spectrometer
  - TD-GC-QTOF
  - Portable TD-GC-MS
- Olfactometry
  - Dilution olfactometry (AS/NZS 4323.3:2001)
  - Olfactory analysis - GC-MS/ODP
- Future instruments
  - Mobile chemical analysis – SIFT-MS

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Research staff

- Dr Eric Sivert (Group manager)
- Dr Gavin Parcsi (Chemical analysis)
- Dr Xinguang Wang (Olfactometry)
- Dr Nhat Le (Chemical analysis and treatment)
- Dr Kate Murphy (Chemometric analysis)

PhD students

- Bei Wang (emission characterisation)
- Hung Le (sulfur degradation and sampling)
- Mark Dunlop (litter emission formation)
- James Hayes (olfactory annoyance-public engagement)

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Research Projects

- Intensive livestock practices (poultry sheds)
- WWTP and biosolid emissions
- Sewer odours
- Landfill emissions
- Composting operations
- Odour abatement performance
- Material emissions
- Taste & odours (drinking water)
- Indoor air quality
- Medical applications (breath analysis)

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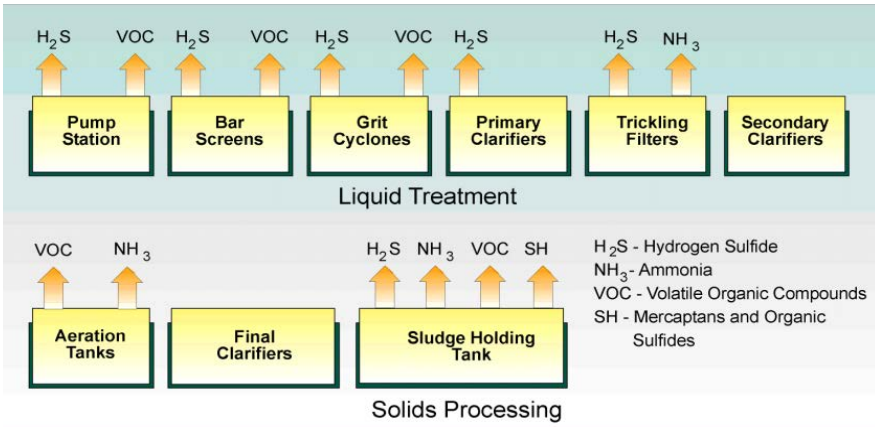
Odorant emissions



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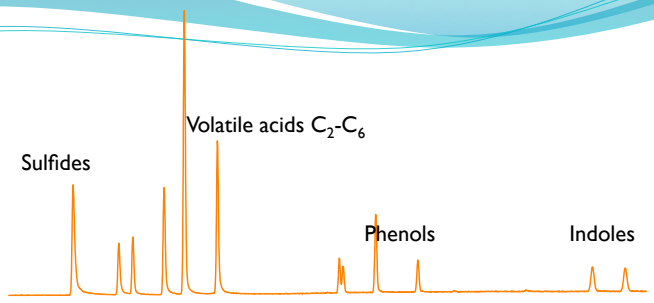
Odorants



Odour thresholds

Hydrogen sulfide – 0.5 ppb

Methyl mercaptan – 0.0014-18 ppb

Dimethyl sulfide – 0.12-0.4 ppb

Methylamine – 0.9-53 ppb

Dimethylamine – 23-80 ppb

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Odorant sampling

- Source - where - type
- Multi-component ppb-ppt range
- Labile components e.g. thiol
- Humidity interferes with the adsorption of polar odorants
- Transportation and transformation of compounds
- Sample collection
- Pre-concentration of samples

Sample collection

- Odour bags
  - Inert bag materials
- Canisters
- Sorbent tubes
  - Porous polymers e.g. Tenax TA
  - Carbon based sorbents e.g. Carbotrap B
  - Others multiple bed sorbent tubes e.g. Chromosorb Silica gel
- Sample pre-concentrations
  - Cryogenic sampling
- Solid-phase micro extraction (SPME)
  - Equilibrium technique based on partitioning of analytes between gaseous and silicone phase

