Identifying diesel particles in ambient PM2.5

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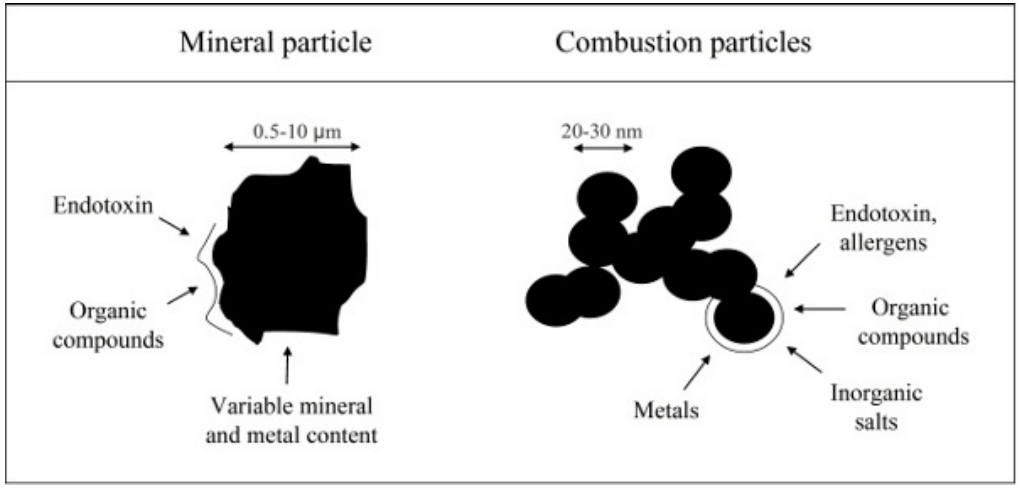
Friday 13 June 2014

