Measurement of Dioxin Emissions from Bushfires in Australia

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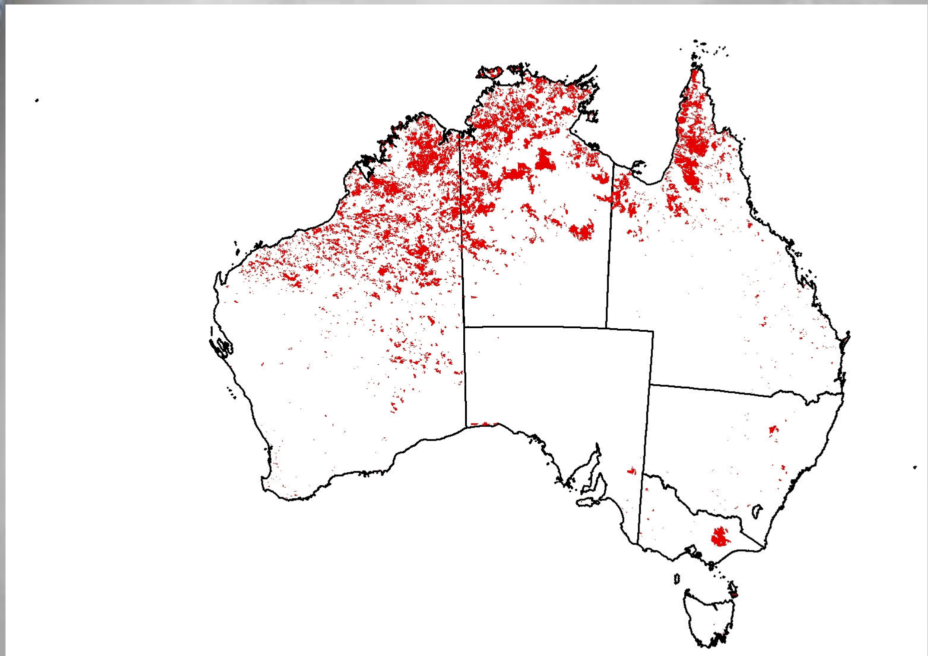


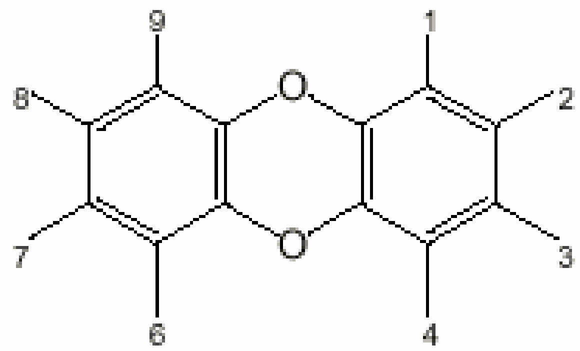
In 2006: 66 Mha

16% of NT,10% of WA, 6% of Qld.

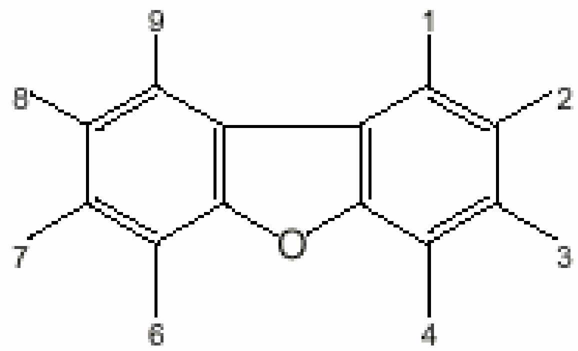
8% of Australia

That produces a lot of dioxins

Dioxins



Dibenzo-p-dioxin



Dibenzofuran

- 210 PCDDs & PCDFs
- the 2,3,7,8 dioxins and furans are toxic
- 7 PCDDs, 10 PCDFs are assigned toxicity weightings
- listed in the Stockholm Convention on POPs

Inventories

Environment Australia (2002)

1994

	Emission factors (ug TEQ.t)	Emission (g TEQ)
Savanna and temperate grasslands	0.5-10	3.5-68
Prescribed burning, stubble burning	0.5-10	62- 1240
Wildfires	0.5-28	7-400
Total		**72-1700** ***(46%-81%)***

National Dioxin Program (2004)

2001

	Mass (t)	Emission factor ug TEQ/t		Emission g	
		To air	To land	To air	To land
Savanna and Temperate Grassland	216,173,000	5	4	1081	865
Prescribed burning of forests	3,505,000	5	4	18	14
Wildfires	10,588,000	5	4	53	42
Agricultural residues- wheat	3,492,000	0.5	10	2	35
Agricultural residues- coarse grains	6,044,000	0.5	10	3	60
Agricultural residues- sugar	653,300	0.5	10	0	7
Total				**1156**	**1023**
All sources				**1410** ***82%***	**1300** ***79%***

Bushfires are the largest source and the most uncertain source in the Inventory

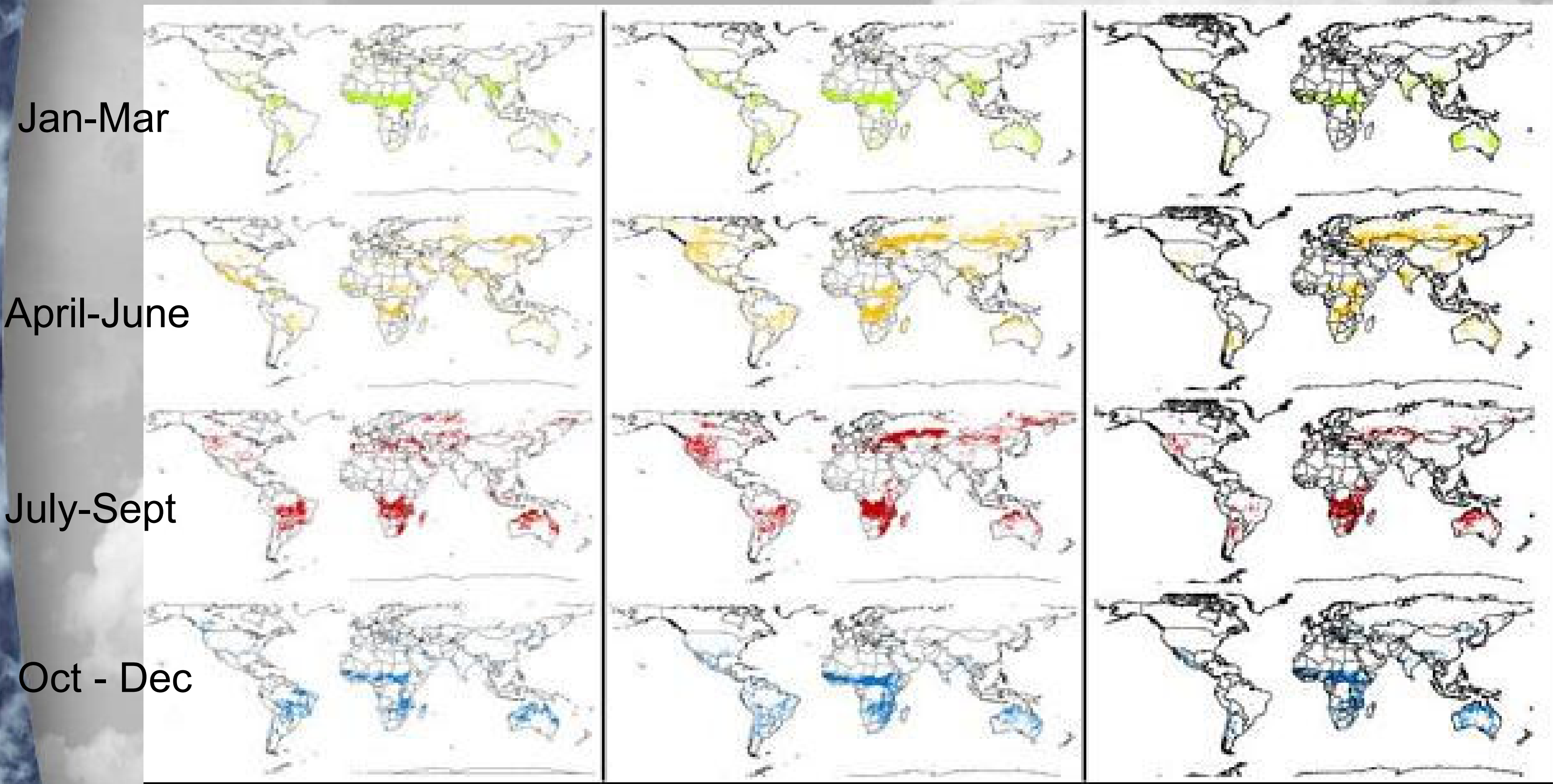
Outline

- Fires
- Measuring emission factors
- Potential measurement artifacts
- Residues
- Dispersion
- Emerging issues

Fires in Australia

CSIRO

Three estimates of global biomass burning in 2002



M. Simon, S. Plummer, F. Fierens, J. J. Hoelzemann, and O. Arino (2004)

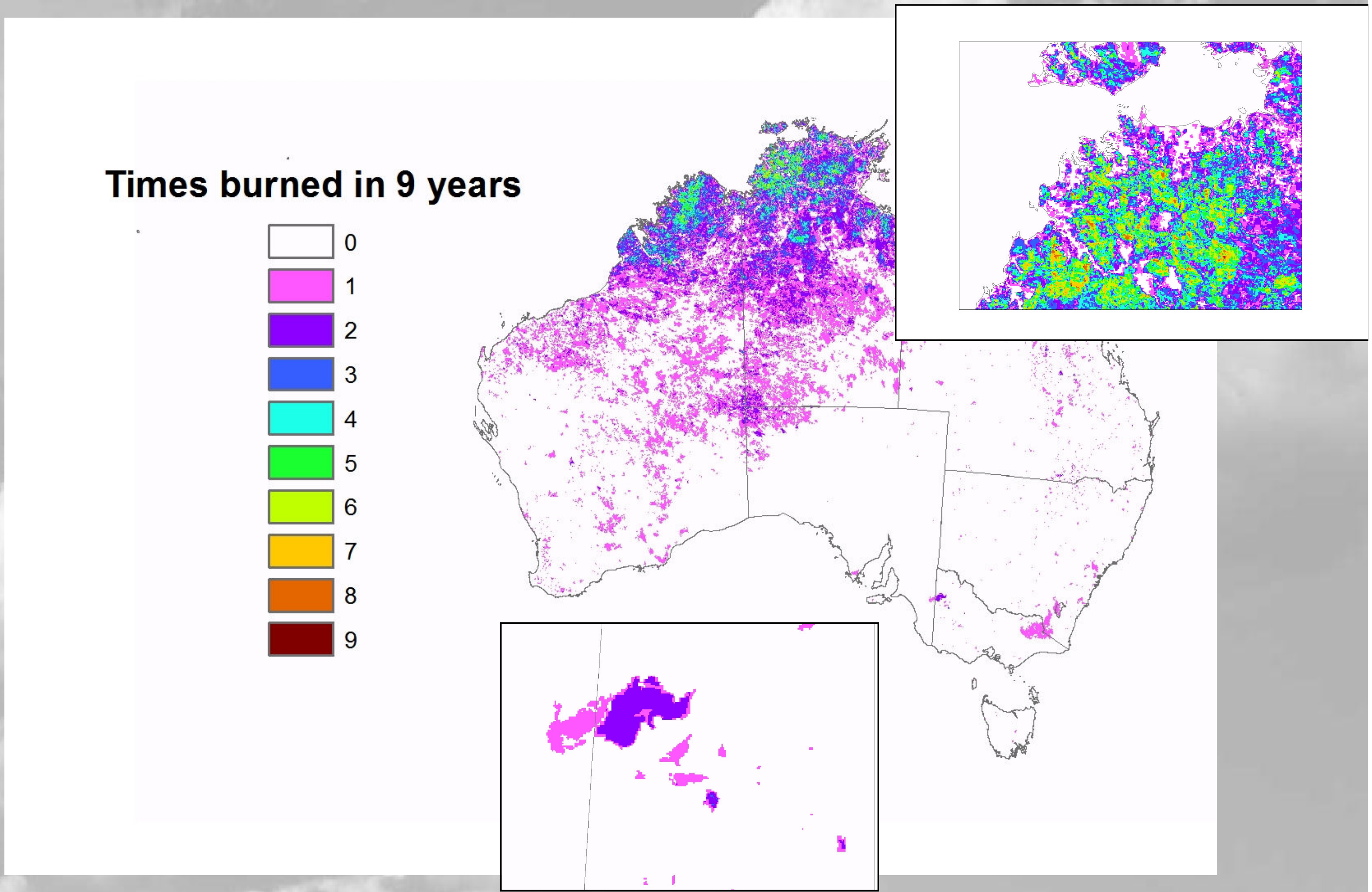
Global emissions

	GLOBSCAR		GBA-2000	
	Area (Mha)	%	Area (Mha)	Percentage
Africa	121	57.4%	224.6	64%
North/Central America	11	5.2%	6.2	2%
South America	13.8	6.5%	11.9	3%
Australia	18	8.5%	55.9	16%
Asia	21.2	10.1%	27.1	8%
Europe	5.8	2.8%	4.3	1%
Russia	20	9.5%	22.2	6%
Global	**210.7**	**100.0%**	**352.2**	**100%**

Australian fire scar analysis
1999/2000 = 52 Mha

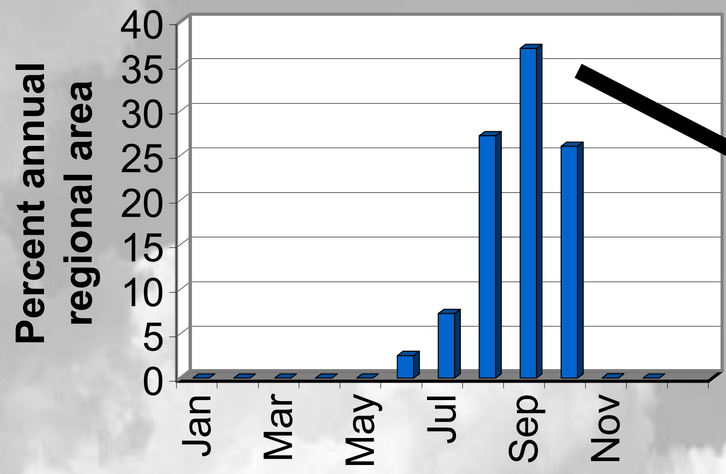
From Kasischke and Penner (2004)

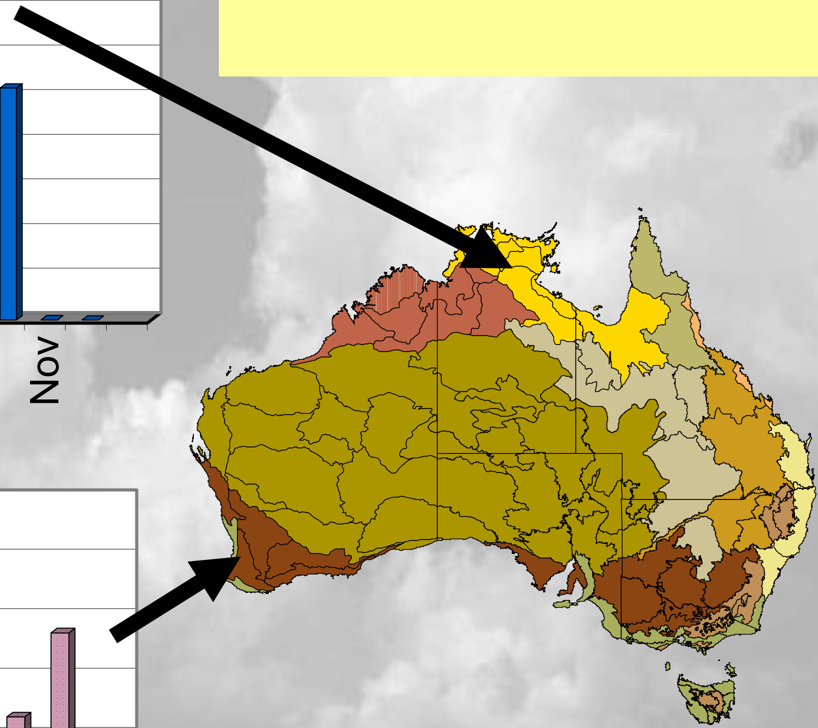
Fire frequency 1998 to 2006

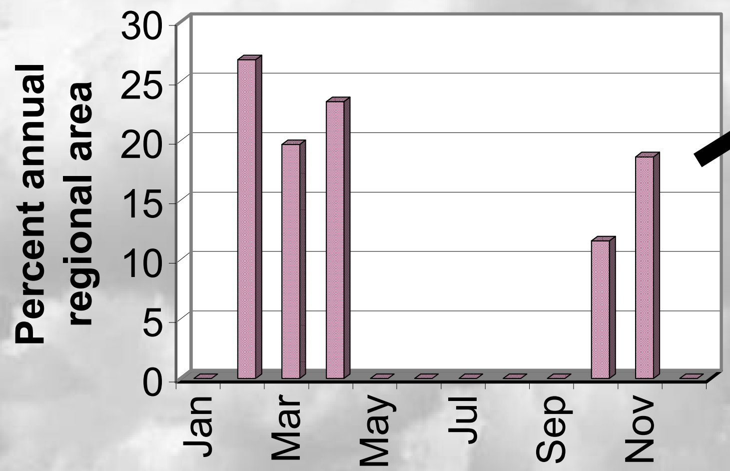


When fires happen

- Fires are fuel limited
- There is always an ignition source







- Fires are **NOT** fuel limited
- Ignition/propagation is weather dependent

Wildfire Causes

Most fires have anthropogenic ignition causes

Causes of fires in State Forests and National Parks in Victoria 1990-1999.