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Chemical analysis

- Online monitoring
  - Odour abatement monitoring
  - Continuous infield measurements
    - sewer systems
- Offline monitoring
  - Spot or grab measurements

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H_2S measurements and methods

- A good marker compound for:
  - Anaerobic processes
  - Acidic conditions
- A poor marker for:
  - Aerobic processes
  - Basic conditions
- Paper tape
  - Lead-acetate / colorimetric
- Gold film
  - Resistance change by adsorption onto gold film
- UV Fluorescence
  - Catalytic conversion of H_2S to SO_2

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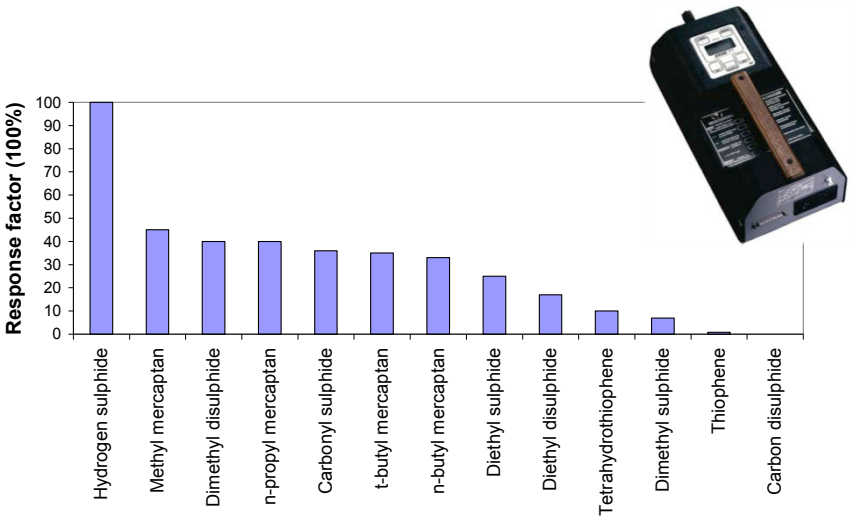
H_2S interference issues



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Gas Chromatography (GC)

- A separation technique
  - Separates individual compounds from complex mixtures
  - Qualitative/quantitative determination of odorants present
- Components detected as they exit the GC column at different times using detectors
- Separation by differential affinities to the column surface
- Column dimensions
  - longer-better separation
- Column surfaces
  - porous solid film for light VOCs/gases
  - thicker films better retention

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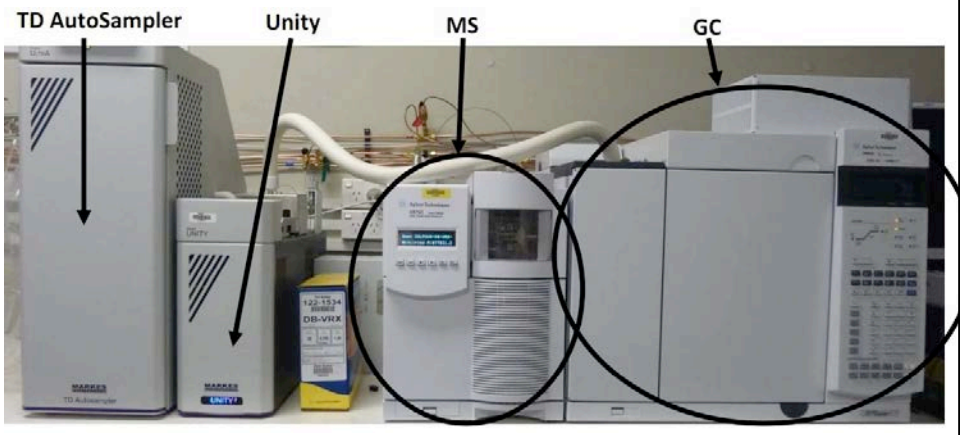
TD-GC-MS



