Australian CCl_4 emissions: a paradigm for a 'missing' global source?

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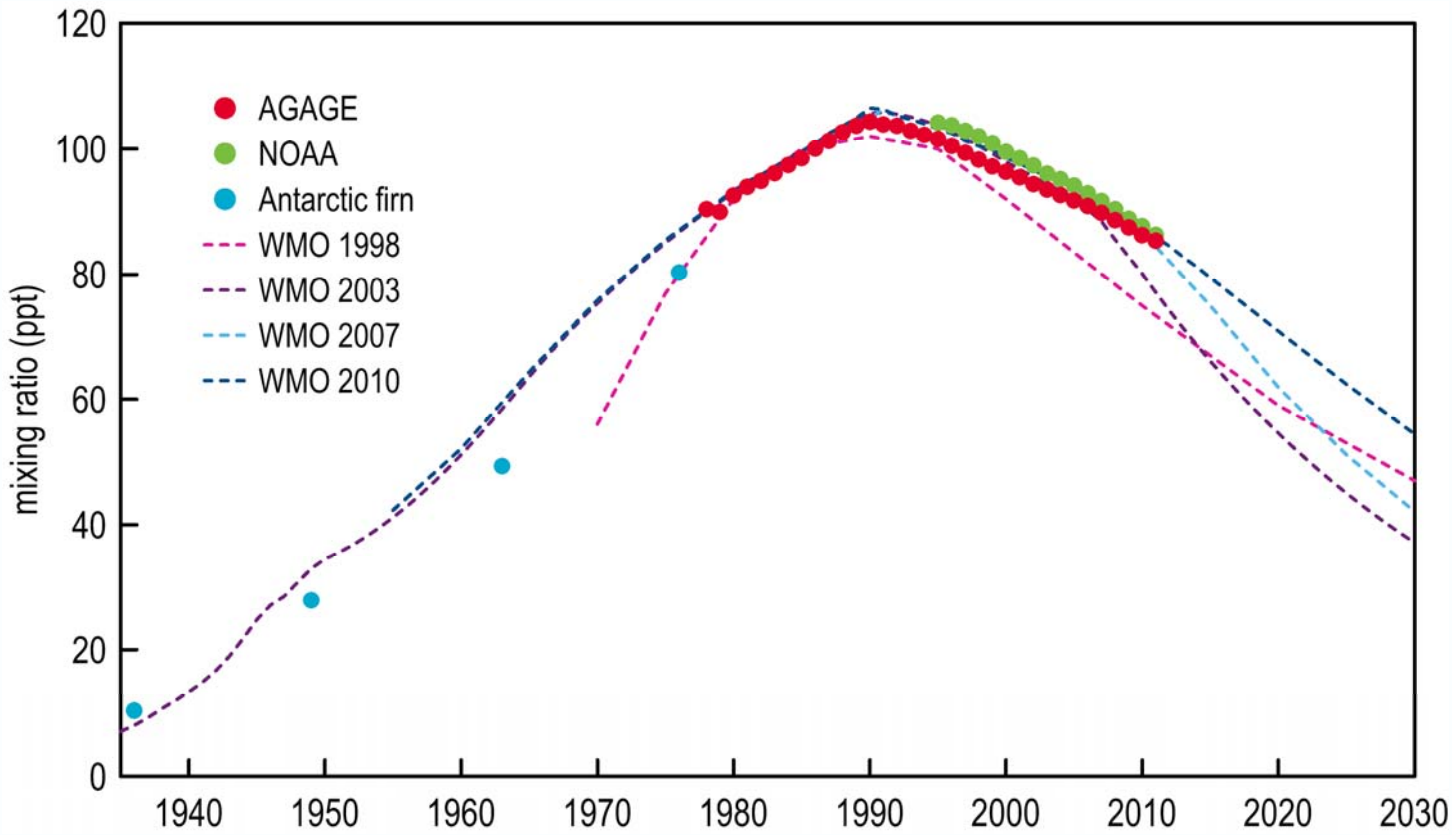
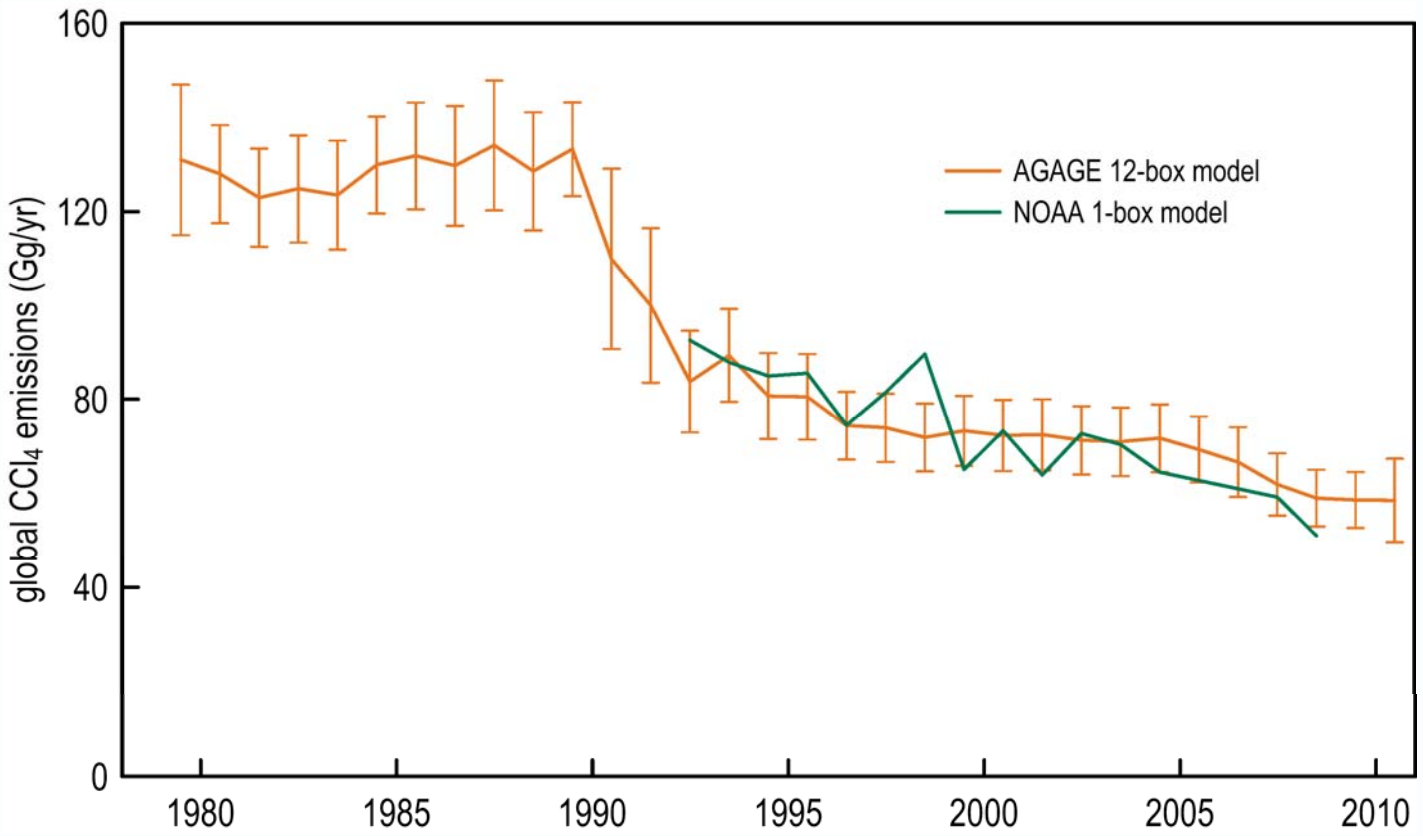
Global CCl_4: NOAA, AGAGE & Antarctic firn