Cause	Number of fires	%
Lightning	*1602*	*25*
Forestry personnel	255	4
Recreational users	600	10
Residents/Farmers	2117	33
Unknown/Arson	1627	26
Unreported	99	2

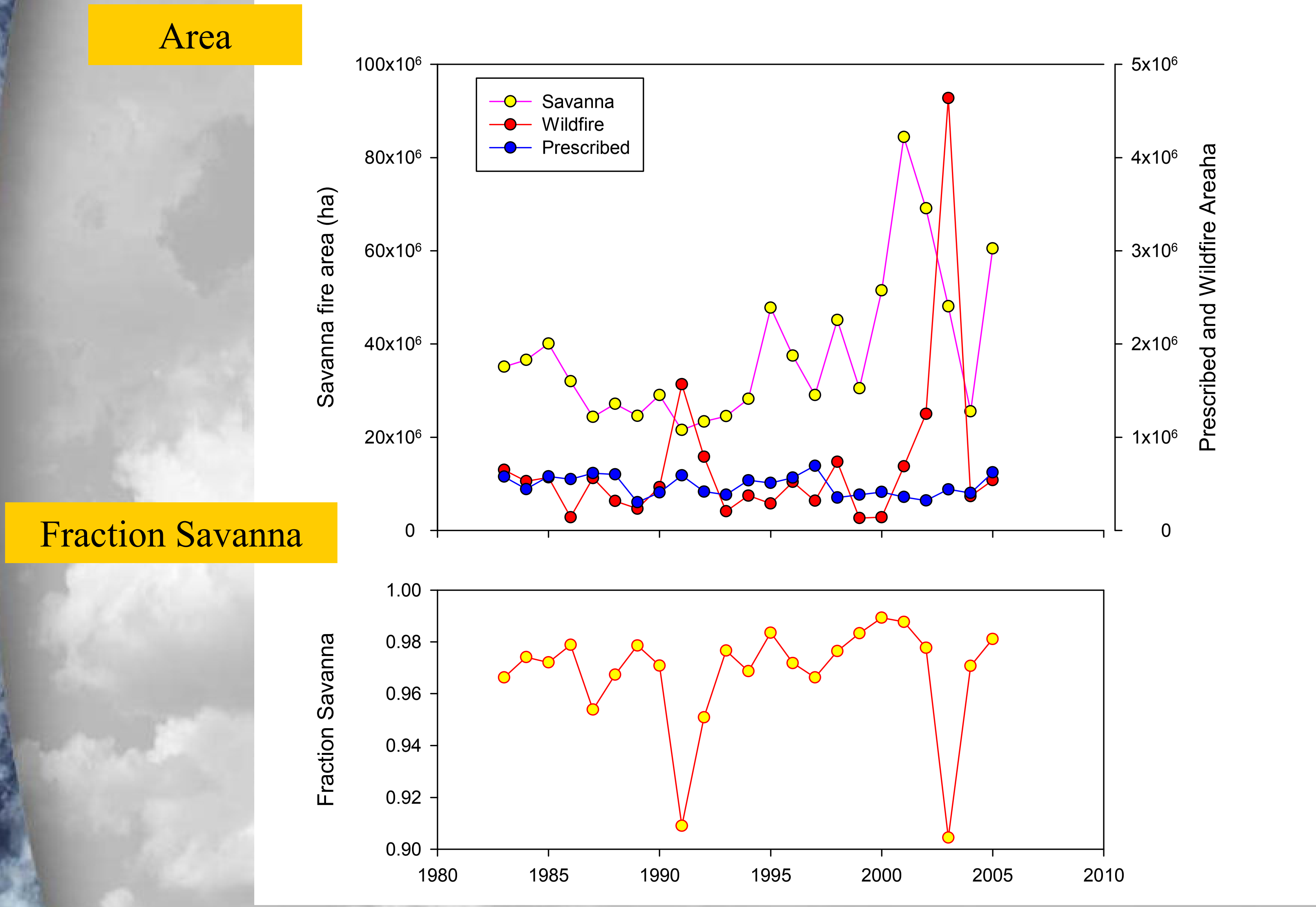
Australian carbon emission estimates (2000)

Vegetation	% Total carbon emitted								
	NSW	Tas	WA	SA	Vic	Qld	NT	ACT	AUST
Tropical savannah	0	0	89	0	0	88	100	0	89
Open woodland and temperate grassland	10	6	-	34	5	0	0	0	
Forest, Prescribed	15	13	2	0	41	2	0	10	2
Forest, Wildfire	49	80	8	0	33	3	0	90	6
Cereals	24	1	2	66	21	3	0	0	3
Sugar	2	0	0	0	0	4	0	0	0
Total	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**
% National emission	1.2	0.12	36.1	0.50	0.4	15.6	40.9	0.0	100
%National emission excluding tropical savannah	1.2	0.1	3.9	0.5	0.4	1.9	0.0	0.0	8.1

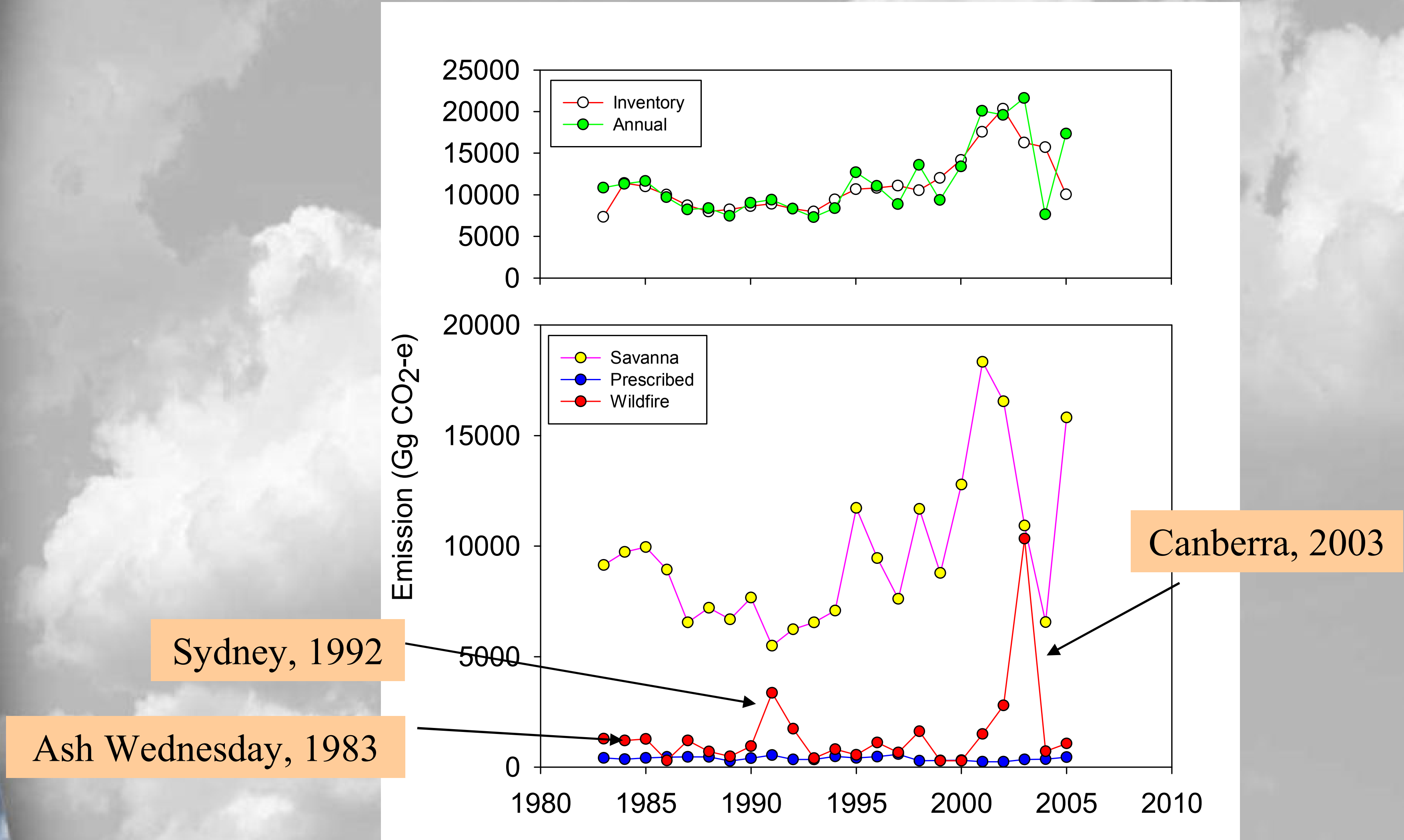
Most of the emissions are from savanna woodland and arid grassland in Northern Australia where the population is low.

Wildfires, agricultural and prescribed fires are where most of the population live-in the South and along the East Coast

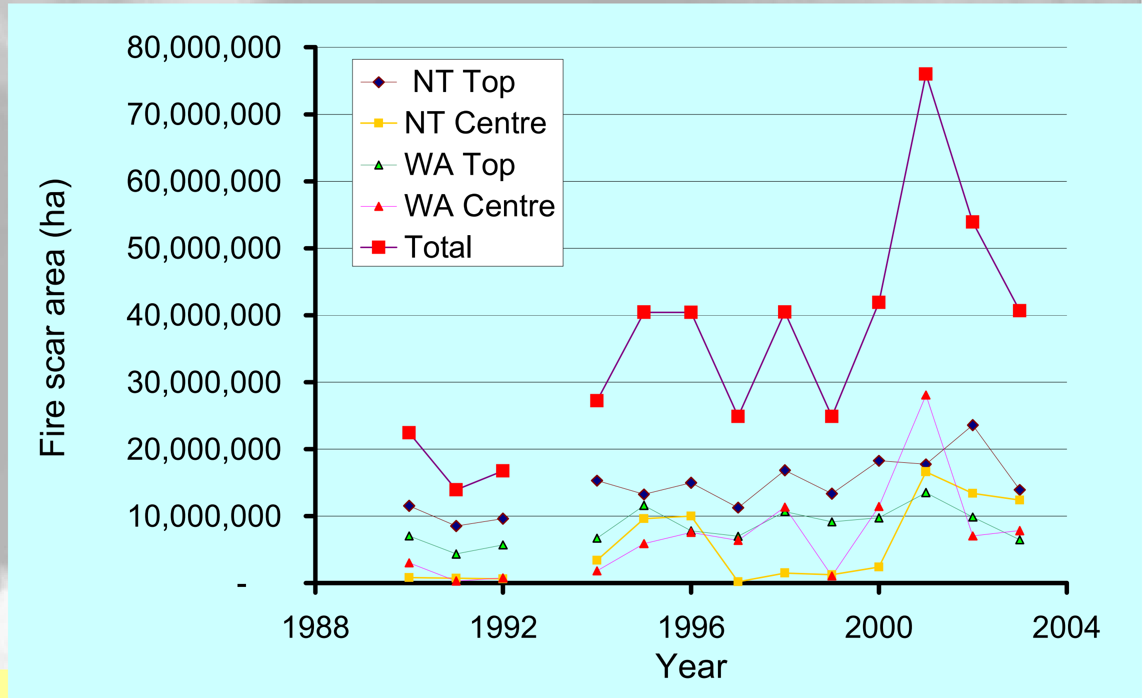
Fire Area

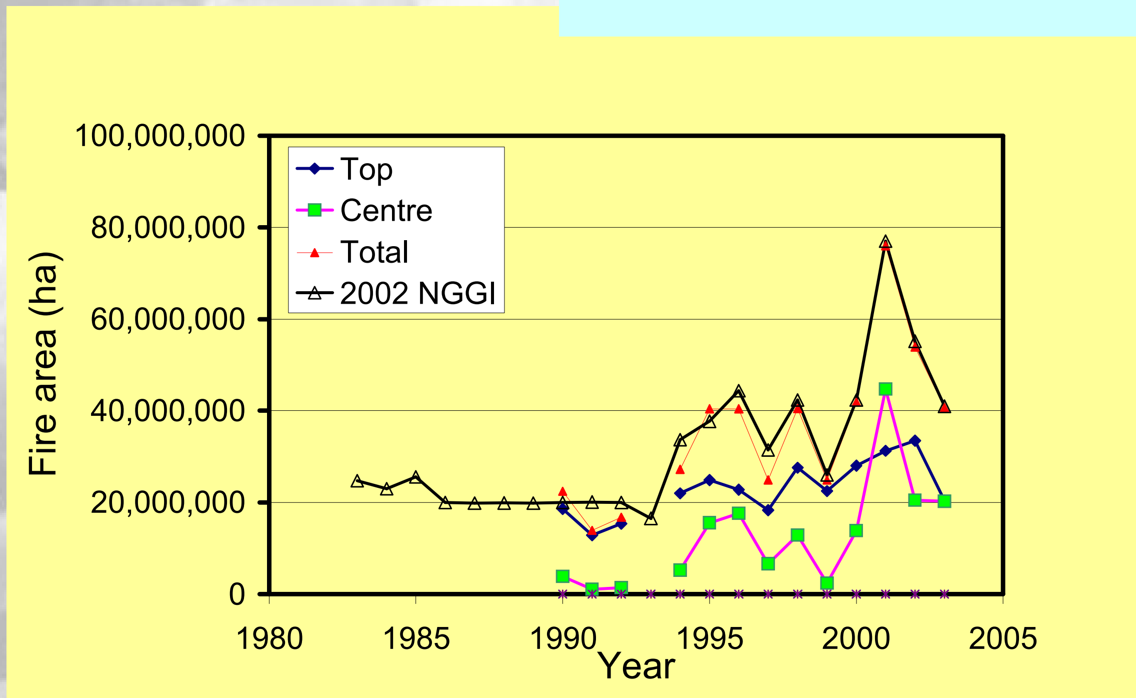

Area
Fraction Savanna
100x10^6
80x10^6
60x10^6
40x10^6
20x10^6
0
Savanna fire area (ha)
5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
Prescribed and Wildfire Areaha
Savanna
Wildfire
Prescribed
1.00
0.98
0.96
0.94
0.92
0.90
Fraction Savanna
1980
1985
1990
1995
2000
2005
2010