CENTRE FOR AUSTRALIAN WEATHER AND CLIMATE RESEARCH/CSIRO MARINE AND ATMOSPHERIC RESEARCH

Diesel $PM_{2.5}$ particles

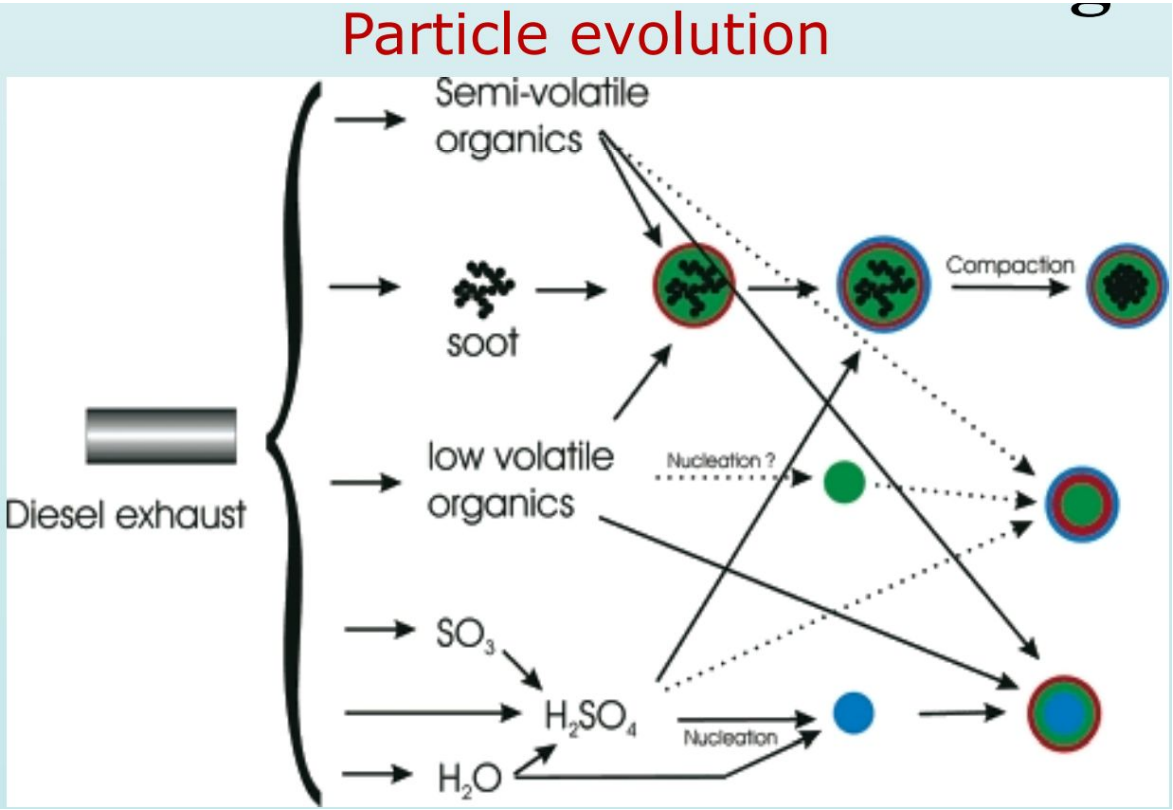


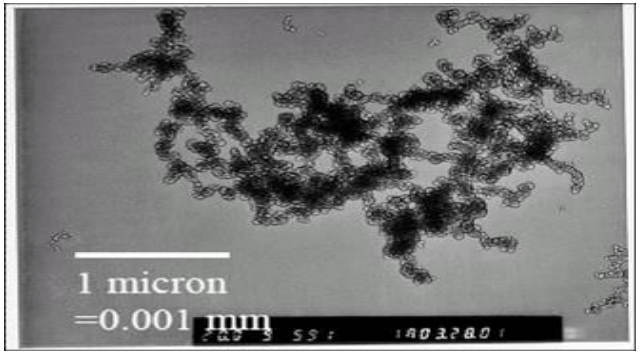
- 45-60% of PM2.5 mass is soot (also called black carbon or elemental carbon)
- Can be measured with light absorption (aethelometers) and thermal-optical techniques

- Organic/lack carbon ratio is much lower (0.4) than for other sources
- Organic carbon – more complex composition than elemental carbon, e.g. vegetation, burns at lower temperatures

Category	Average OC/BC ratio
Diesel engines	0.4
Petrol engines	5 – 10
Domestic woodheaters	7
Bushfires	10
Fuel reduction burns	12
Fugitive road dust	22

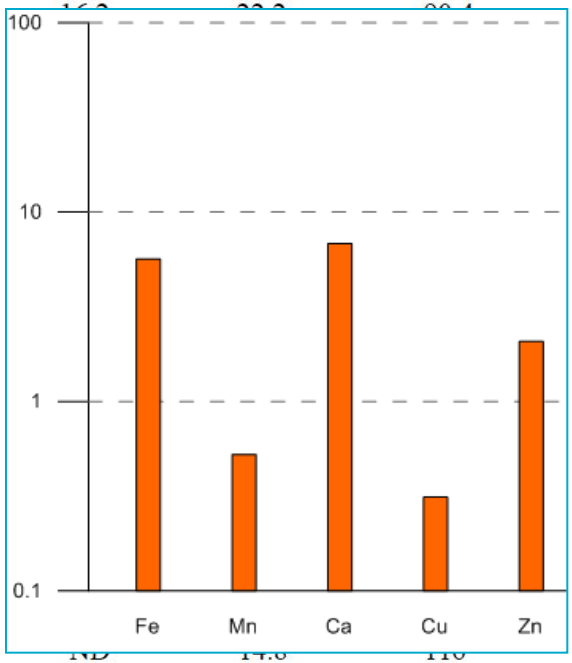
Diesel particle formation





Some of the chemical species in diesel $PM_{2.5}$

Element	$PM_{2.5}$			
	Idling	40 km/h	M-15	60%/40%
Na	44.1	44.6	65.3	290
Mg	ND[a]	ND	ND	139
Si	23.8	37.6	28.4	538
S	130	81.6	63.0	274
Cl	13.0			
Ca	2.0			
Ti	ND			
V	ND			
Cr	0.4			
Mn	0.4			
Fe	0.6			
Ni	0.1			
Cu	0.3			
Zn	1.5			
Pb	0.3			
F^-	ND[a]			
Cl^-	ND			
NO_2^-	23.9			
Br^-	ND			
NO_3^-	23.9			
PO_4^{3-}	ND			
SO_4^{2-}	200			
$C_2O_4^{2-}$	ND			
Na^+	ND			
NH_4^+	48.1	32.0	29.6	233
K^+	ND	10.6	14.8	116
Mg^{2+}	ND	ND	ND	ND
Ca^{2+}	7.9	10.6	14.8	58.2