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Choice of Detector

- Known analytes
  - FID - C & H 10^6 dynamic range
  - ECD - electron affinity - halides & N
  - Sulfur – sulfur chemiluminescence detector (SCD)
  - Nitrogen – nitrogen chemiluminescence detector (NCD)
- Unknown analytes
  - Mass spectrometer (MS) - almost universal

- MS detection
  - Molecular identification
  - pg detection limits
  - set mass range and single ion monitoring (SIM) e.g. 64 SO_2
  - gas flows are important
  - concentration stage
  - mostly laboratory based but transportable systems now available

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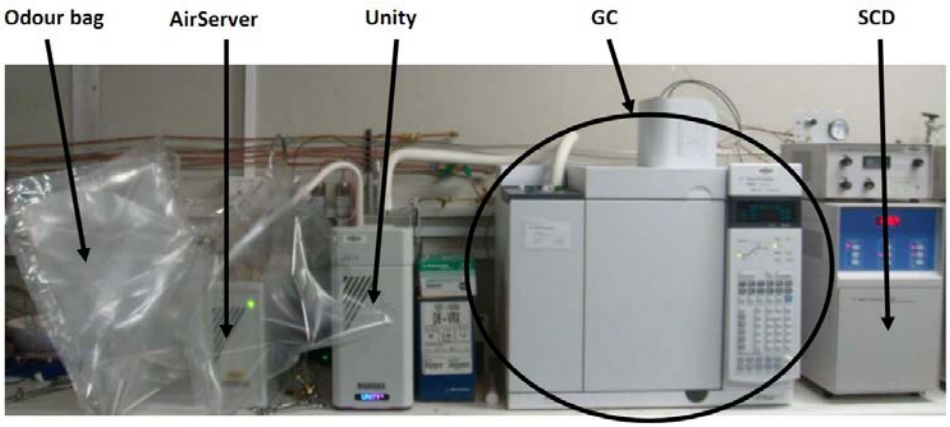
Air server-TD-GC-SCD



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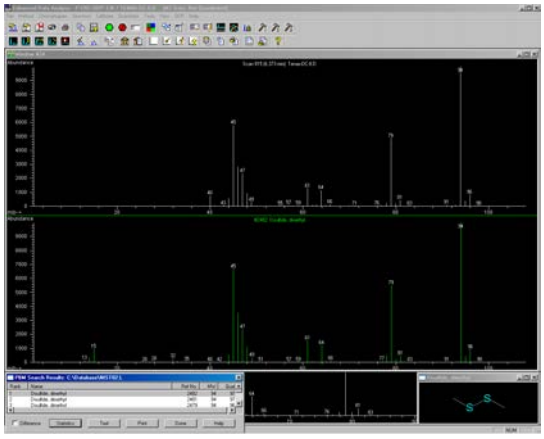
MS data presentation



- Qualitative assessment
- Relative quantification
- Quantification
  - standard solution
  - calibration curves
  - method detect limits
  - storage recovery
    - sulfur compounds

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Analytical methods

US EPA Method TO-17

- Standard Method for Air Toxics
  - BTEX, halo-hydrocarbons
  - 44 compounds ~ 50 minutes
- Last Revision 1999
- Few known odorants in the matrix