National Emission Timeseries



Inter-annual Variability of Savanna Fires



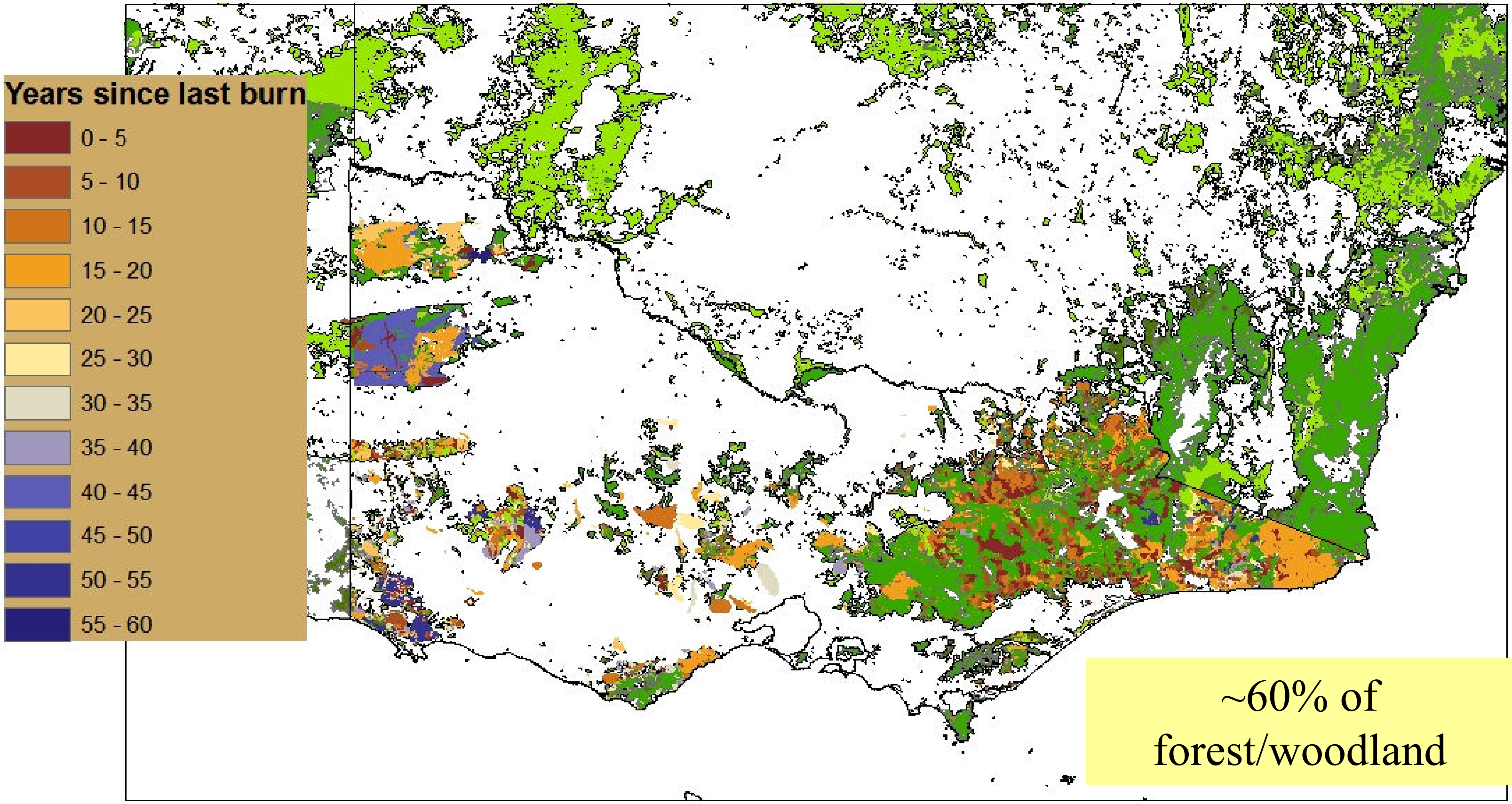


Range min to max

Woodlands ~2

Grasslands ~80

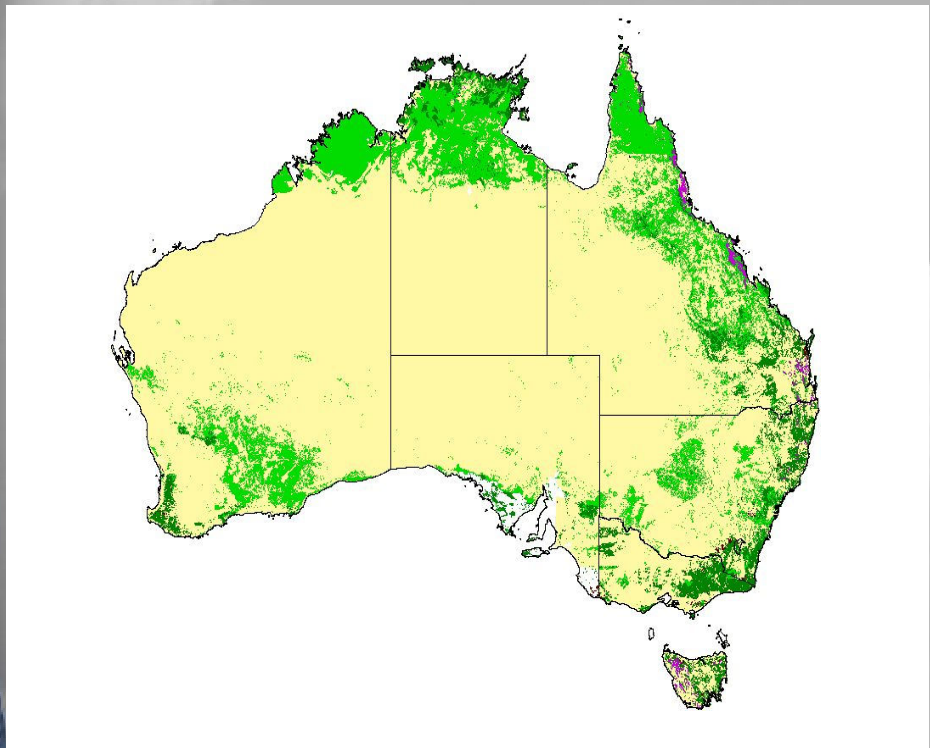
Fire History in Victoria 1940-1999



~60% of forest/woodland

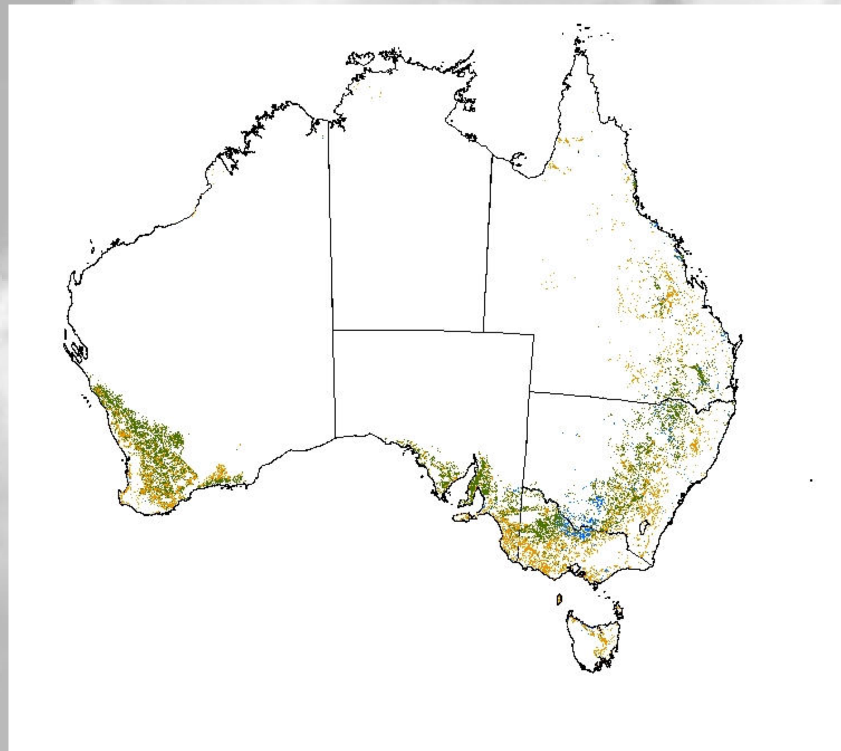
Landscape uses

Forest, woodlands, Arid Grasslands (Wildfire, Prescribed fires)



Agricultural cropping

(Agricultural residues)



Fires are:

- A natural part of the Australian landscape
- Highly variable from year to year
- A major component of the carbon cycle

Fires from land clearing are very different

- Occur once
- Often on topsoils with high carbon content

How do we measure dioxin emissions

Emission = Fuel burned x emission factor

$Fuel_{burned}$ = Area x fuel load x combustion efficiency

How to determine emission factors:

- Direct measurement – mass dioxin emitted/mass fuel burned - possible in laboratory
- From atmospheric concentration measurements using a dual tracer technique – field method

Dioxin emissions from biomass burning

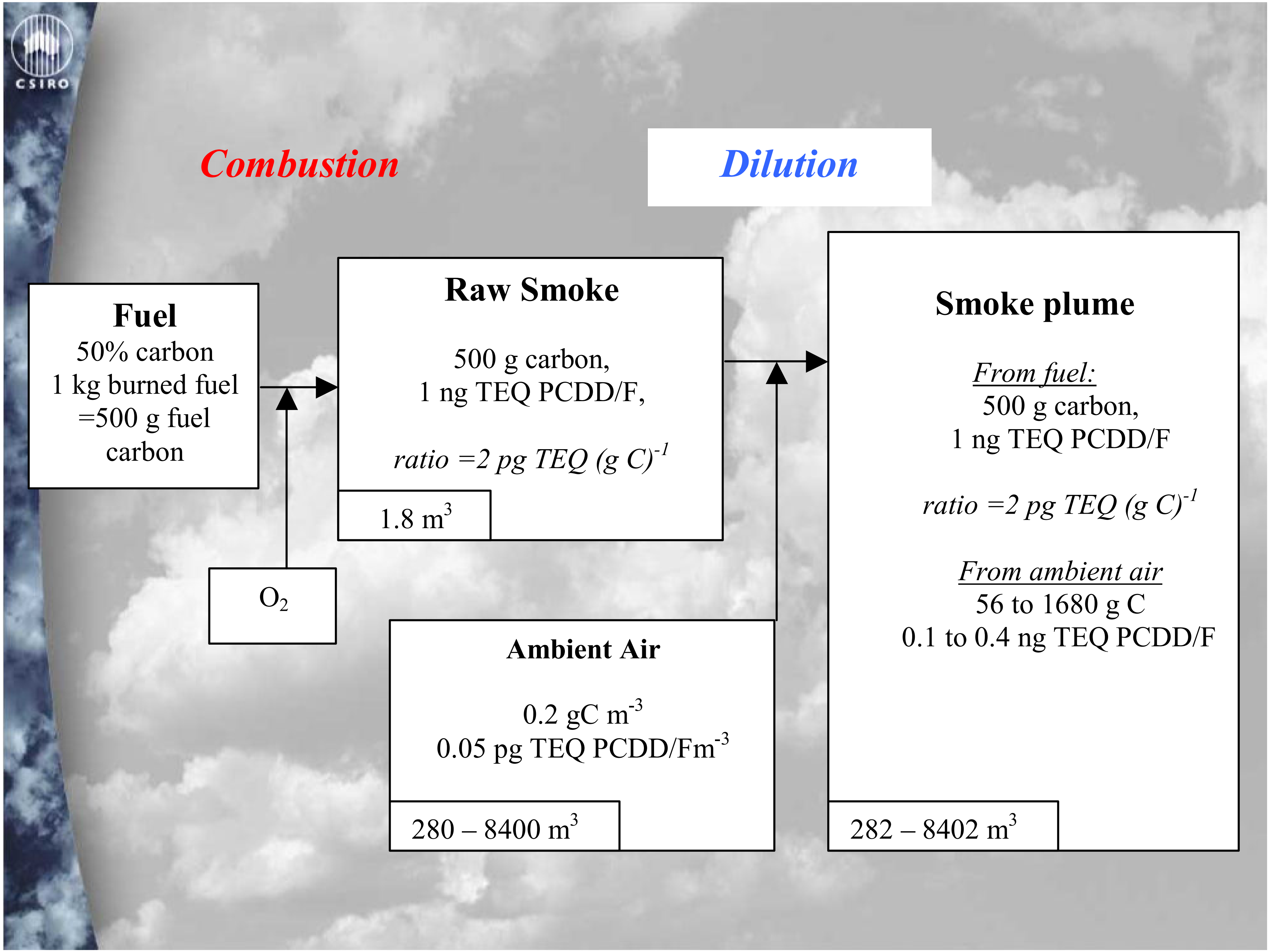
- Surrogate estimates were made using wood combustion heaters were made using open combustion chambers (0.5 to 30 ug TEQ/kg)
- Field measurements (e.g (Prange, Mueller et al. (NRCET)
  - Low rates, OCDD dominated
- Combustion rooms e.g. Gullett and Touati (US EPA)
  - 0.5 - 55 ug TEQ/kg
  - Fuel dependent

Measurement Principle

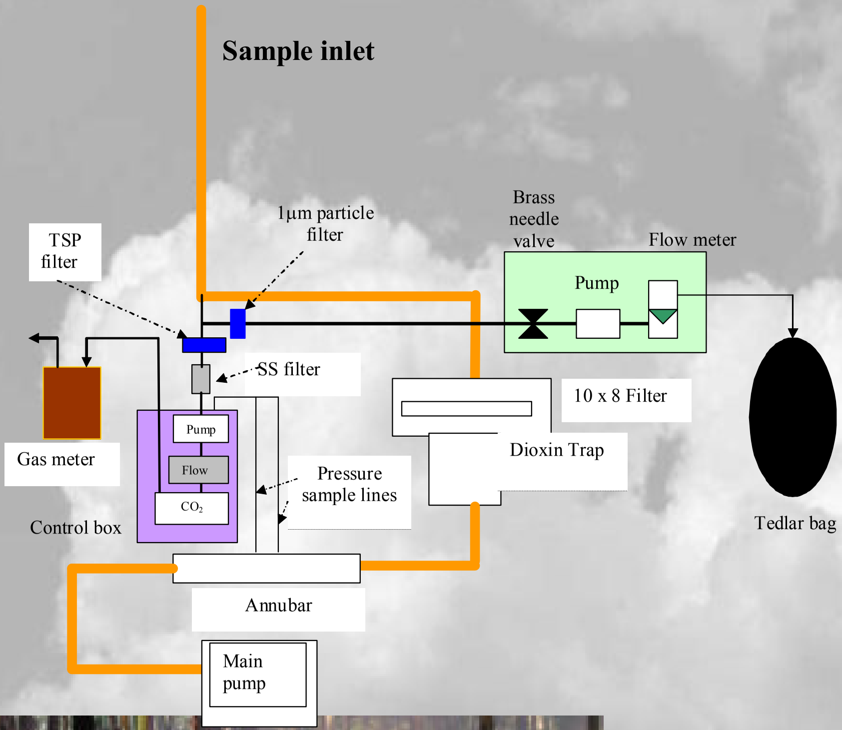
Dual tracer technique

$$E_{PCDD} = E_C \times [PCDD] / [C]$$

Tracer (E_c) is total volatilised fuel carbon


Combustion
Dilution
Fuel
50% carbon
1 kg burned fuel
=500 g fuel
carbon
O_2
Raw Smoke
500 g carbon,
1 ng TEQ PCDD/F,
ratio =2 pg TEQ (g C)$^{-1}$
1.8 m^3
Ambient Air
0.2 gC m^{-3}
0.05 pg TEQ PCDD/Fm^{-3}
280 – 8400 m^3
Smoke plume
From fuel:
500 g carbon,
1 ng TEQ PCDD/F
ratio =2 pg TEQ (g C)$^{-1}$
From ambient air
56 to 1680 g C
0.1 to 0.4 ng TEQ PCDD/F
282 – 8402 m^3

Field sampling



The challenge is to sample sufficient smoke to get a dioxin sample that can be reliably analysed