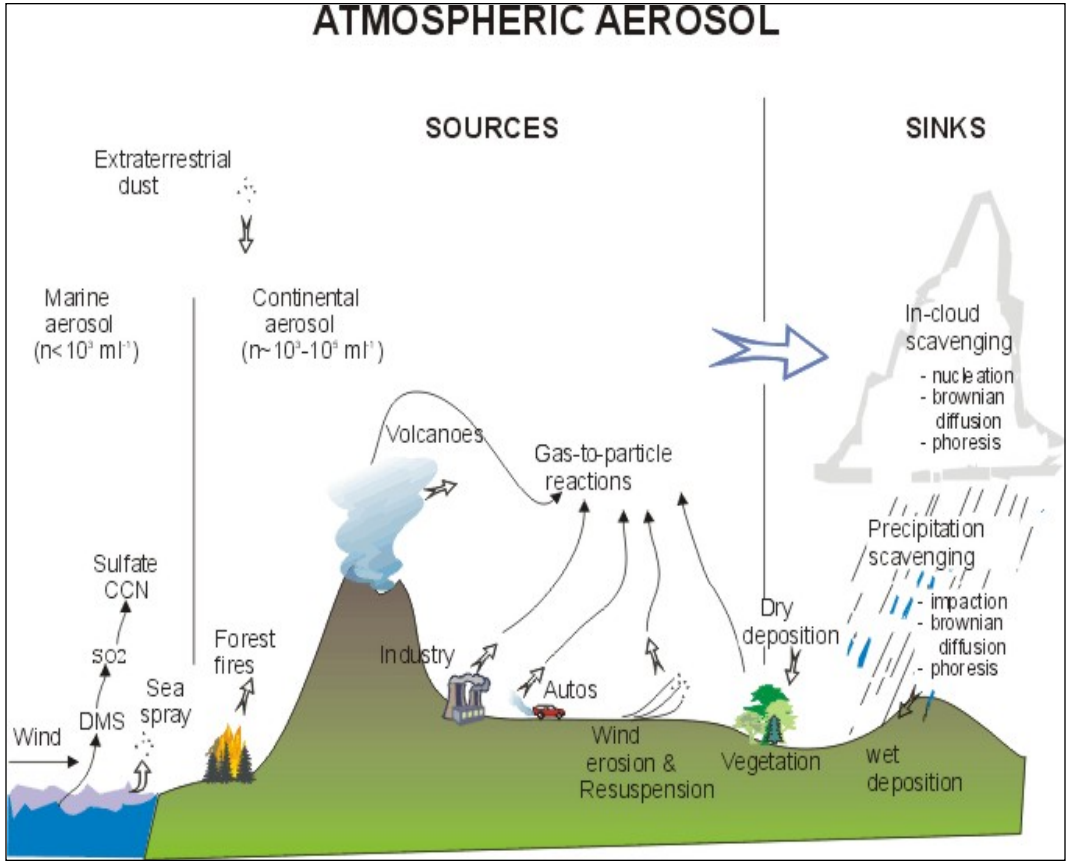
Factors affecting diesel emissions

- Engine type and power
- Engine operating conditions, e.g. idle, accelerate, decelerate
- Fuel formulations, e.g. sulfur content
- Dilution and aging
- Meteorology, e.g. temperature, relative humidity, sunlight

Ambient $PM_{2.5}$

Ambient PM2.5 includes

- **Diesel engine emissions**
- Brake and tyre wear
- Road dust
- Other engine emissions
- Sea salt
- Smoke - fires
- Industrial emissions
- Vegetation
- Dust from duststorms
- Biogenic emissions
- Secondary particles formed in the atmosphere



Source Apportionment to identifying diesel emissions in ambient $PM_{2.5}$

Method used in

- Upper Hunter Particle Characterisation Study in 2012
- Current Lower Hunter Particle Characterisation Study
- ANSTO's long-running aerosol sampling program

1. Collect samples of ambient PM2.5
2. Analyse chemical composition of samples
3. Positive Matrix Factorisation (PMF) technique identifies fingerprints and their contributions
4. Interpret fingerprints to determine sources