Need a benchmarked method that addresses relevant odorous compounds

Halocarbon 114
1,2-Dichloroethane
1,3,5-Trimethylbenzene
Methyl Acetate
Halocarbon 11
Trichloroethene
1,2,4-Trimethylbenzene
Methyl tert-Butyl Ether
Halocarbon 113
1,2-Dichloropropane
Dichlorobenzenes
Methyl Ethyl Ketone
1,1-Dichloroethene
cis-1,3-Dichloropropene
1,2,4-Trichlorobenzene
Ethyl Acrylate
Methylene Chloride
Toluene
Hexachloro-1,3,-butadiene
Methyl Acrylate
1,1 Dichloroethane
Trans-1,3-Dichloropropene
1,3 Butadiene
Methyl Isobutyl Ketone
cis-1,2-Dichloroethene
Furfural
Acetonitrile
Tetrachloroethene
Chloroform
1,2-Dibromoethane
Acetone
Chlorobenzene
1,1,1-Trichloroethane
Ethylbenzene
2-Propanol
m-Xylene
Carbon tetrachloride
p-Xylene
Acrylonitrile
o-Xylene
Benzene
1,1,2,2-Tetrachloroethane
Isoprene

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Odorants of interest

Key Compounds

- Volatile Organic Compounds (VOCs)
  - Butyl compounds
  - Aromatics
  - Terpenes

GC-MS

- Volatile Organic Sulfur Compounds (VOSCs) and H_2S
  - Sulfides
  - Thiols
- Volatile Nitrogen Compounds (VNCs)

GC-SCD/NCD

- Non-permeable Gases (NPGs) - Methane

GC-FID

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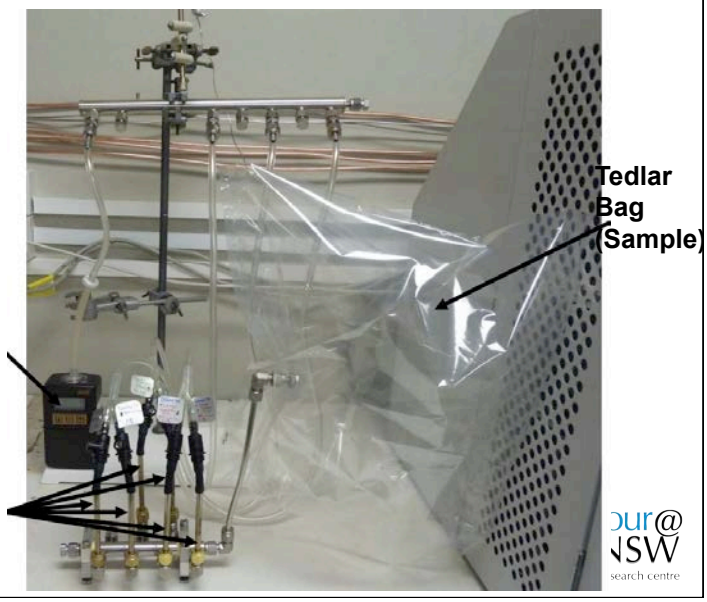
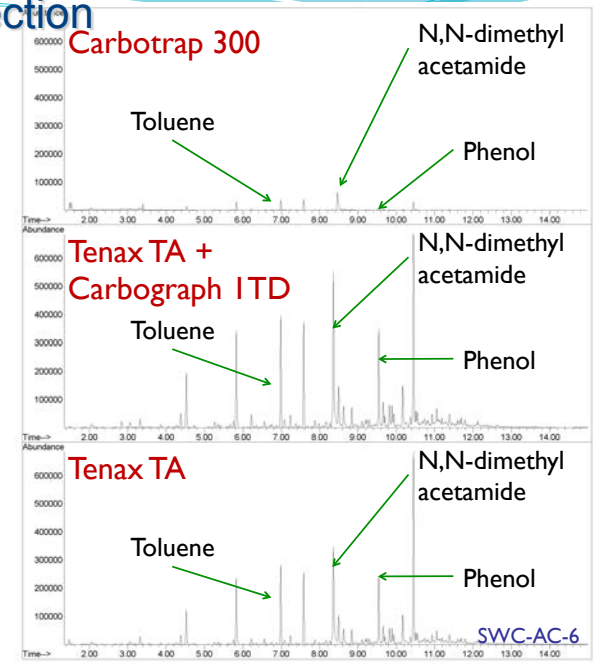
Sorbent tube selection