>5g C, >200 m^3 air, in approx 1h

In the Field

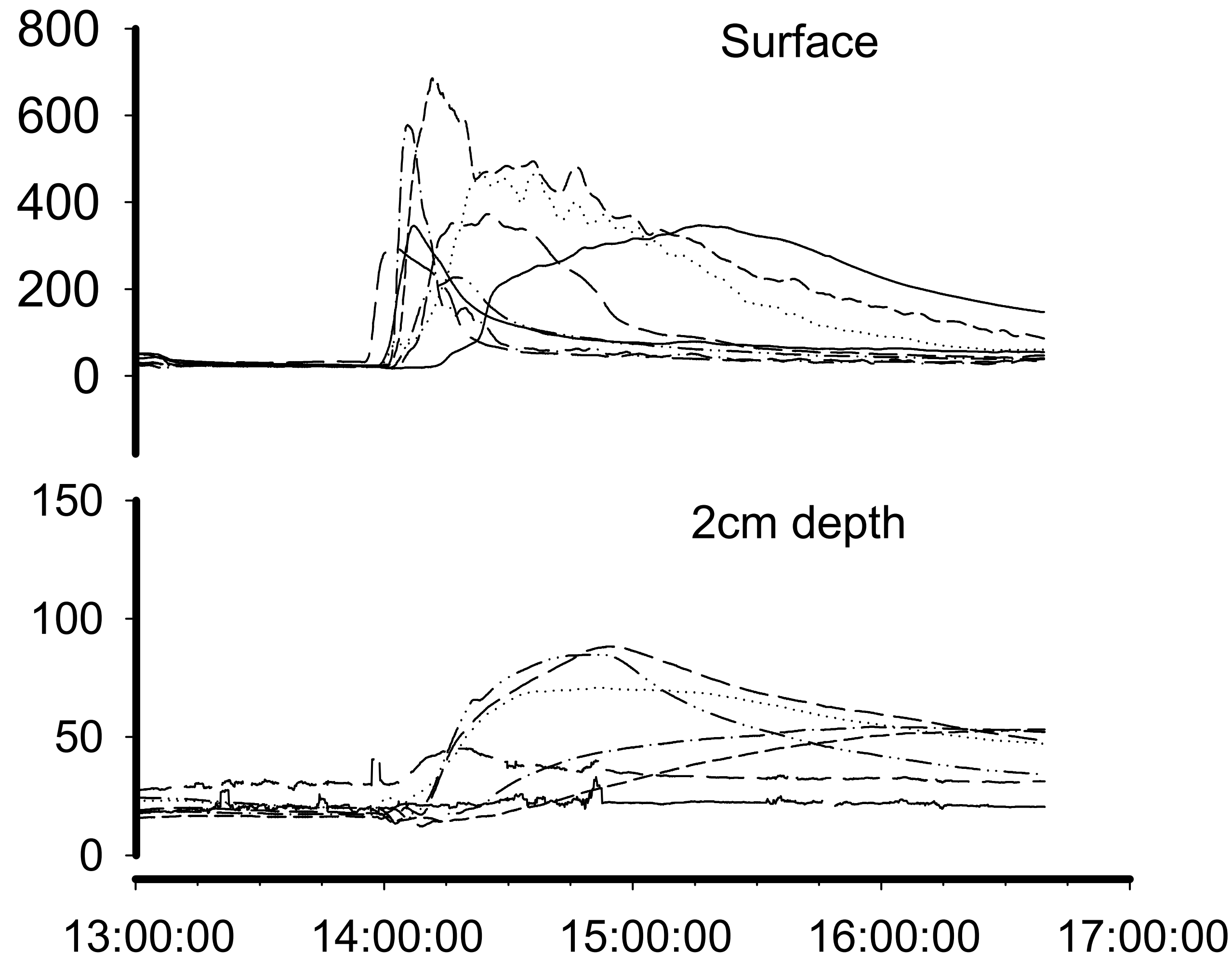


Savanna Fires

Early season

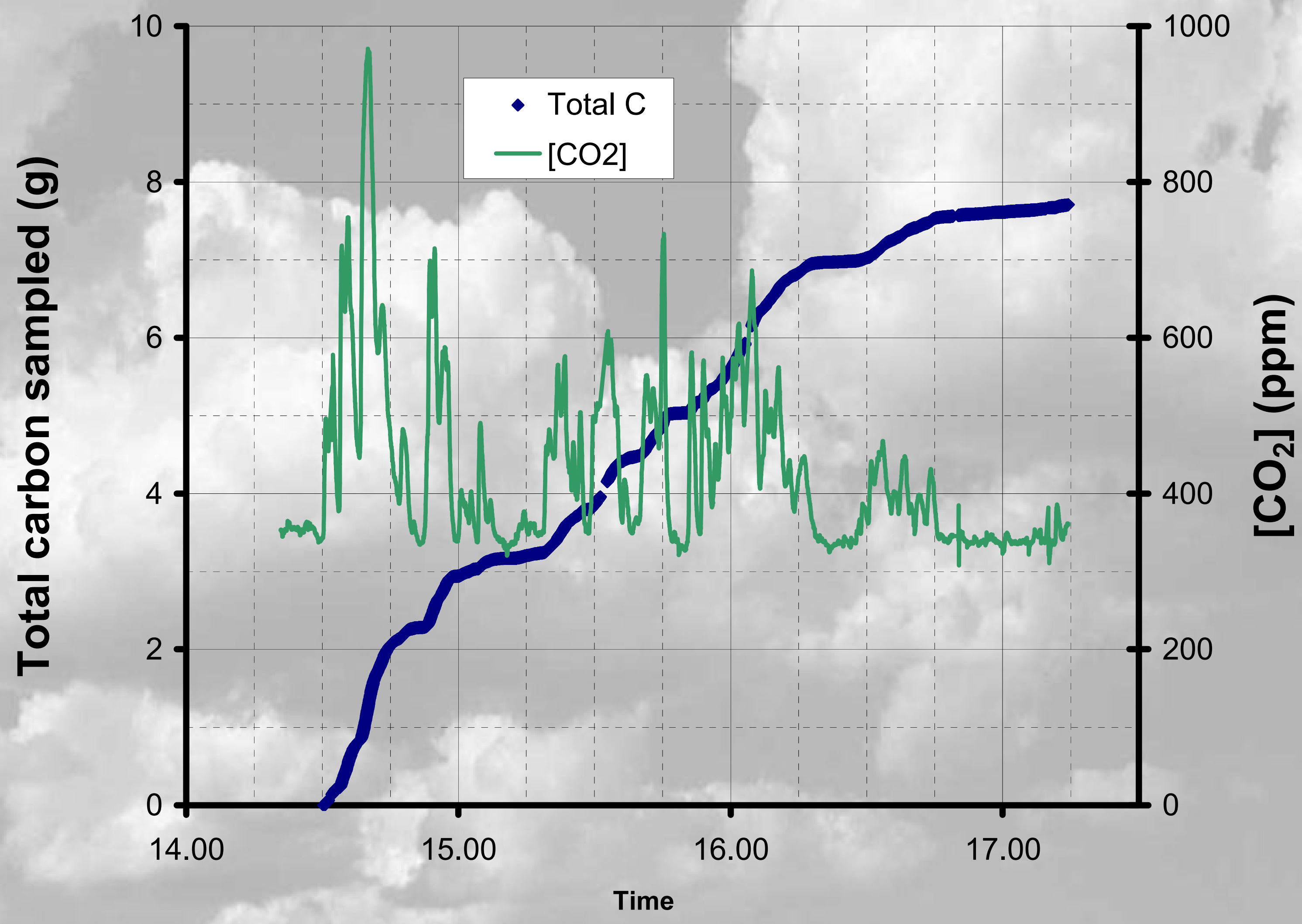
Late season

Fuel bed and soil temperatures Prescribed burn, Victoria

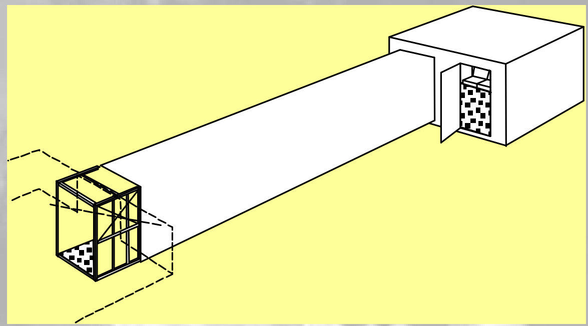


Sugar Cane

CO_2 concentrations near a low intensity prescribed fire



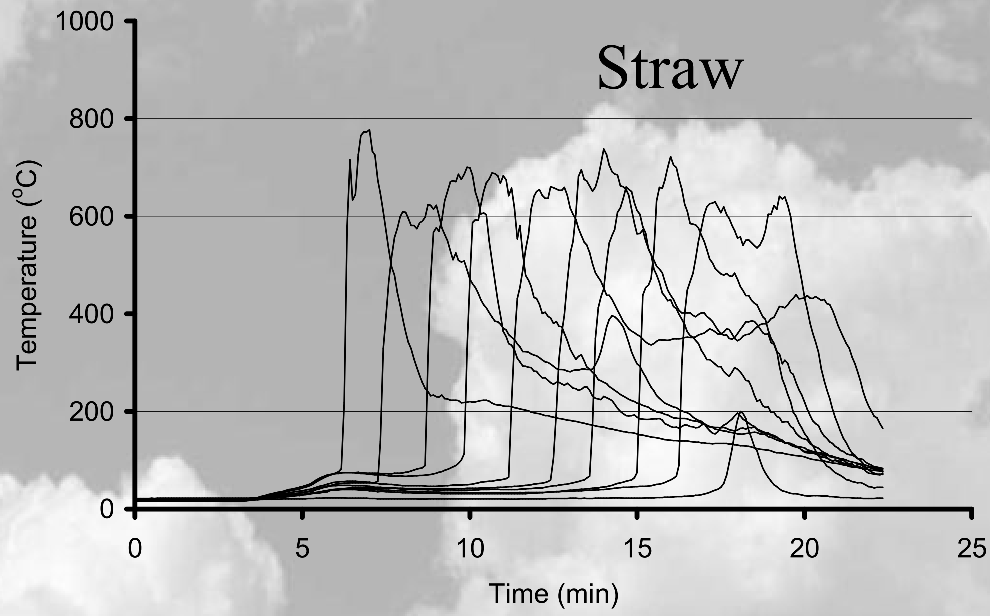
Laboratory sampling

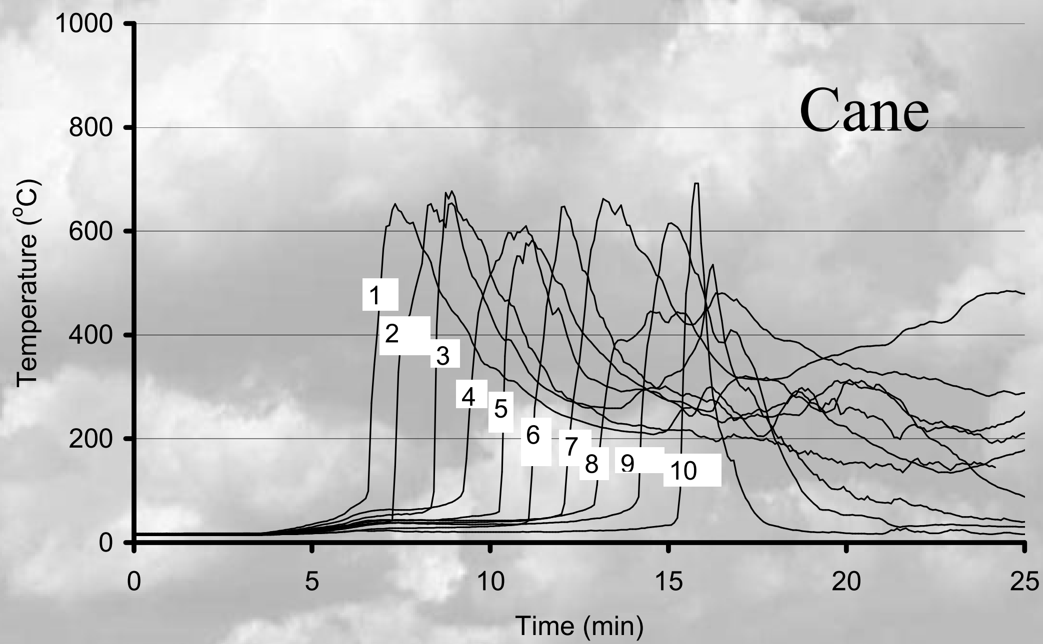


- Fire progresses across a fuel bed on the floor of the corridor
- Smoke is sampled from the exhaust hood
- Simulates a backing fire; either stubble or prescribed fuel reduction fire in forests

Leaf litter
Burn

Timecourse of fire along the bed





In the field- at close quarters

(sampler version 2)

Wildfires

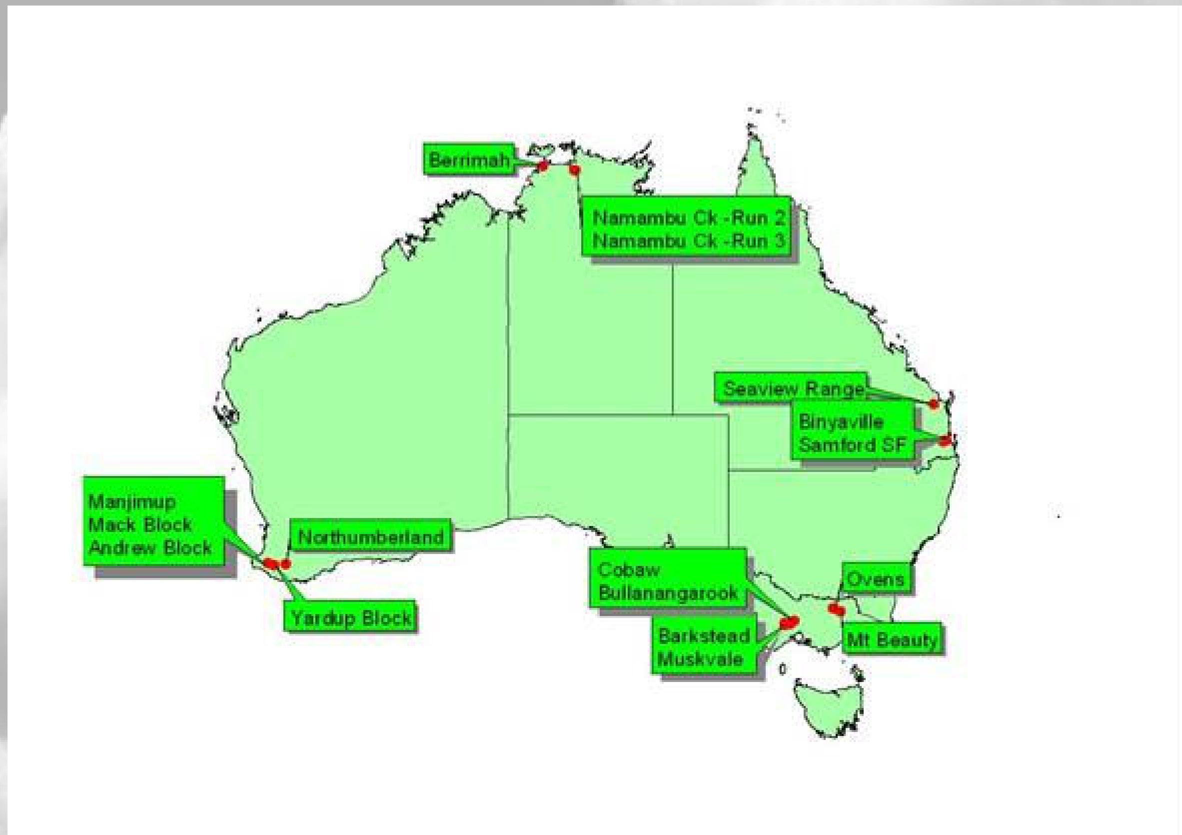
For safety, you never see to fire front.

- The energy release is 50- 100 MW m^{-1} compared with 1 -5 MW m^{-1} for prescribed fires.
- The front can move at 10-20 km h^{-1}

Measurements

CSIRO

Locations of field measurements



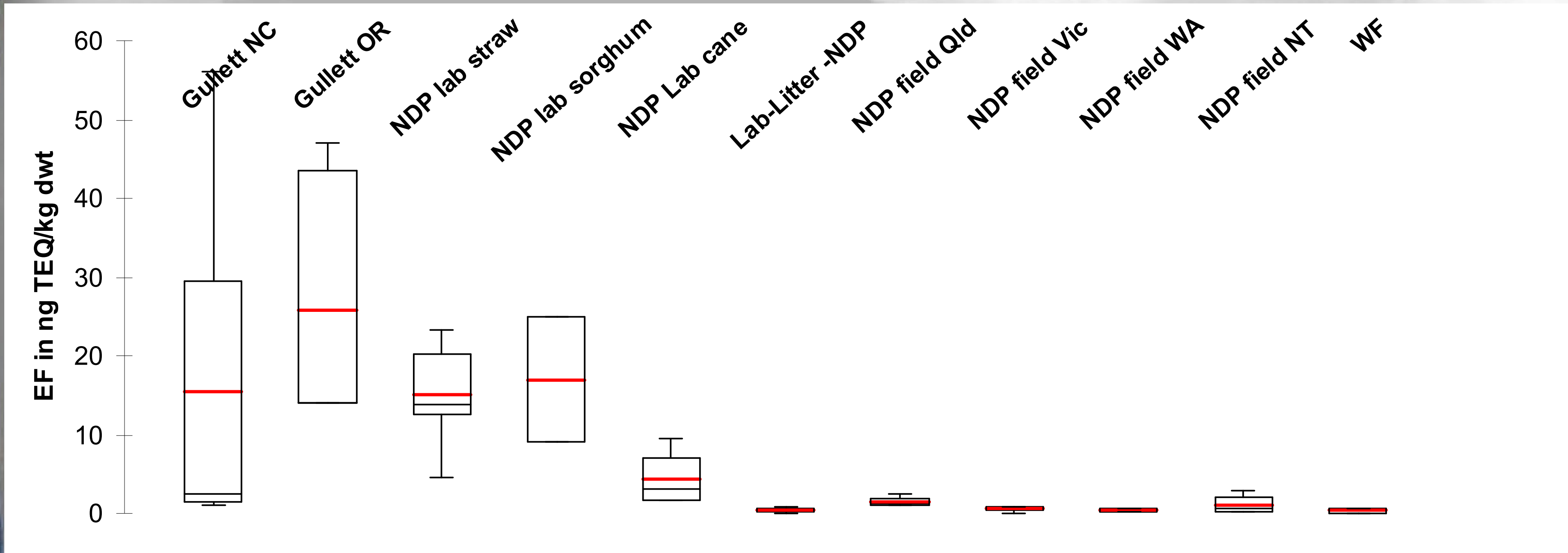
Results

Emission ratios (pg TEQ gC^{-1})