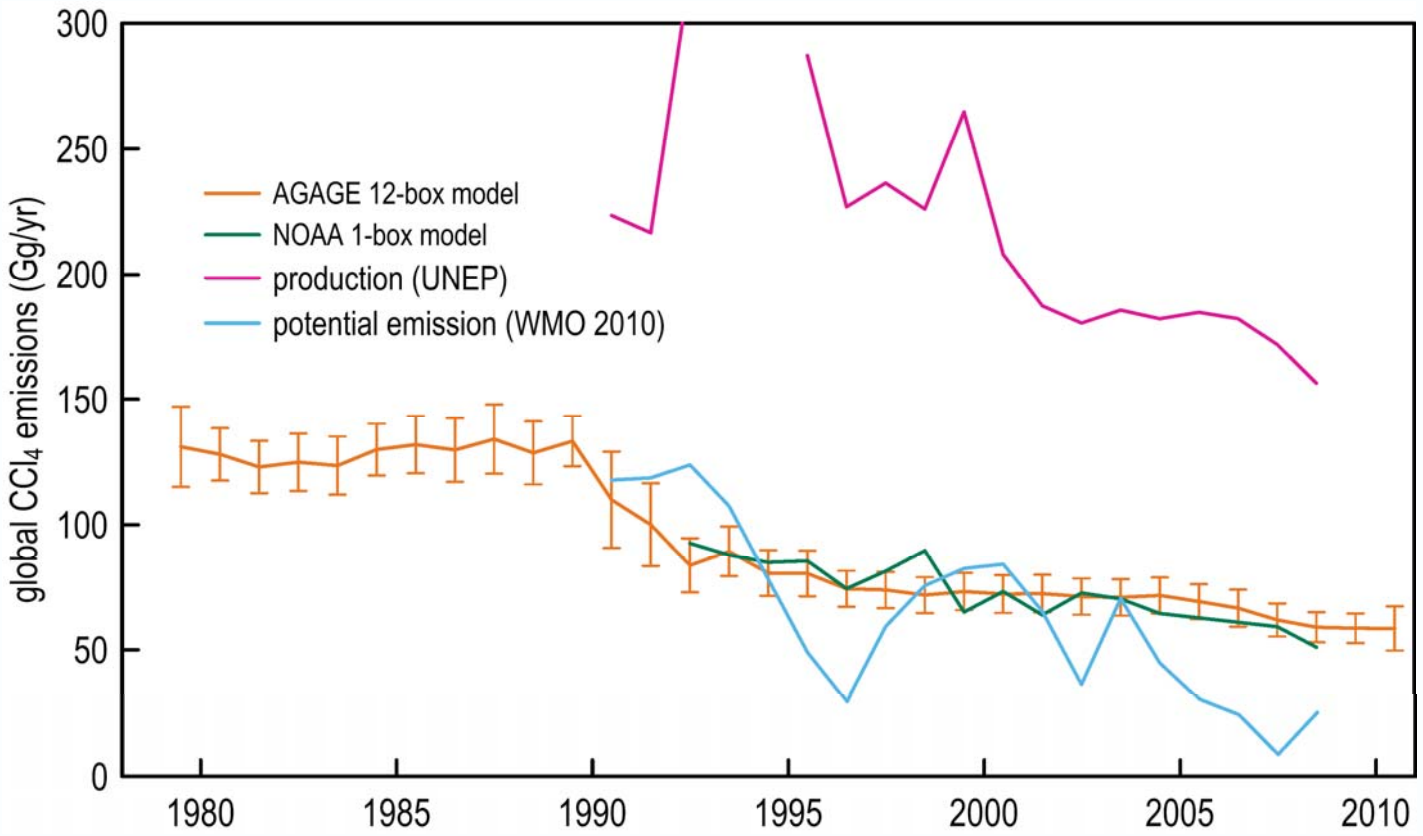
- WMO scenarios consistently over-predict rate of decline
- Unaccounted-for sources?