- Field samples
- Tedlar bags
- Drawn onto sorbent tubes
- 3 sorbents



Sorbent tube selection

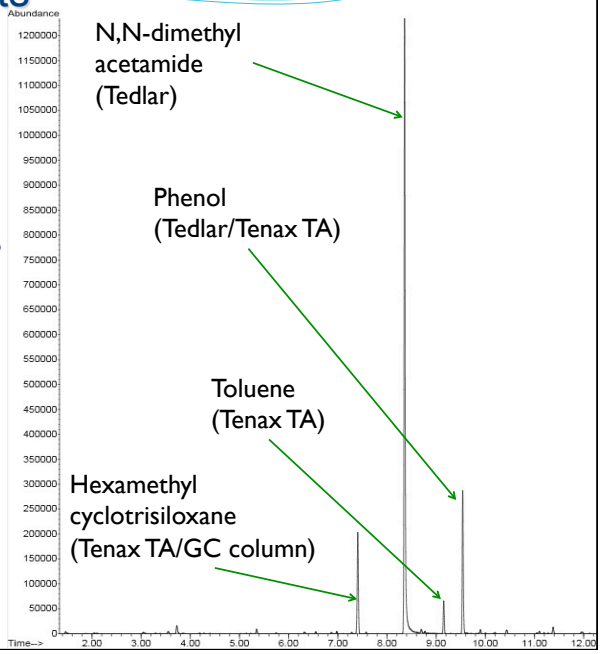
- 3 significant compounds detected in all samples



Sampling artifacts

- Blank sample
- Tenax TA sorbent
- Tedlar bag
- Significant artefacts from the Tedlar bag

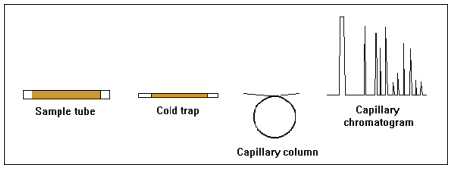
Bags not suitable for VOC sample collection



Sample pre-concentration

Thermal desorption (TD)

- Improves resolution of GC peaks
- Samples are heated in a flow of inert gas to extract target compounds into the vapour stream via a process of dynamic gas extraction
- The techniques combines sample extraction, with selective analyte concentration and transfer of target compounds to the detector