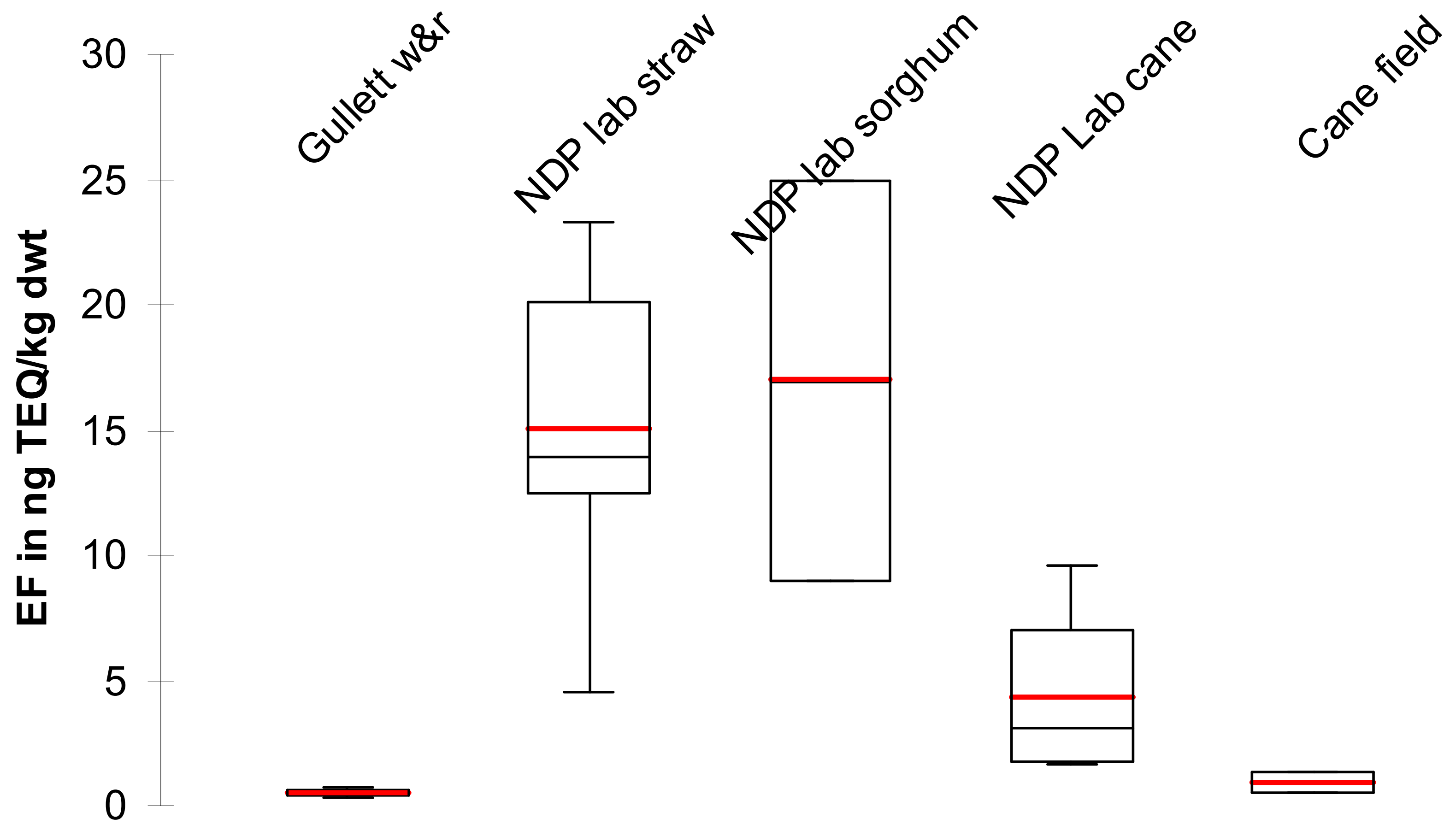
Field samples				
Species	**Cane**	**Prescribed**	**Wildfire**	**Savanna**
PCDD	1.8	1.23	0.65	2.03
PCDF	0.14	0.36	0.13	0.16
PCB	0.07	0.18	0.13	0.07
Total	**1.98**	**1.78**	**0.91**	**2.3**

Laboratory samples				
Species	**Cane**	**Forest**	**Sorghum**	**Straw**
PCDD	3.7	0.42	11.5	11.4
PCDF	5.1	0.33	22.4	18.7
PCB	0.2	0.09	0.35	0.35
Total	**8.9**	**0.83**	**34.2**	**30.5**

Forest and Savanna fuels



Agricultural Residues



Congener Profile for homologue groups (by mass)

	Cane	Wildfire	Savanna	Prescribed
TCDD isomers	1	19	4	16
PeCDD isomers	1	9	3	6
HxCDD isomers	2	21	6	9
HpCDD isomers	11	15	10	9
OCDD	**79**	**17**	**51**	**41**
TCDF isomers	4	11	25	17
PeCDF isomers	0	3	0	1
HxCDF isomers	0	2	0	0
HpCDF isomers	1	1	0	0
OCDF	**2**	**1**	**0**	**0**
Total CDD	**93**	**82**	**74**	**82**

Congener profiles- toxic congeners by mass

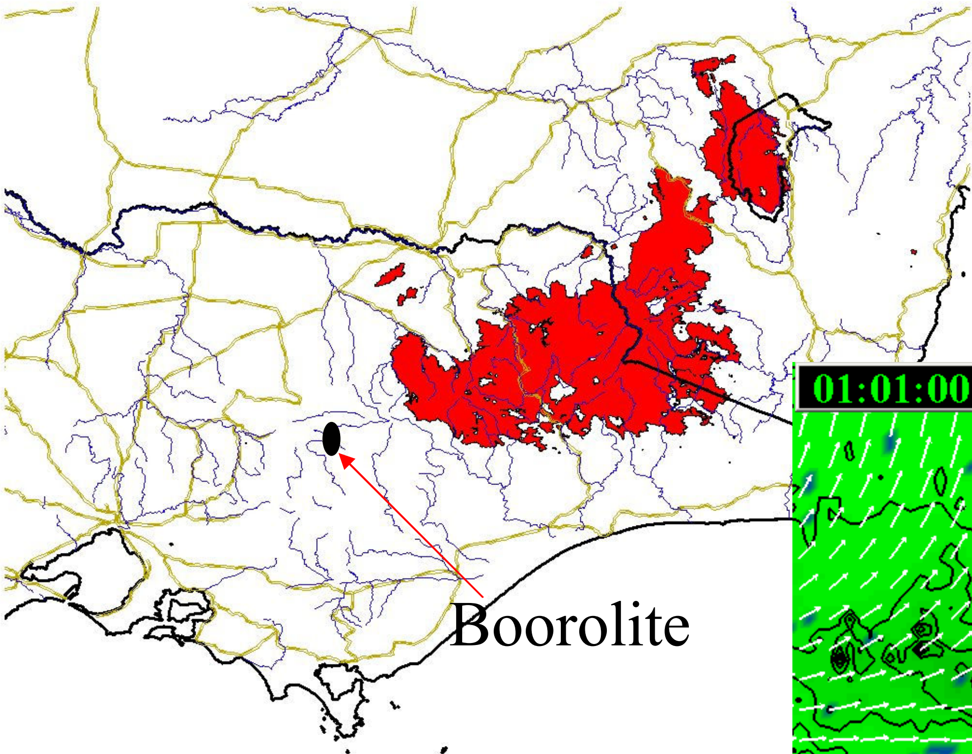
Congener	Cane	Wildfire	Savanna	Prescribed
1,2,3,7,8-PeCDD	0	2	1	0
1,2,3,4,7,8-HxCDD	0	2	0	1
1,2,3,6,7,8-HxCDD	0	2	1	1
1,2,3,7,8,9-HxCDD	0	2	1	1
1,2,3,4,6,7,8-HpCDD	6	24	7	8
OCDD	**91**	**62**	**89**	**88**
OCDF	**2**	**2**	**0**	**0**
Total CDD	**97**	**93**	**99**	**98**

Congener profiles – toxic congeners by toxicity (TEQ)

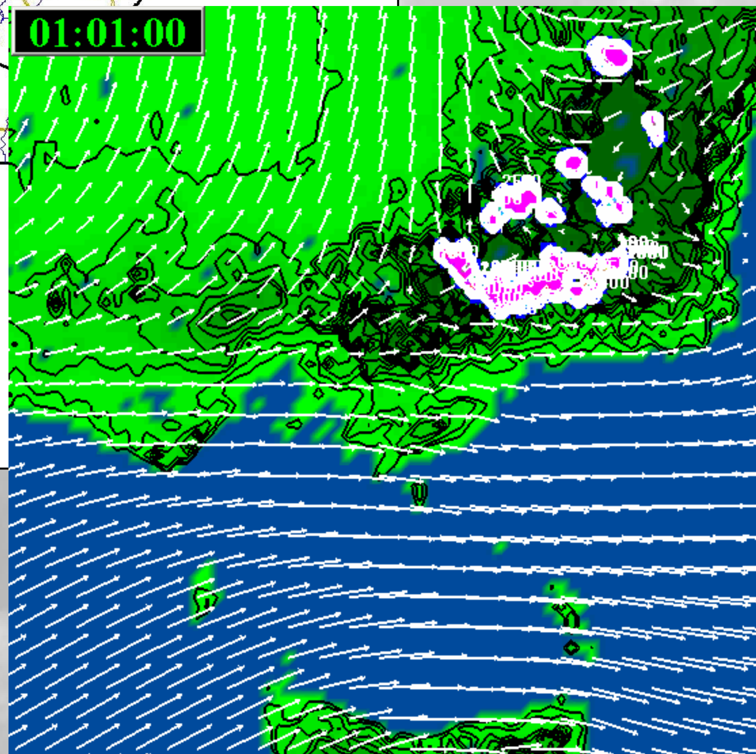
	Cane	Wildfire	Savanna	Prescribed
2,3,7,8-TCDD	12	5	16	7
1,2,3,7,8-PeCDD	47	54	49	40
1,2,3,4,7,8-HxCDD	5	6	4	5
1,2,3,6,7,8-HxCDD	7	7	6	8
1,2,3,7,8,9-HxCDD	2	5	9	7
1,2,3,4,6,7,8-HpCDD	17	7	7	8
OCDD	**3**	**0**	**1**	**1**
2,3,7,8-TCDF	2	1	1	4
1,2,3,7,8-PeCDF	0	1	0	1
2,3,4,7,8-PeCDF	2	9	4	12
Total CDD	**93**	**83**	**93**	**76**

Are wildfires really low emitters of PCDD/PCDF ?

Fire Scar Area from Jan/Feb 2003 bushfires



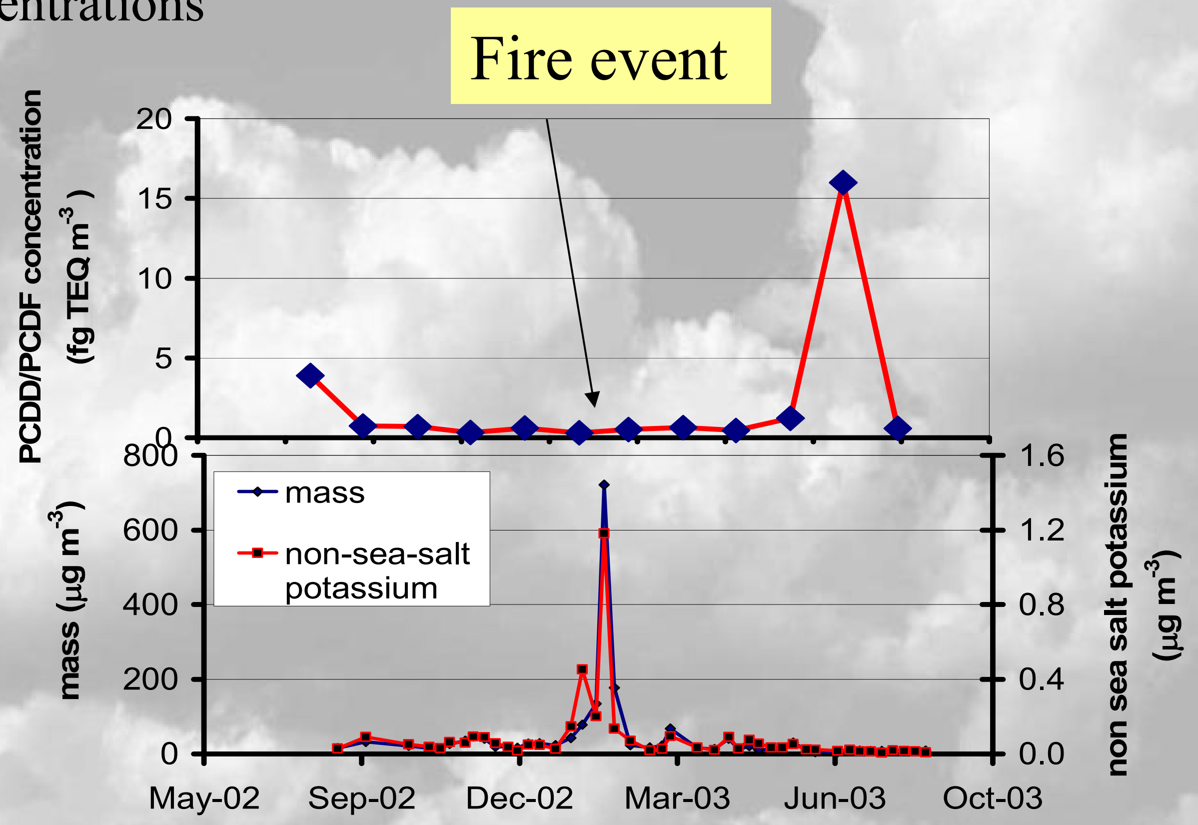
1.7 Mha fire area



The smoke plume from the NE fires impacted Boroolite in Jan/Feb

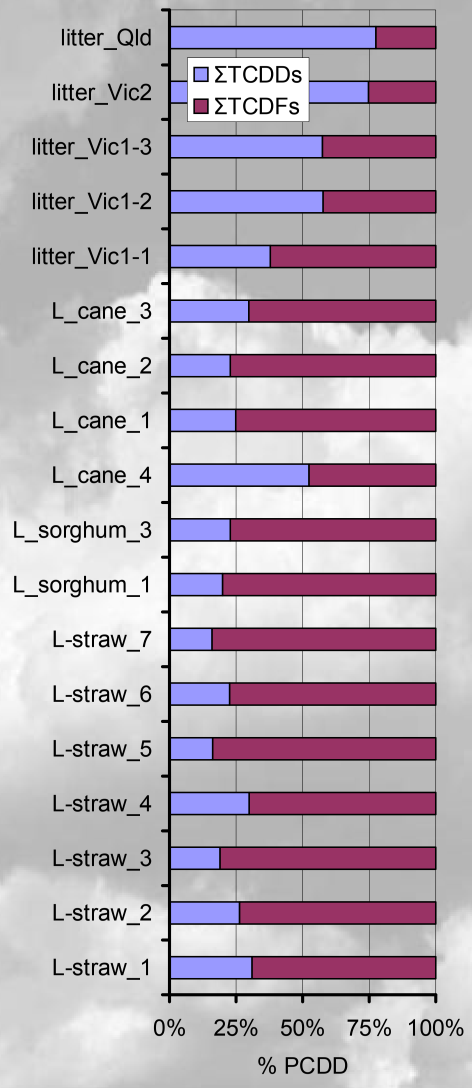
TSP and NSS-K concentrations were very high from impact a dense smoke plume BUT