Global CCl_4 emissions: AGAGE & NOAA



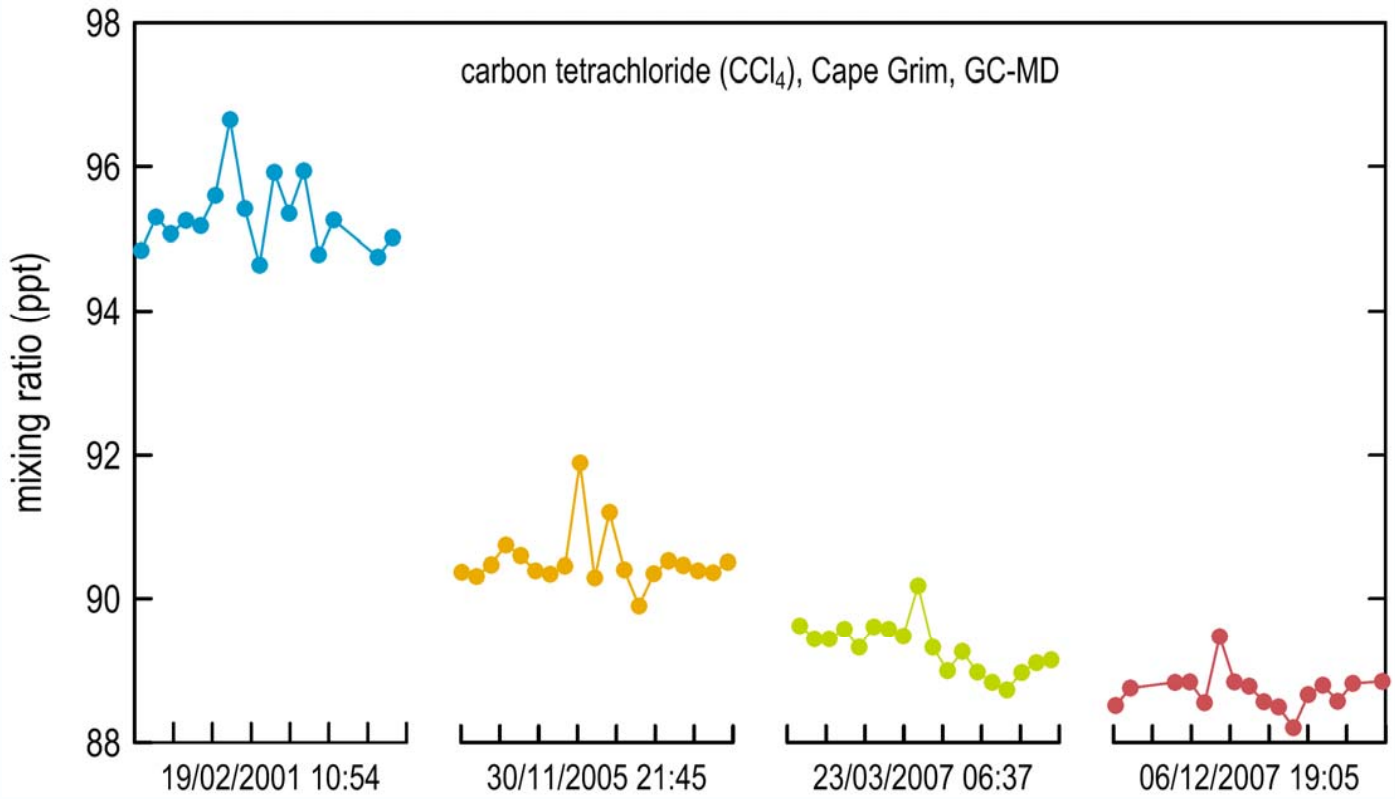
- pre-1990: 130 k tonnes/yr
- post-1995: 80 to 60 k tonnes/yr
- early-1990s rapid decline: developed world CFC phase-out

Global CCl_4 emissions: 'bottom-up' v 'top-down'



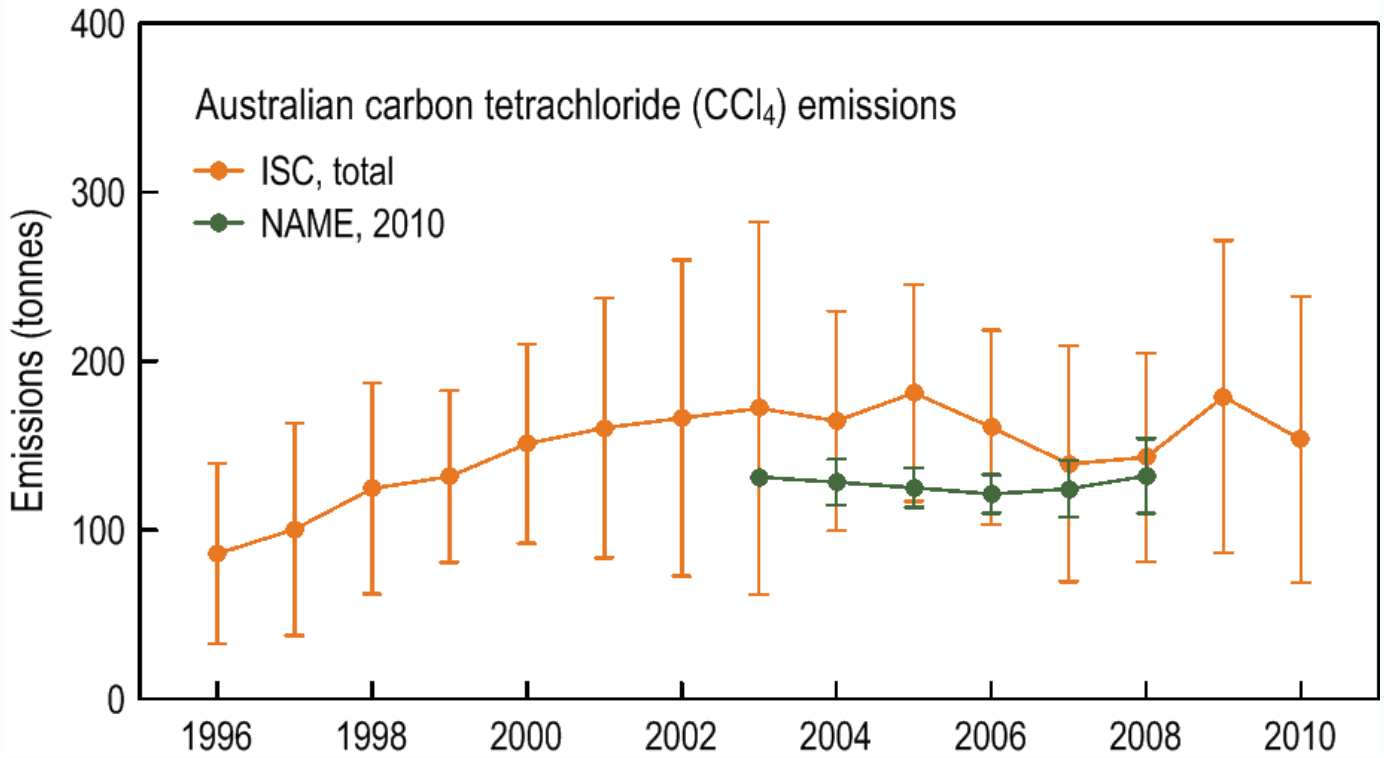