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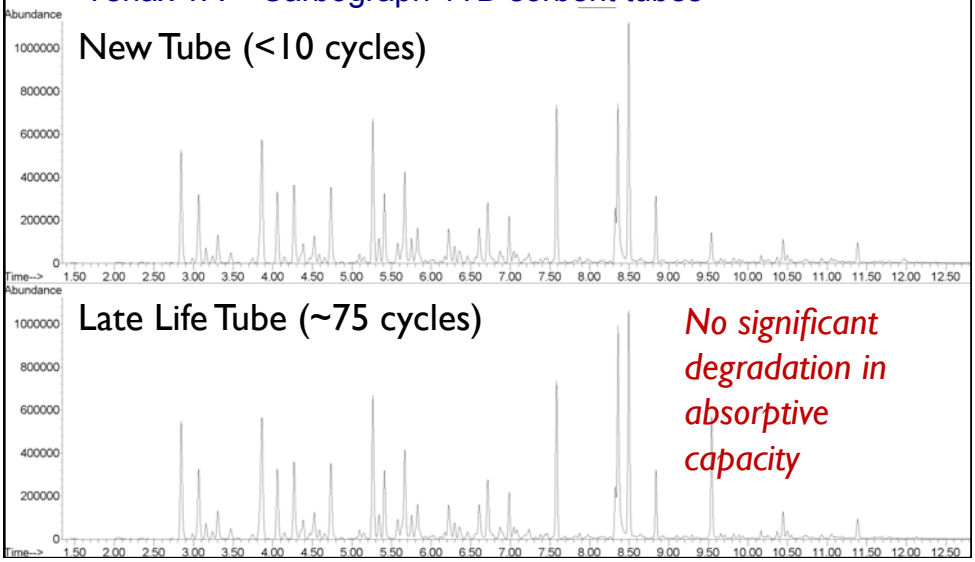
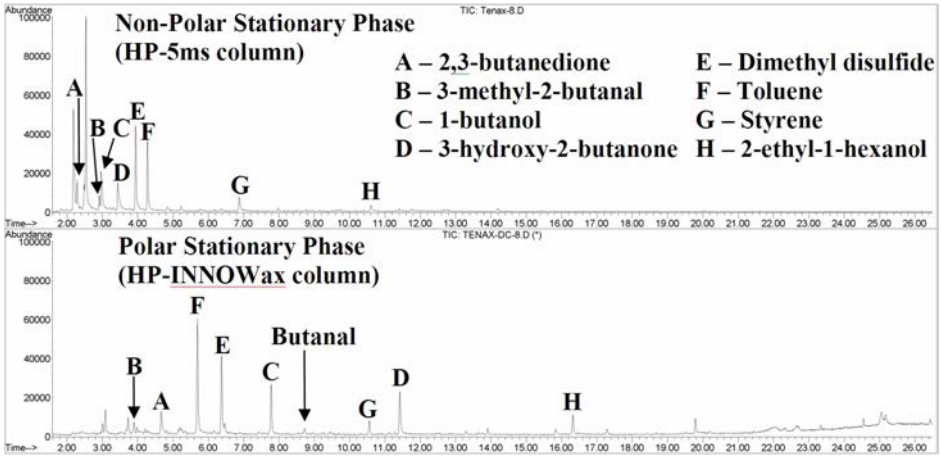
Impact of sorbent tube age on compound capture

Tenax TA + Carbograph 1TD sorbent tubes



No significant degradation in absorptive capacity

Column selection



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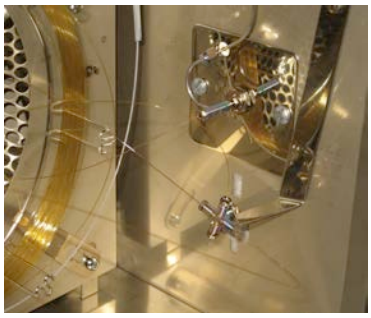
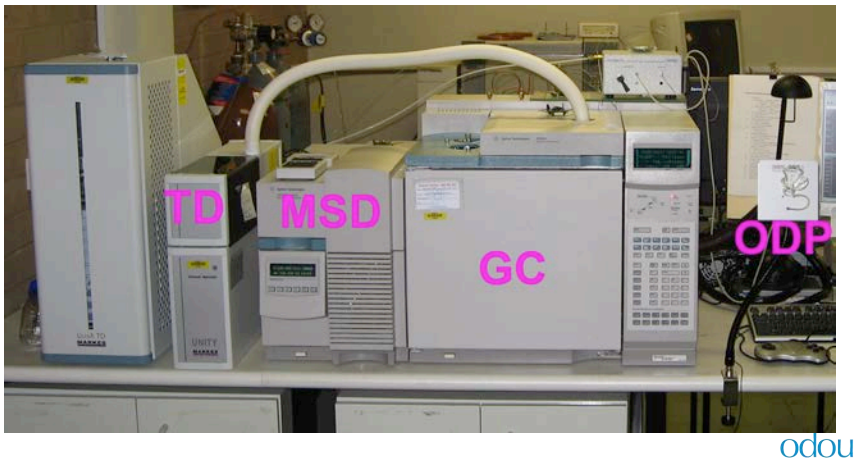
ODP analysis

- Coupling an olfactory detection port (ODP) to a GC-MS or GC
- Techniques allows odorants to be separated and identifies individually



TD-GC-MS/O

- Allows odour contribution for each compound to be characterised in terms of character and intensity