Collect PM2.5 samples on filters

1 day in 3 sampling

24-hour sample

Analysis

- Gravimetric mass
- Black carbon (laser integrated plate method)
- Elemental concentrations using IBA
  - Hydrogen (H)
  - Sodium (Na)
  - Aluminium (Al)
  - Silicon (Si)
  - Phosphorous (P)
  - Sulfur (S)
  - Chlorine (Cl)
  - Potassium (K)
  - Calcium (Ca)
  - Titanium (Ti)
  - Vanadium (V)
  - Chromium (Cr)
  - Manganese (Mn)
  - Iron (Fe)
  - Cobolt (Co)
  - Nickel (Ni)
  - Copper (Cu)
  - Zinc (Zn)
  - Bromine (Br)
  - Lead (Pb)
- Organic carbon
- Elemental carbon
- Soluble ions
  - Chloride (Cl^-)
  - Nitrate (NO_3^-)
  - Sulphate (SO_4^{2-})
  - Oxalate
  - Phosphate
  - Methanosulfonate (MSA)
  - Sodium (Na^+)
  - Ammonium (NH_4^+)
  - Magnesium (Mg^{2+})
  - Calcium ($Ca^{2+)}$
  - Potassium (K^+)
- Anhydrous sugars (woodsmoke)
  - Levoglucuosan
  - Mannosan