- potential emissions = production – 98% * feedstock – 75% * destruction
- AGAGE – potential emissions 'gap' = ~40 k tonnes (2005-2008)

Australian CCl_4 emissions: Cape Grim CCl_4 pollution episodes



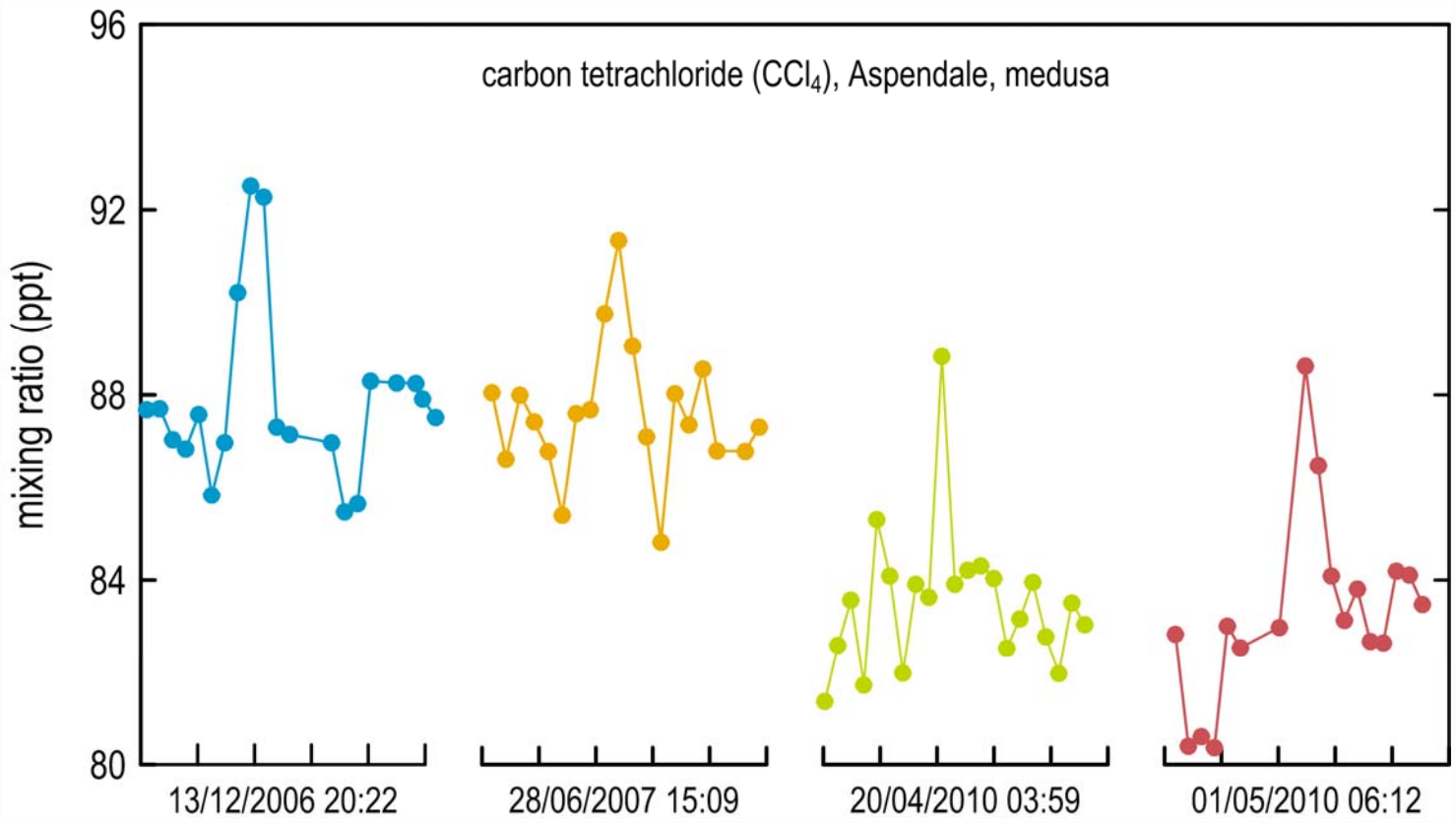
- Cape Grim CCl_4 pollution episodes maximum 1-2 ppt
- correlate with other urban emission species: CO, HFC-134a