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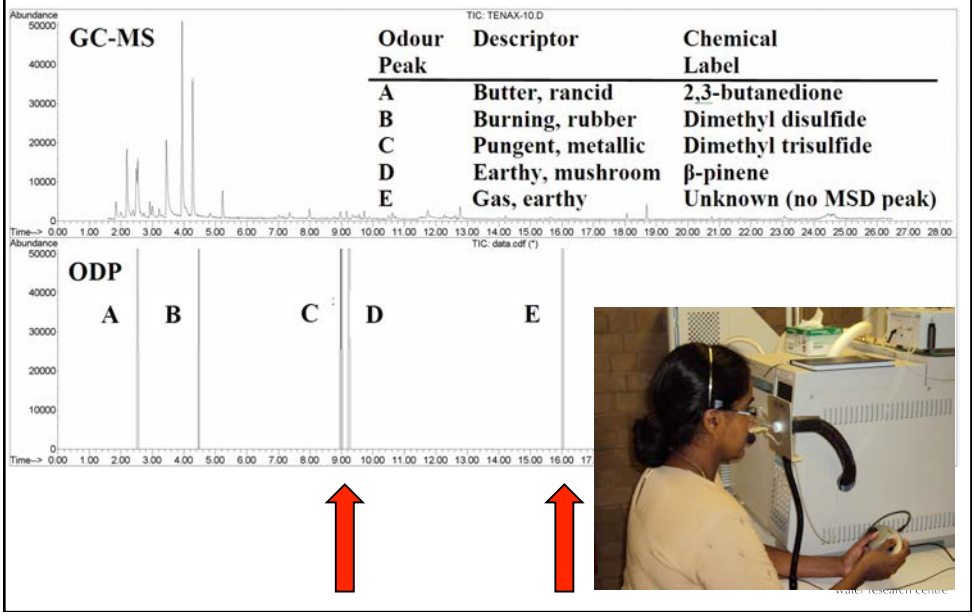
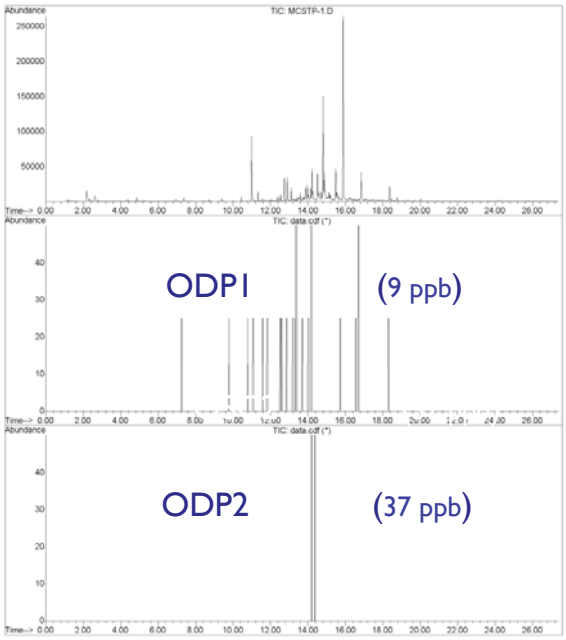
TD-GC-MS/O analysis



Odour Peak	Descriptor	Chemical Label
A	Butter, rancid	2,3-butanedione
B	Burning, rubber	Dimethyl disulfide
C	Pungent, metallic	Dimethyl trisulfide
D	Earthy, mushroom	β-pinene
E	Gas, earthy	Unknown (no MSD peak)