PCDD/PCDF concentrations were at ambient background concentrations

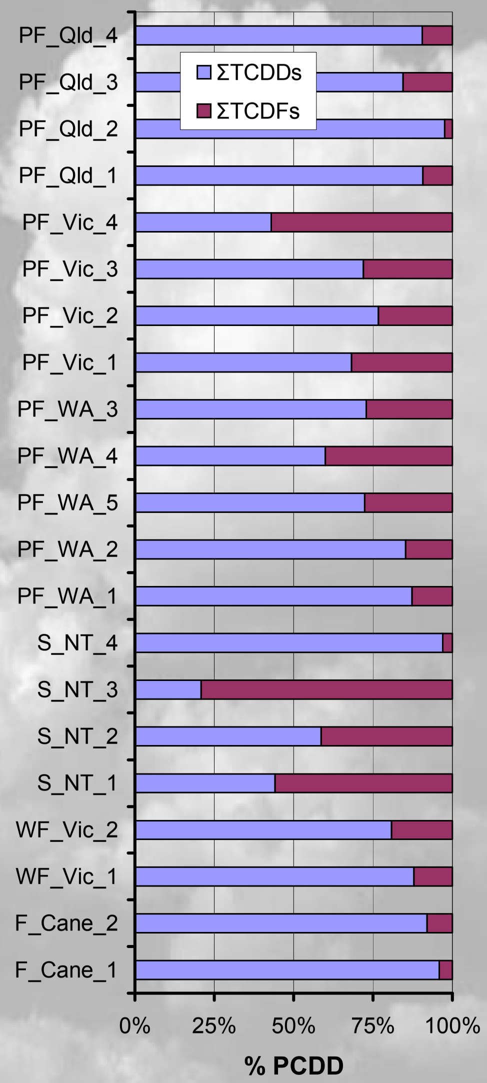


Compare field and laboratory measurements

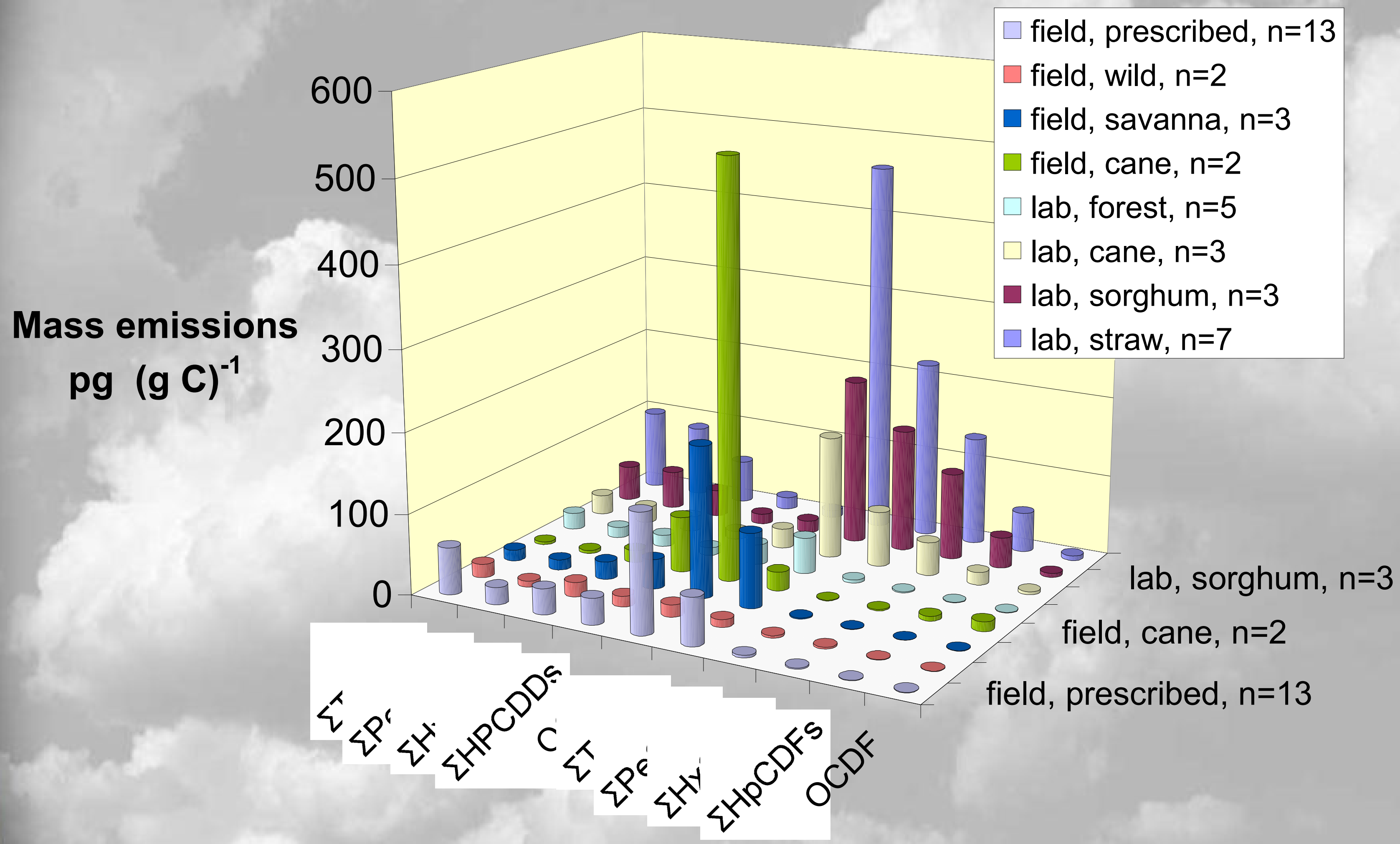
Laboratory tests



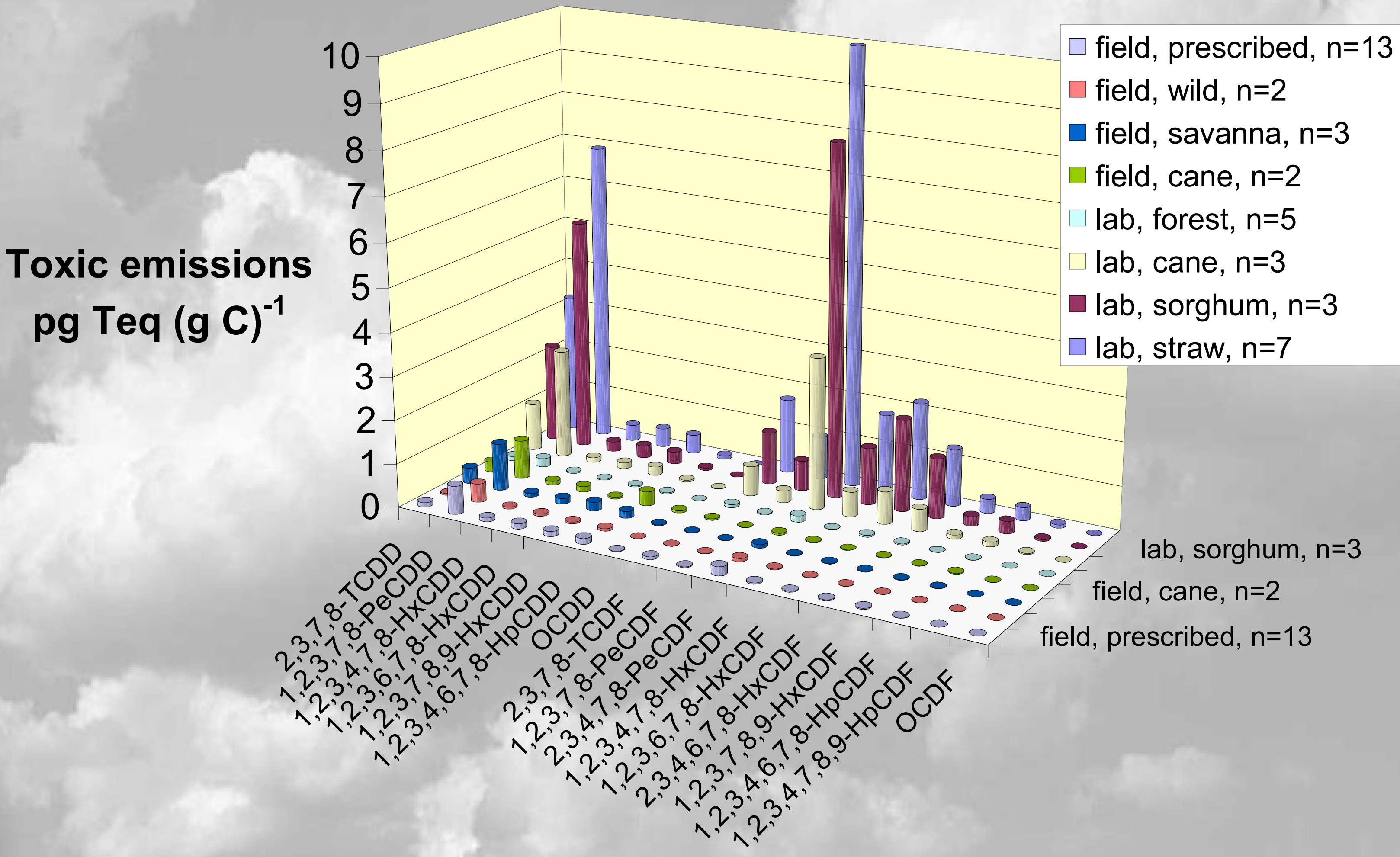
Field measurements



PCDD/PCCF homologue mass profiles



PCDD/PCCF toxic congener profiles



Mechanisms

Dioxins form by

- gas phase chemistry at 400 – 600^{o}C
- heterogeneous chemistry at 200 - 450^{o}C.

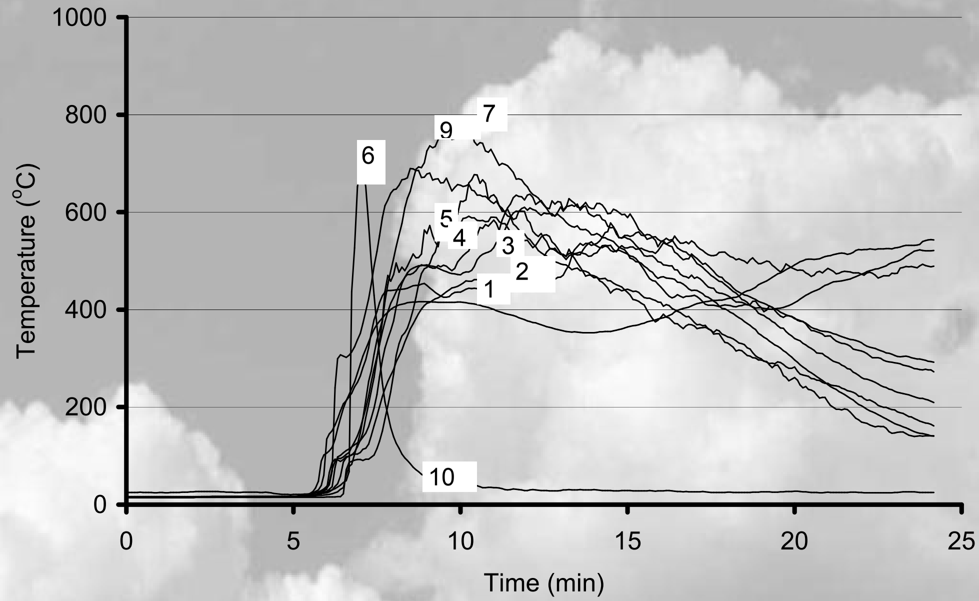
In furnaces, in slow combustion heaters and in open fire places the combustion gases are retained at high temperature in the flue.

And we see PCDD/PCDF production

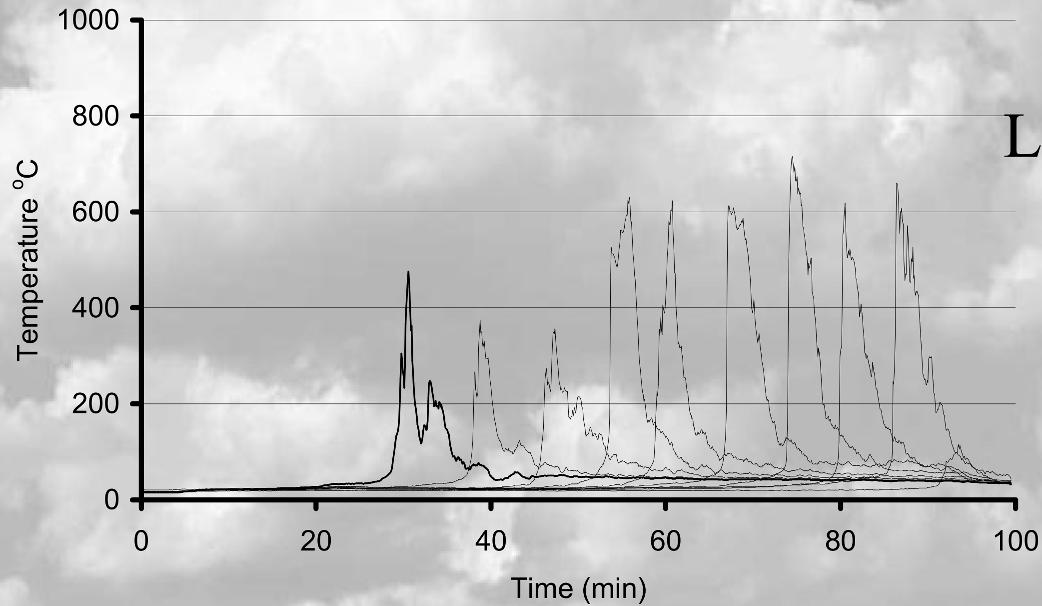
Leaf litter
Burn

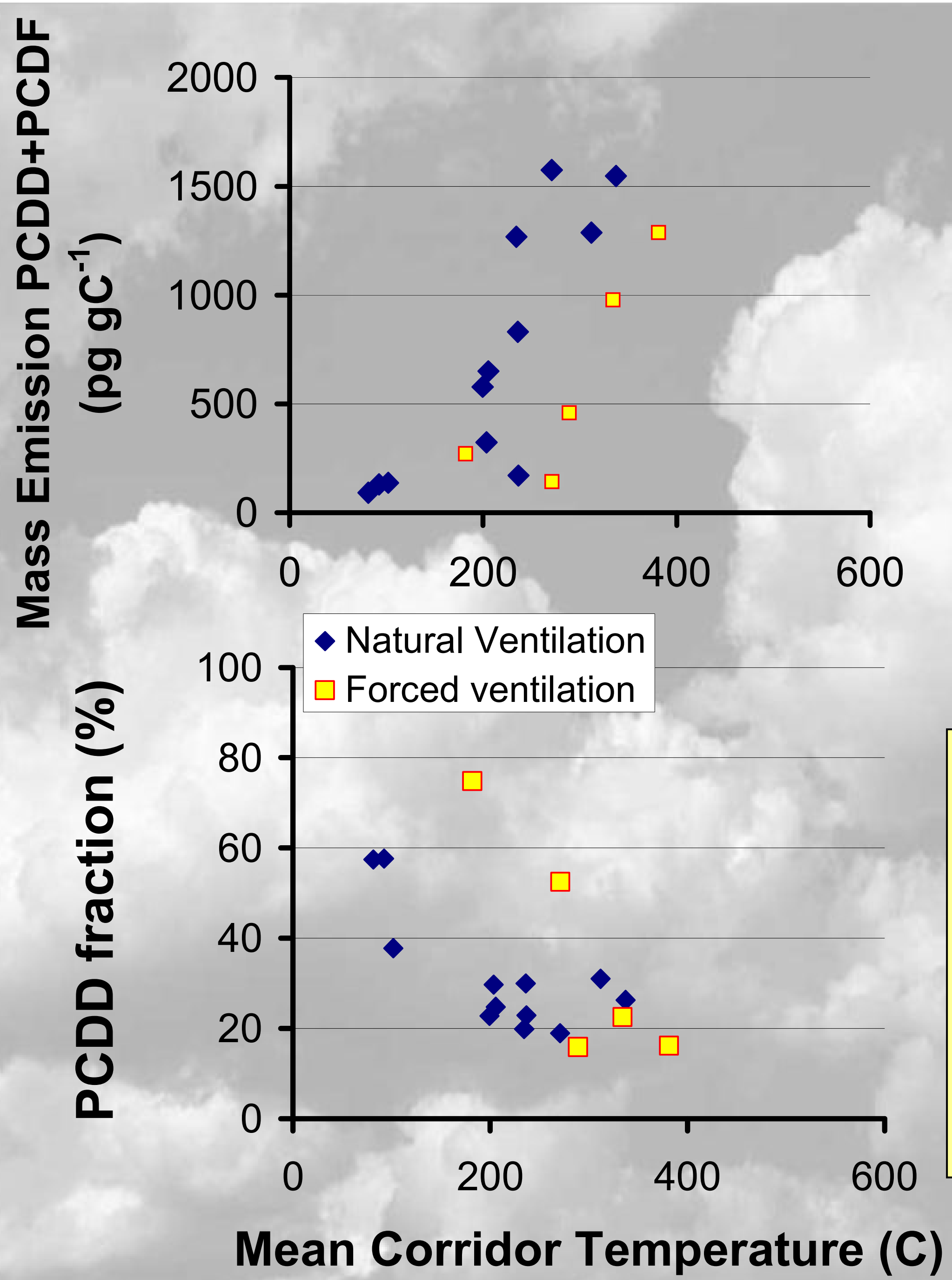
Timecourse of fire along the bed

Straw- fan assisted



Leaf litter





With fan-assisted ventilation air flow is more turbulent and smoke residence time is shorter