- air mass trajectories show these episodes come from Melbourne

Australian CCl_4 emissions from Cape Grim data



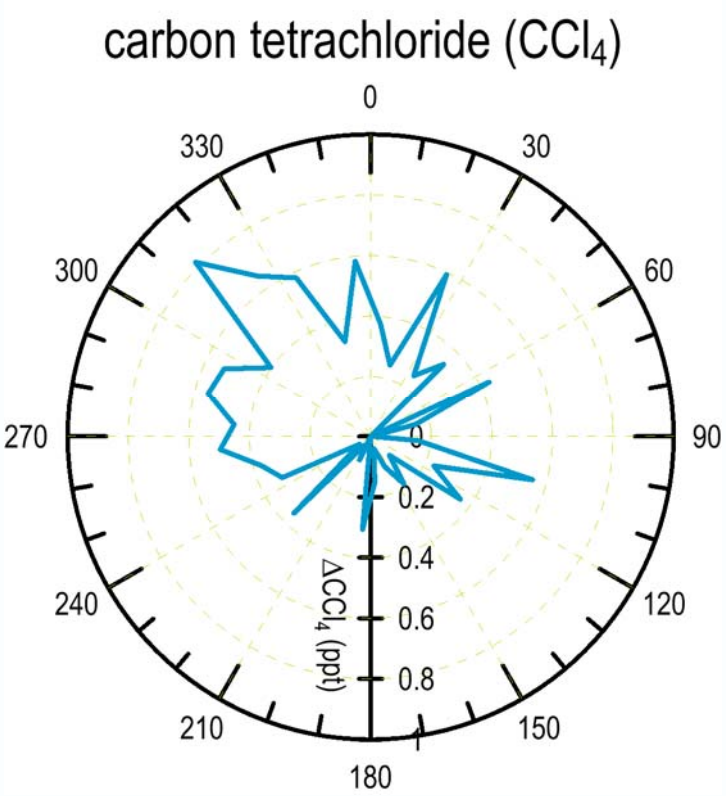
- **ISC**: interspecies correlation, CO reference species (Dunse *et al*., 2005)
- **NAME** inversion: Lagrangian particle dispersion model (Manning *et al*., 2011)