Results spreadsheet of chemical analysis

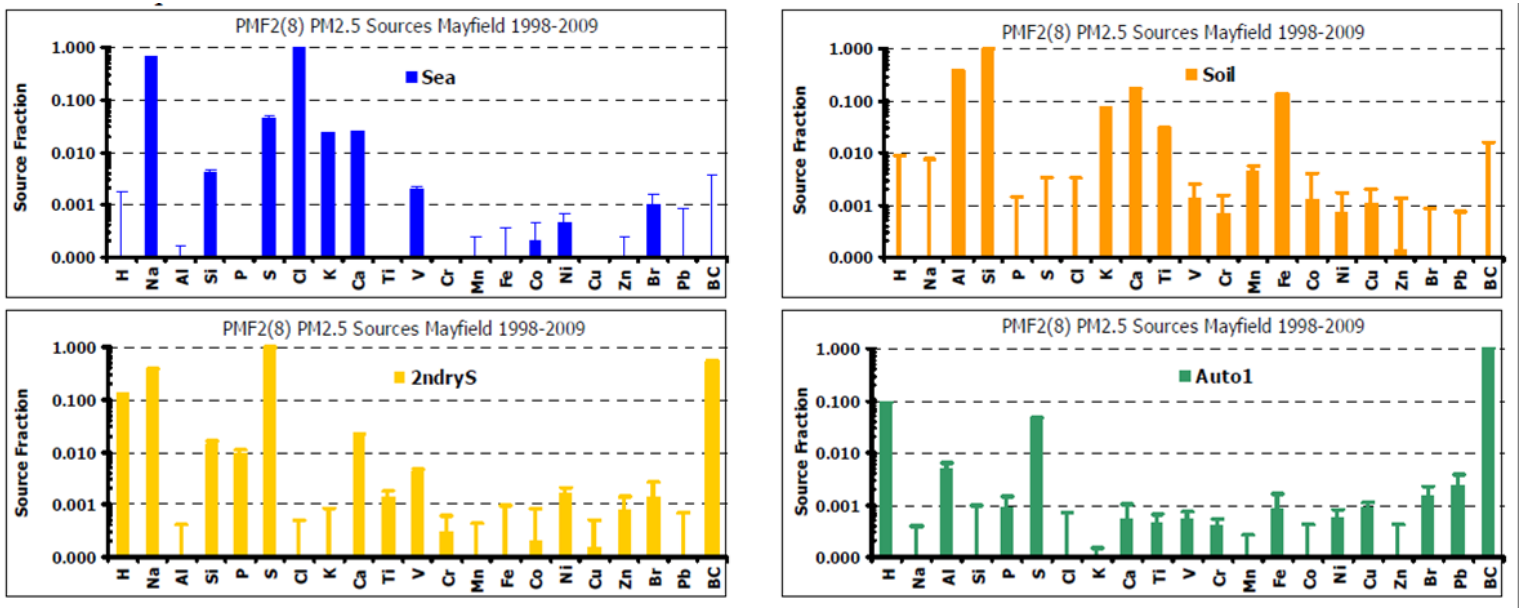
	A	B	C	D	E	F	G	H	I	J	K	L	M
1		Na+	Mg2+	Cl-	NH4+	SO42-	NO3-	Levoglu	Mannos	OC1	OC2	OC3	OC4
2	Date	*ng/m3*	*ng/m3*	*ng/m3*	*ng/m3*	*ng/m3*	*ng/m3*	*ng/m3*	*ng/m3*	*ng c/m3*	*ng c/m3*	*ng c/m3*	*ng c*
3	4/01/2012	475.0	61.4	20.9	389.1	1926.3	136.4	7.8	0.2	389.3	823.5	1917.7	65
4	7/01/2012	748.5	89.5	537.8	120.8	1095.9	185.9	7.2	0.2	181.0	366.7	717.1	24
5	10/01/2012	799.9	97.0	234.4	324.7	1793.3	741.9	2.9	0.2	223.9	560.6	970.5	42
6	13/01/2012	491.5	58.3	582.7	68.4	506.2	51.0	14.2	0.2	225.4	422.0	879.7	32
7	16/01/2012	476.6	58.1	129.9	188.5	1187.4	279.4	1.1	0.2	134.5	353.9	525.3	19
8	19/01/2012	410.2	51.2	16.6	572.0	2505.9	75.2	2.2	0.2	165.0	329.1	425.4	25
9	22/01/2012	879.1	104.5	866.7	180.9	1245.4	159.7	7.6	0.2	69.1	231.9	393.7	11
10	25/01/2012	459.9	52.4	400.7	71.7	633.1	125.6	2.2	0.2	33.8	157.2	239.0	6
11	28/01/2012	490.4	58.4	377.6	145.1	952.6	95.4	0.2	0.2	70.9	223.5	310.2	10
12	31/01/2012	698.9	85.1	659.0	106.9	901.4	142.8	2.6	0.2	114.4	293.2	530.3	17
13	3/02/2012	94.0	10.5	3.6	262.1	1008.8	23.6	2.7	0.2	58.4	139.6	208.4	8
14	6/02/2012	364.3	48.7	9.8	992.1	3727.6	19.6	7.5	0.2	183.4	459.8	478.5	35
15	9/02/2012	924.3	110.5	978.6	167.7	1138.4	193.2	2.7	0.2	180.4	366.7	603.3	13
16	12/02/2012	125.0	14.9	2.3	333.2	1279.4	25.4	12.1	0.2	107.2	248.6	437.2	19
17	15/02/2012	250.6	30.9	145.5	110.1	598.4	128.8	1.9	0.2	95.9	231.5	357.5	16
18	18/02/2012	176.8	25.7	2.4	1117.3	3712.1	30.9	7.4	0.2	173.9	530.6	457.1	30
19	21/02/2012	214.6	21.1	29.2	181.4	932.6	82.0	8.6	0.2	94.0	208.5	339.1	14
20	24/02/2012	166.1	20.8	6.5	255.3	1061.0	16.3	2.4	0.2	82.5	256.9	450.4	20
21	27/02/2012	245.1	33.9	12.4	138.8	849.3	127.7	3.9	0.2	138.8	398.6	846.0	34
22	1/03/2012	356.1	37.2	42.4	133.7	1053.1	123.4	0.2	0.2	187.1	494.3	1423.1	53
23	4/03/2012	399.7	50.7	241.4	128.6	735.1	237.3	27.6	2.7	72.4	337.8	705.2	30
24	7/03/2012	398.2	38.8	115.8	115.4	893.8	259.8	2.4	0.2	119.4	218.6	437.0	18

20+ species

100+ days

Analysis using Positive Matrix Factorisation (PMF)