In the open, ambient air is entrained into the smoke plume. It

- rapidly dilutes and
- rapidly cools

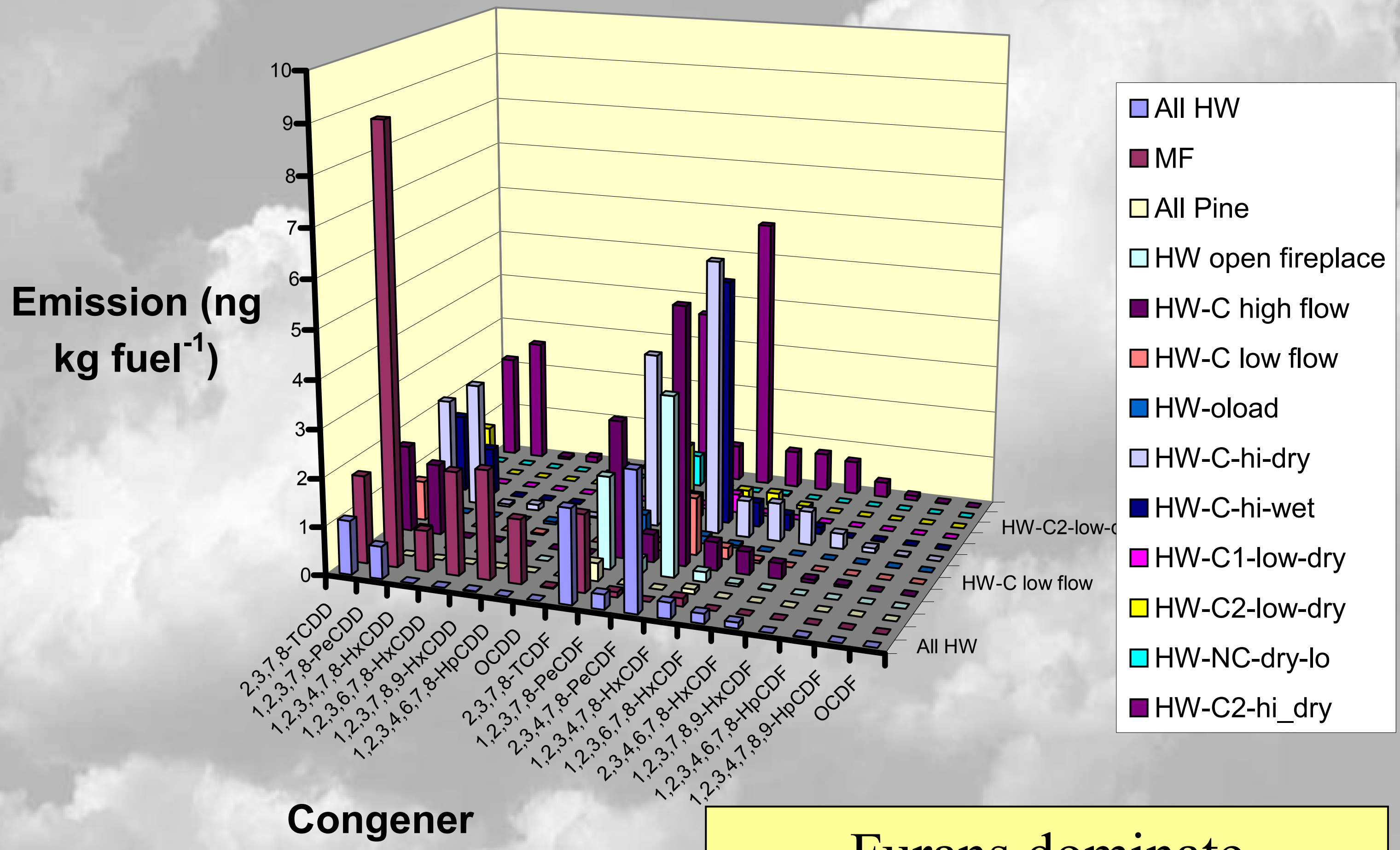
This is very difficult to reproduce precisely therefore laboratory tests should be interpreted with caution.

Who else has seen these patterns

Slow combustion woodheaters

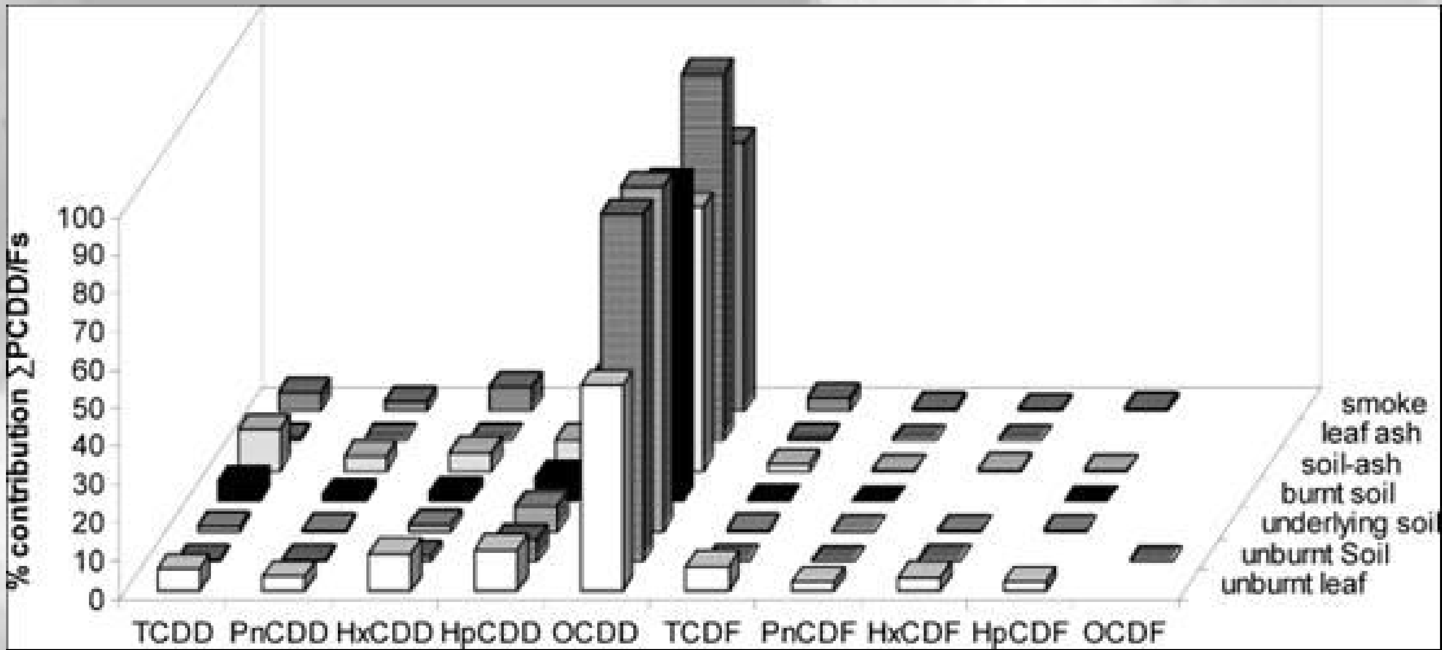
(Gras et al. , 2002)

Mean 4 ng TEQ (g fuel)$^{-1}$



Furans dominate

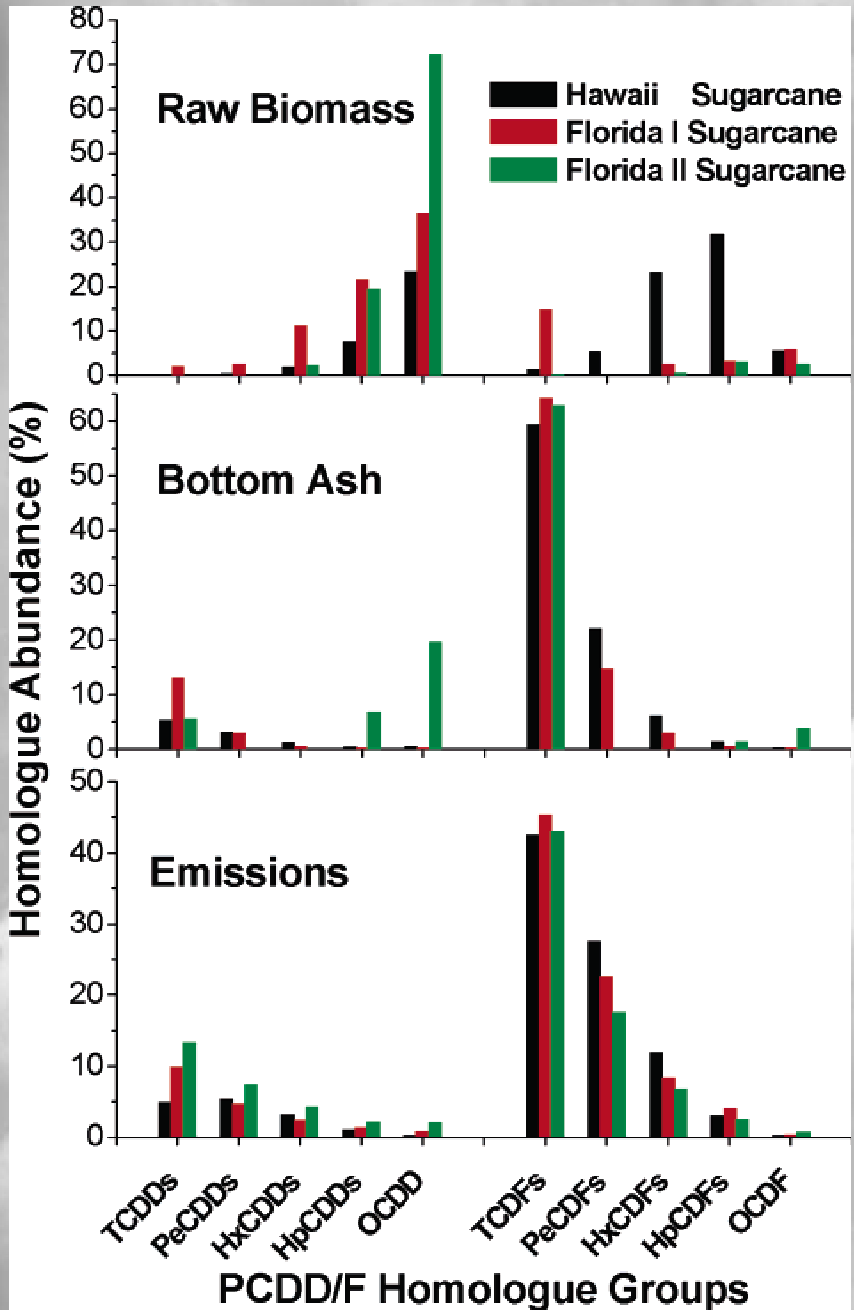
Dioxins in smoke, Combustion hood test

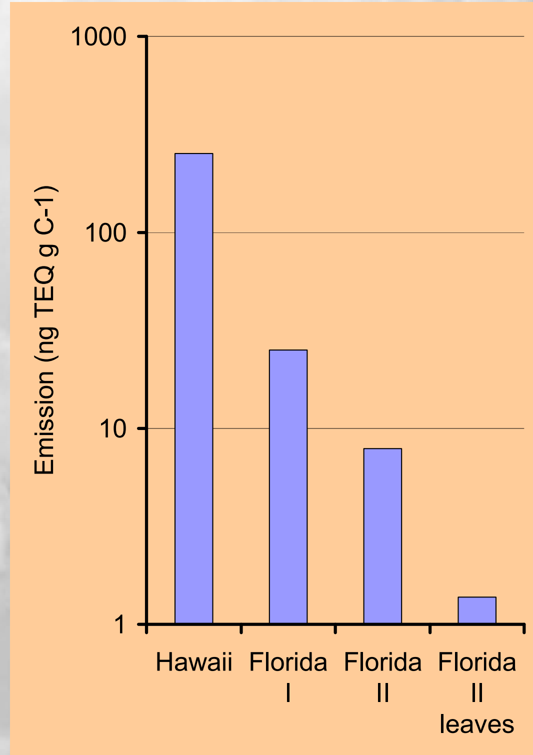


Prange et al., (2002)

Gullett and Touati (2003) saw similar patterns for wheat and rice

Sugar Cane- burn hut





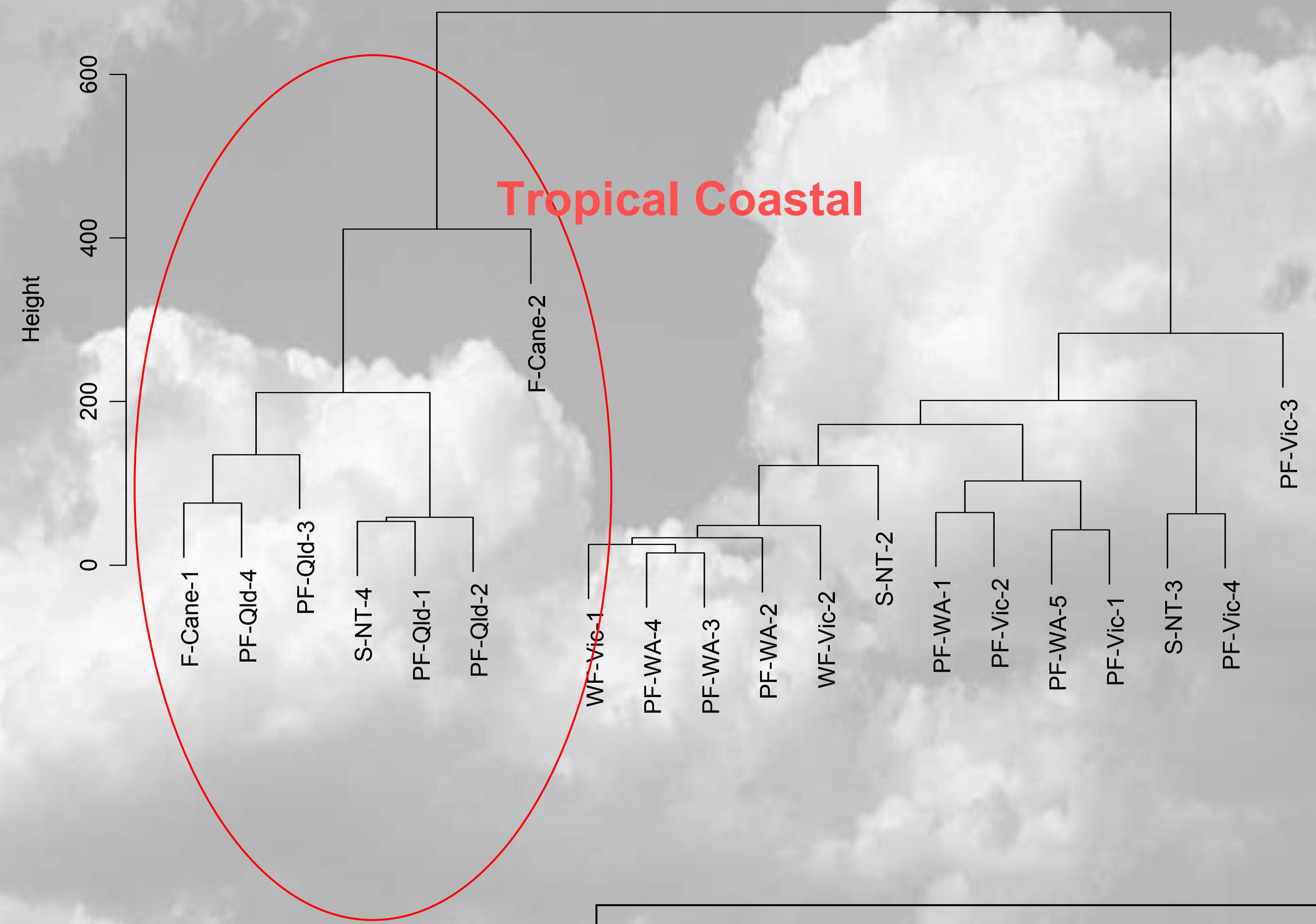
Gullett et al. (2006)

Also Oregan and North Carolina forest fuels

Why the differences

- Fuel (residues, or formation chemistry)
  - **– possible but not large**
- Soil (volatilisation or formation from pyrolysis of soil carbon
  - **- some evidence for this in recent work**
- Fractionation of smoke in the field (flaming combustion smoke rises in the plume, smouldering remains)
  - **Little evidence that this occurs to any substantial extent**
- Sampling artifacts
  - **Most likely in our study**

Cluster analysis of field emission factors by PDCC/PDCF homologue groups

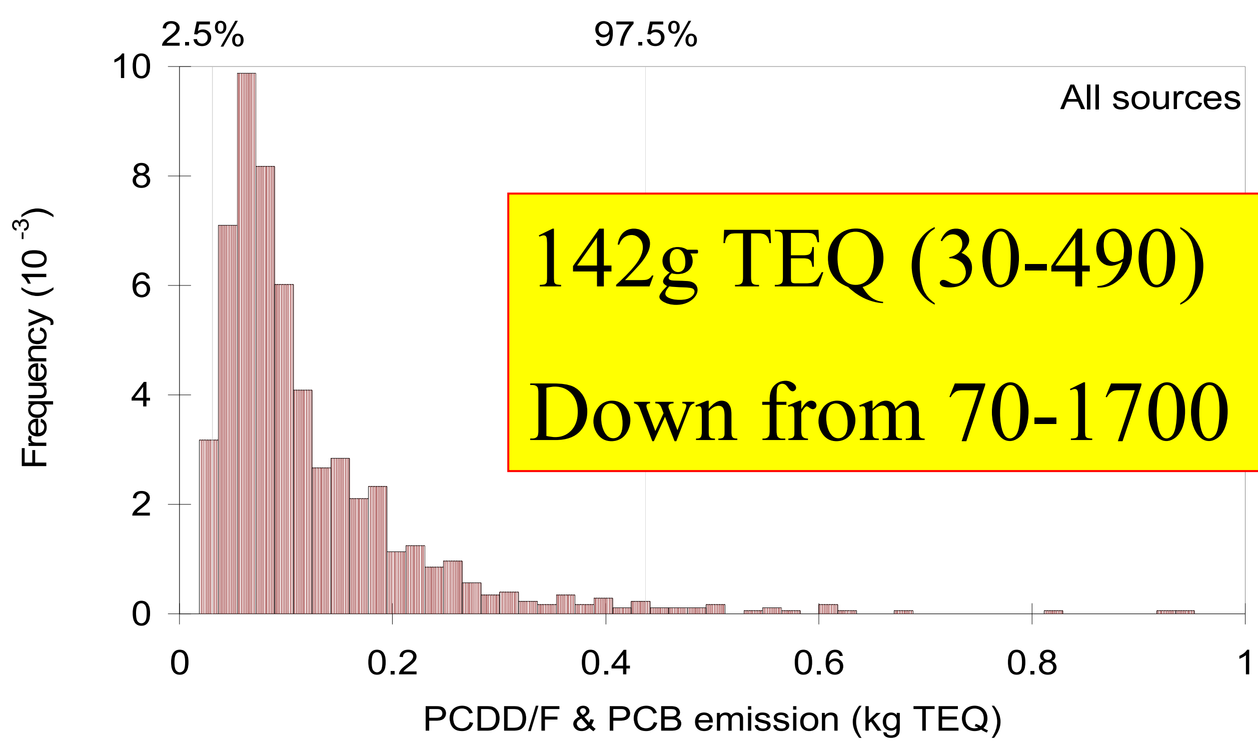


There is something in the location of the fire.