ODP analysis

- Variations between ODP operators based n-butanol threshold

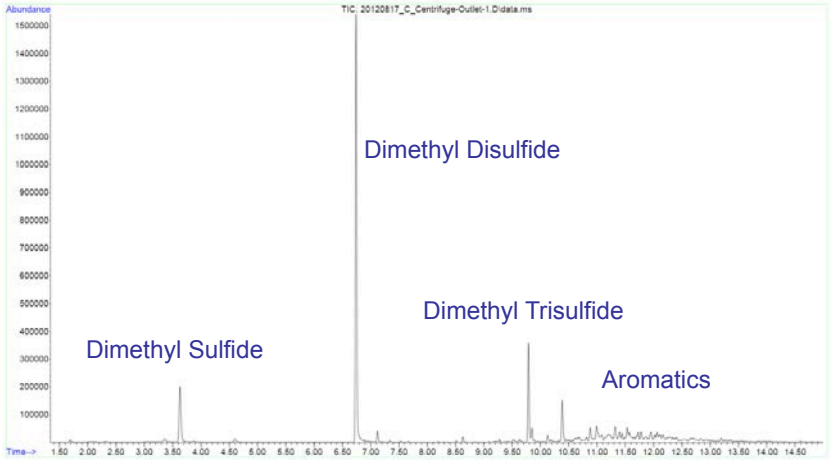


Biosolid sampling

Sorbent tubes and bag samples being collected

Sample preparation using US EPA Flux Hoods

Biosolid emissions (VOCs and VOSCs)



Low abundance and diversity, dominated by sulfurs

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Sulfur Compounds: Odorants

- Different characters
- Low detection thresholds

Chemical	Character	OTV (mg/m^3)
H_2S	Rotten egg	0.002
DMS	Sulfury onion	0.049
MeSH	Decomposing cabbage	0.0013
DMDS	Sulfurous vegetable	0.82
EtSH	Sulfurous fruity	0.0008
DEDS	Gassy ripe onion	0.09
EMDS	Sulfurous truffle	0.062
DMTS	Sulfourous cooked onion	0.014

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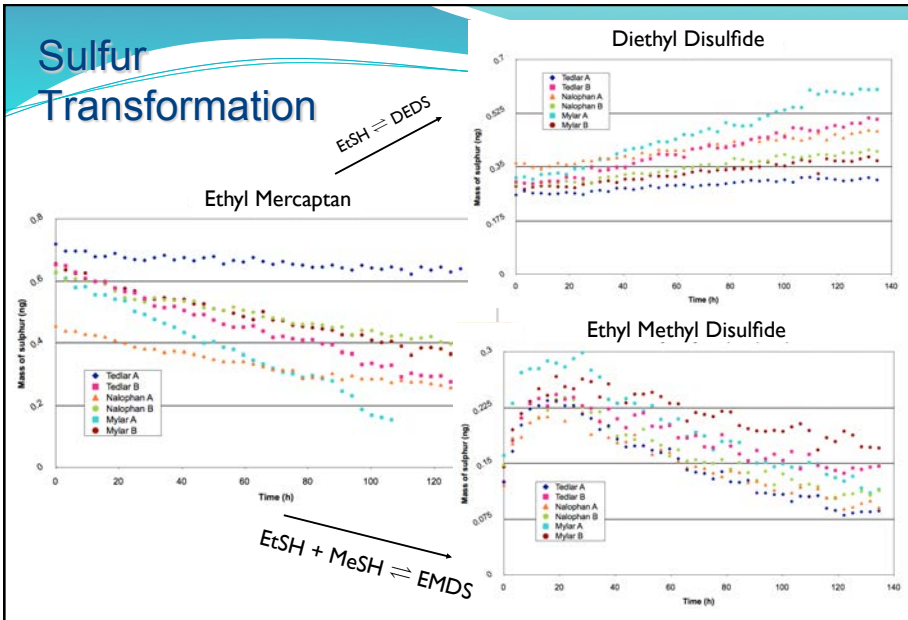
Sulfur Transformation



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Summary

- In order to compare VOC emissions from different sources we need to benchmark sampling and analysis approaches
- Several hundred different VOCs and VOSCs are present in odour emissions, often compounds in low abundance are most odorous
- Sites-specified VOCs are often present and can be related to the source or the process functionality
  - eg. sewer catchment, household waste, compositing operation, biosolids processing

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