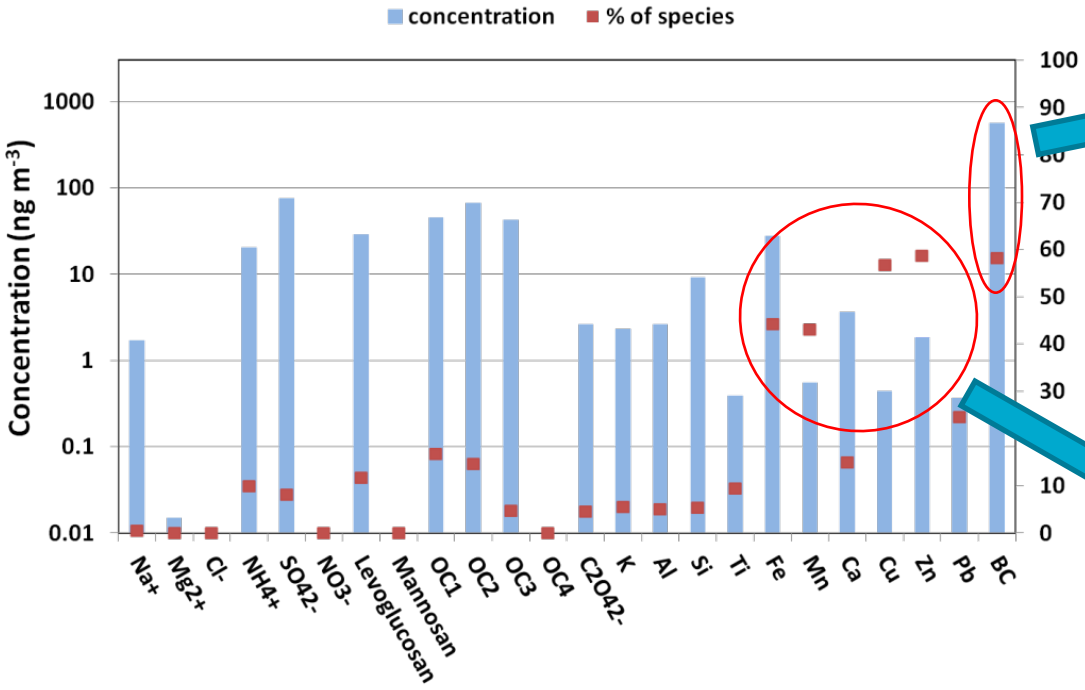
- PMF is a statistical data analysis tool with output of
  - fingerprint profiles
  - fingerprint contributions to total PM2.5



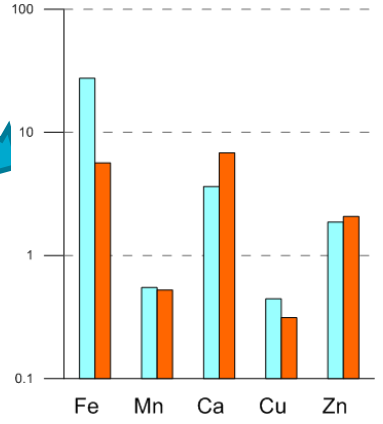
PMF fingerprints → Sources of PM2.5

- PMF fingerprints can include
  - single source
  - multiple sources
  - secondary particles that form in the atmosphere
- Interpretation of fingerprints to determine sources using:
  - information about known sources
  - knowledge of atmospheric chemistry
  - wind sector analysis
  - seasonal variations

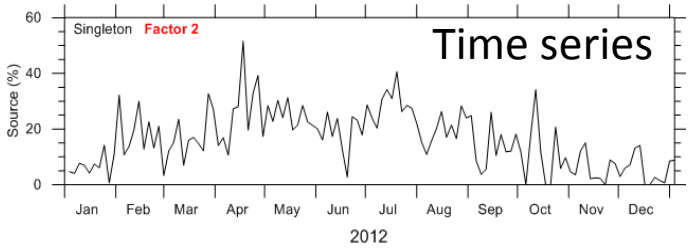
Diesel/Industry factor



OC/EC ratio



Compare with emissions data



OC/EC ratio in Upper Hunter PMF factors

Factor	OC/EC ratio
Diesel/Industry	0.3
Sea salt	1.0
Industry aged sea salt	1.6
Secondary sulfate	1.8
Soil	3.4
Domestic woodsmoke	3.8
Secondary nitrate	6.0
Biomass burning	11.4