Is it fuel? Is it soil?

Revised Emissions

1994 – Revised EA (2002)



142g TEQ (30-490)

Down from 70-1700

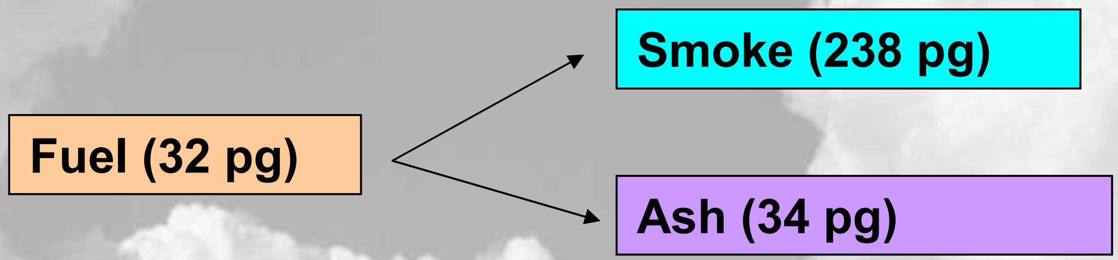
2001 Estimates

	Mass (t)	Emission factor ug TEQ/t		Emission g		Revised
		To air	To land	To air	To land	To air
Savanna and Temperate Grassland	216,173,000	5	4	1081	865	230
Prescribed burning of forests	3,505,000	5	4	18	14	3
Wildfires	10,588,000	5	4	53	42	4.7
Agricultural residues- wheat	3,492,000	0.5	10	2	35	2.9
Agricultural residues- coarse grains	6,044,000	0.5	10	3	60	5
Agricultural residues- sugar	653,300	0.5	10	0	7	0.45
Total				**1156**	**1023**	**246.05**
All sources				**1410** ***82%***	**1300** ***79%***	**500** ***49%***

Emissions to air reduce by a factor of 4, but still comprise 50% of emissions (with a high range of uncertainty)

Residues

Mass Balance- Coastal savanna woodland

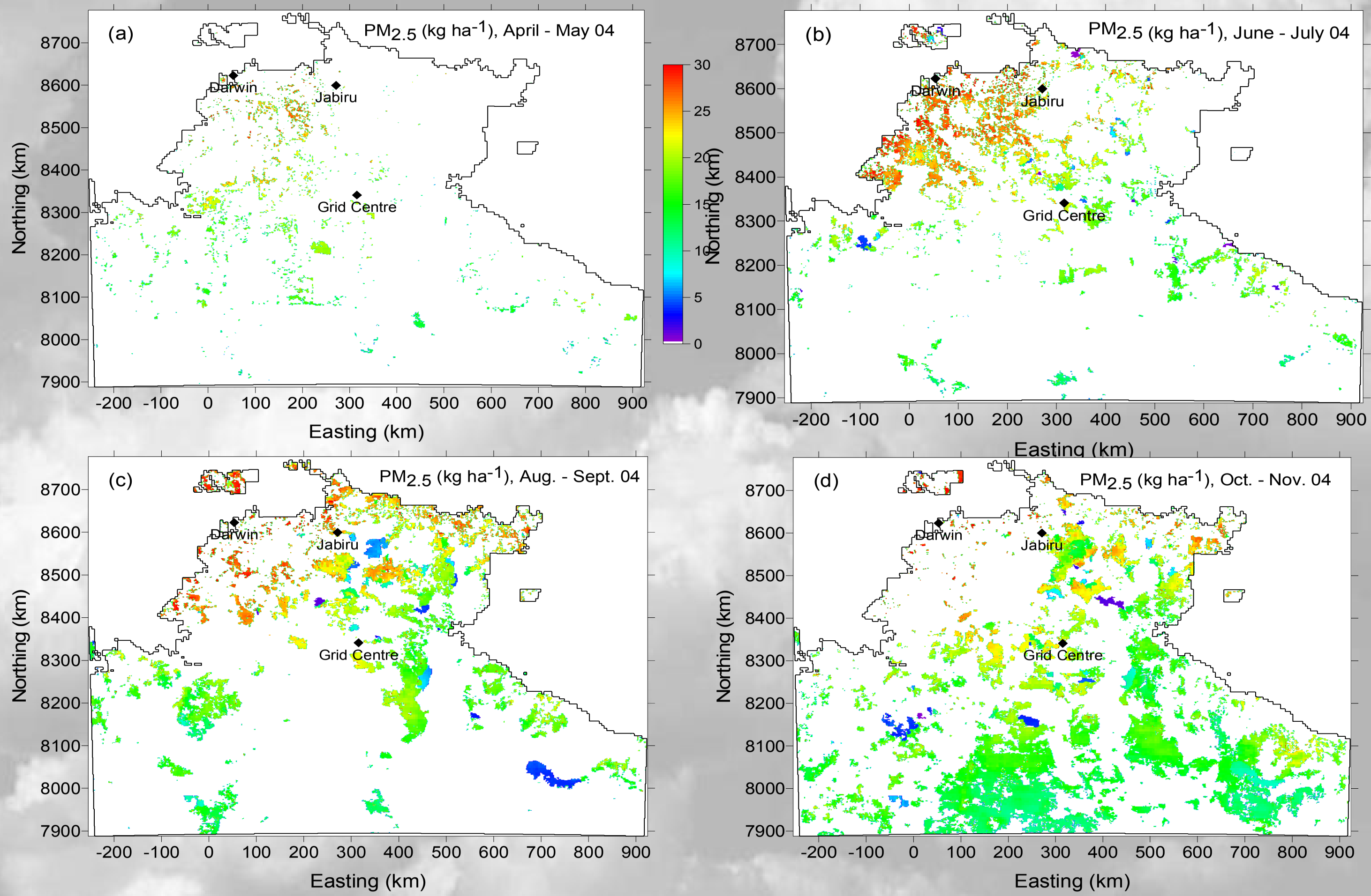


Homologue group	pg (g fuel)$^{-1}$		
	Fuel	Smoke	Ash
Total TCDD isomers	0.18	10.3	0.2
Total PeCDD isomers	0.1	15.5	0.2
Total HxCDD isomers	0.61	26.9	1.9
Total HpCDD isomers	2	40.4	4.1
OCDD	29	182.2	27.0
Total TCDF isomers	0.2	6.4	0.3
Total PeCDF isomers	0.1	1.2	0.2
Total HxCDF isomers	0.1	0.6	0.2
Total HpCDF isomers	0.05	0.1	0.1
OCDF	0.02	0.1	0.1
Total	**32.4**	**283.8**	**34.1**

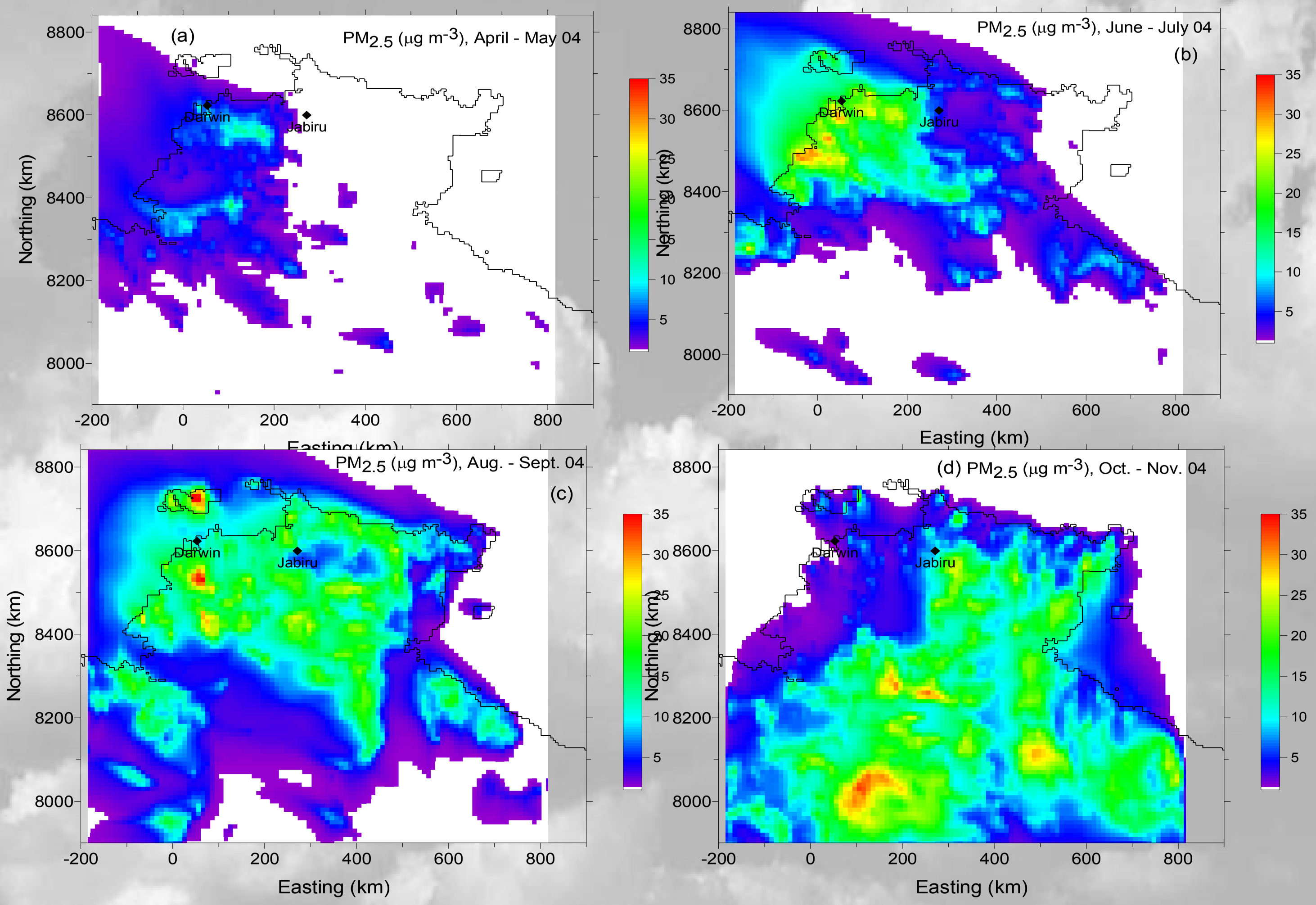
Dispersion- where does it fall

- Smoke plumes are transported hundreds to thousands of kilometers
- Where the smoke contacts the surface, there is surface deposition

PM2.5 Emissions (kg ha^{-1})

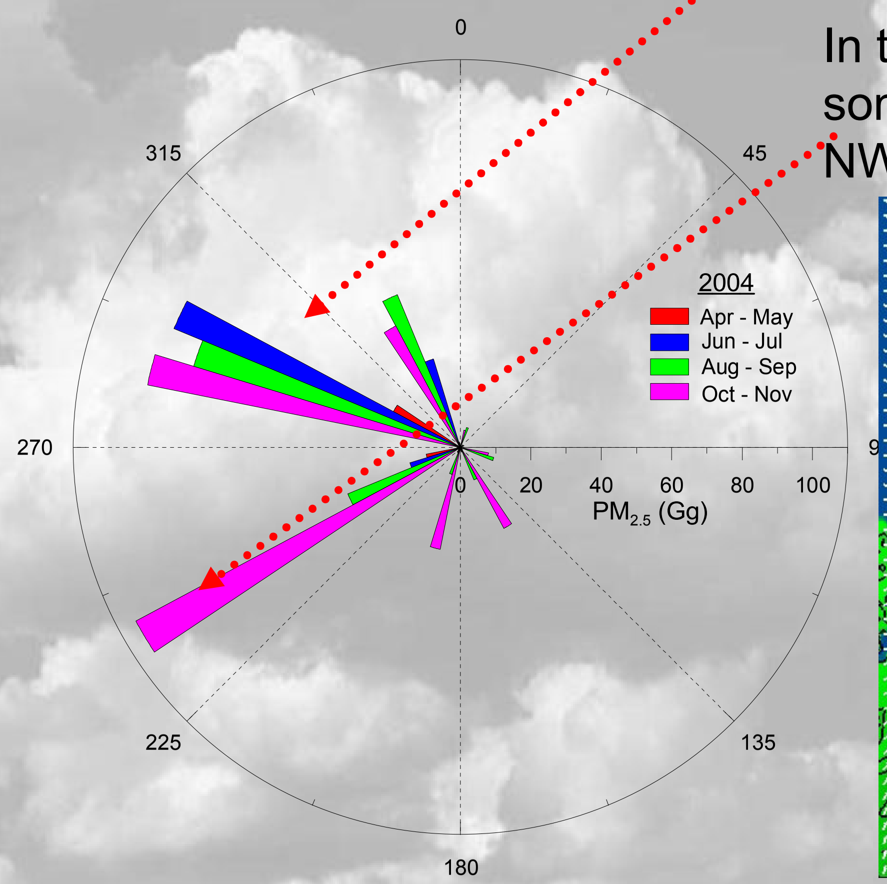


PM2.5 Surface Concentrations



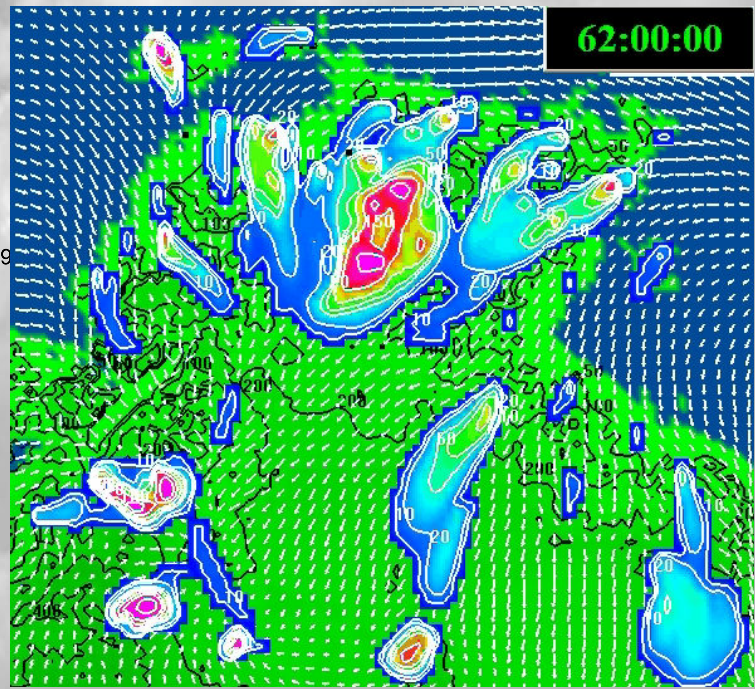
Where does it end up: PM2.5 leaving the domain

Total emitted 668 Gg



A large proportion is transported into the Timor Sea

In the late fire season, some is transported SW to NW WA.



Quantifying the emissions is only the start- to understand impacts of dioxins we first need to understand the dispersion and deposition.

Conclusions/ Emerging Area

- The emissions in Australian ecosystems are low
- Measurement artifacts may be a problem
  careful measurement protocols are required
- Emissions to land require review
- Long-range transport can be significant
  The impact may be distant from the source.

But that may not be universal –

- other fuels and soils may have different emissions
- Soil pyrolysis. What happens when there is substantial soil heating e.g.
  - Slash burns from forest clearing
  - Peat fires in forests