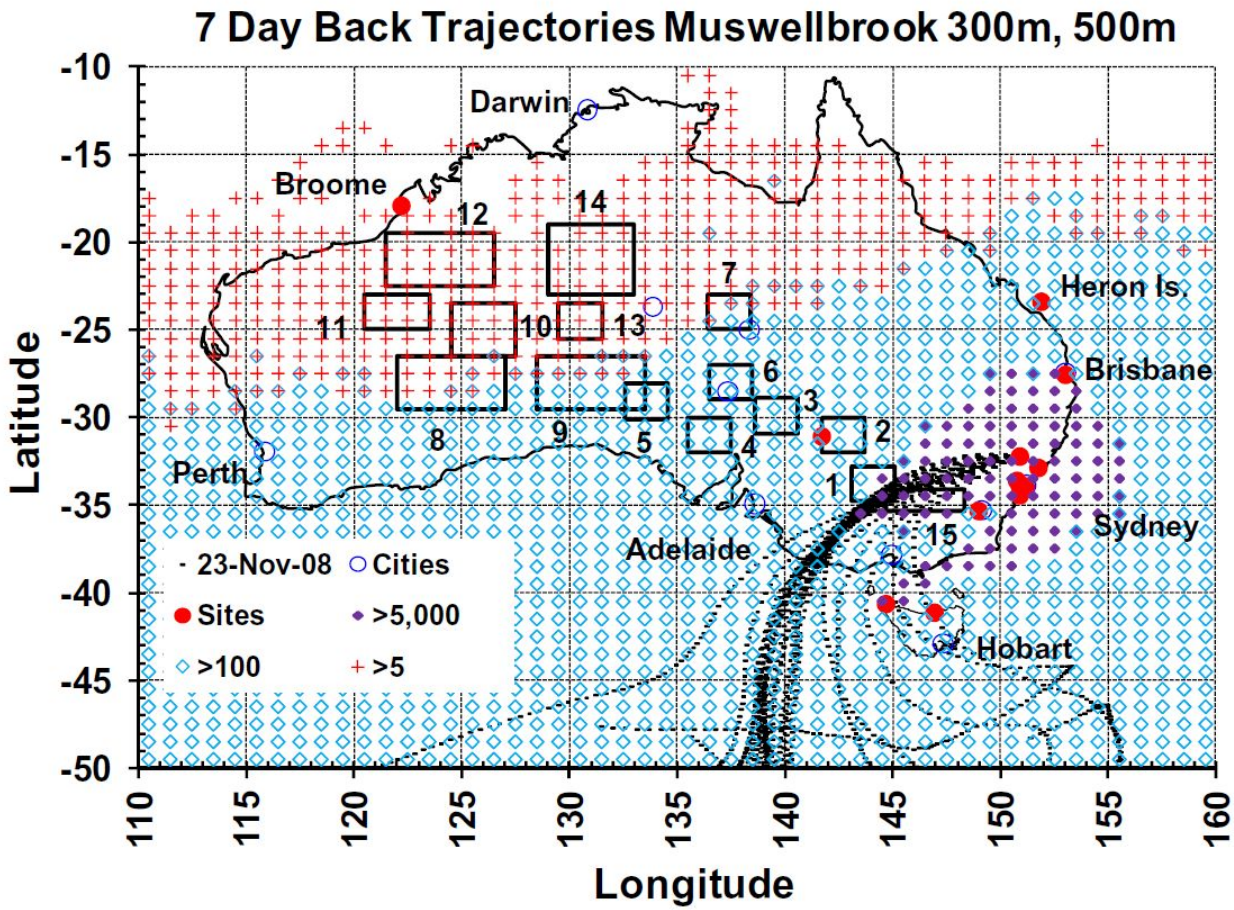
Pinpointing sources with wind data

Diesel/Industry factor

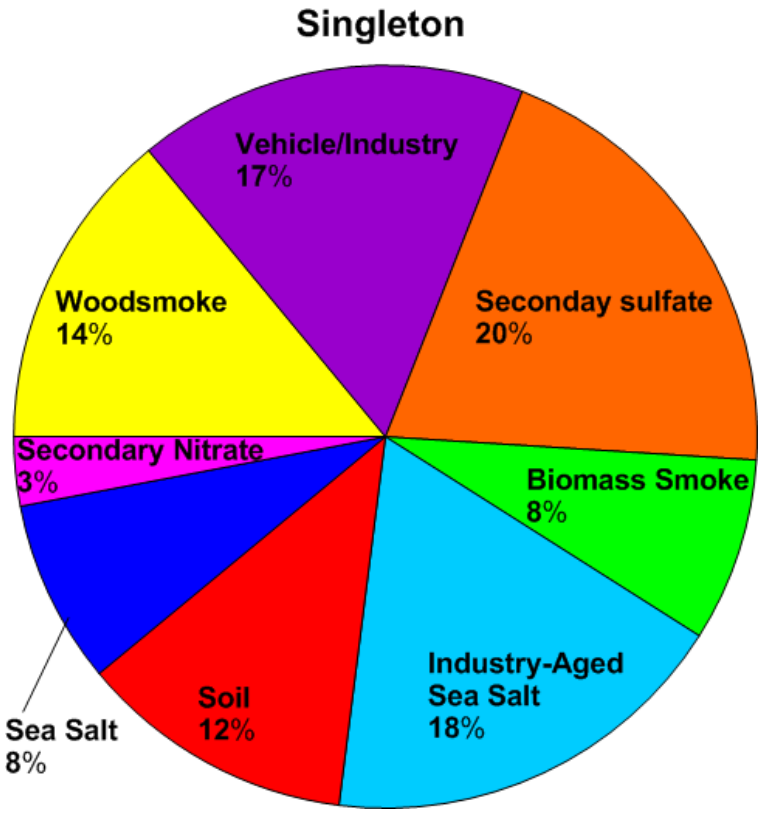
Soil factor

Sea salt factor

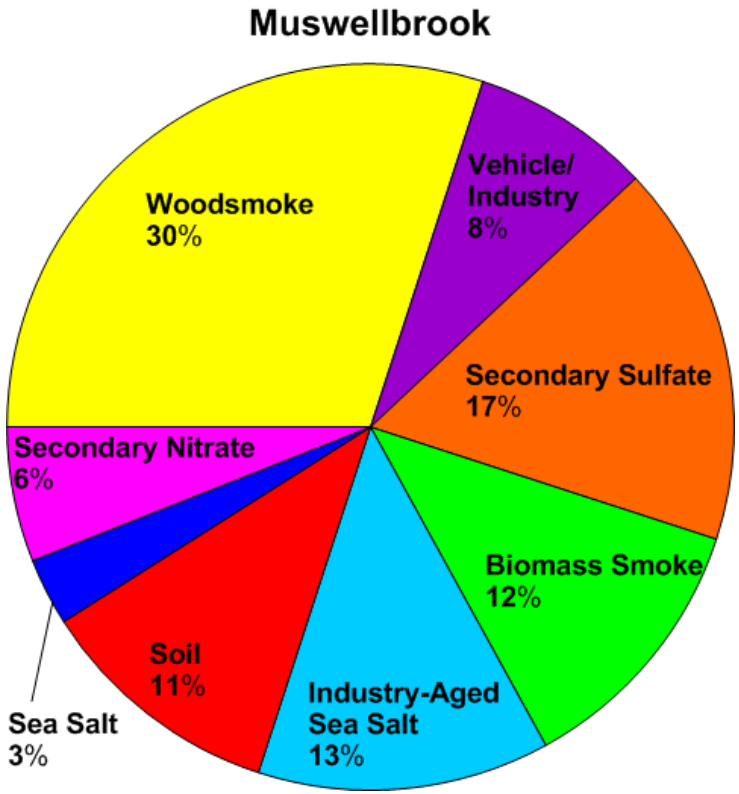
Back trajectory analysis to identify sources



Summary of $PM_{2.5}$ results for Upper Hunter



Annual average 6 µg m^{-3}



Annual average 8 µg m^{-3}

Conclusions

- Ambient $PM_{2.5}$ is a complex mix of chemical species from many sources and with a wide range of sizes
- 45-60% of the mass of diesel engine emissions are elemental carbon (soot)
- OC/EC ratio for diesel emissions is much lower than other sources
- Source apportionment (PMF) can identify the fraction of diesel emissions in ambient $PM_{2.5}$, and also its sources

Thank you

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