- Australian emissions ~constant at 160 tonnes/yr (2000-2010)
- Australian CCl_4 production ceased early 1980s, imports ceased late 1980s
- UNEP data: Australia has zero CCl_4 consumption (~emissions) since the 1990s

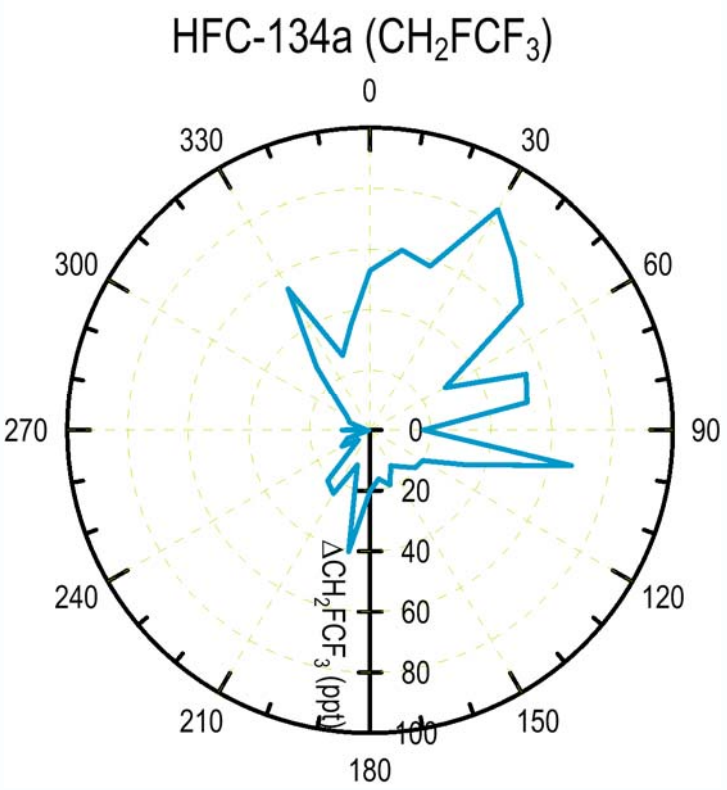
Aspendale CCl_4 pollution episodes



- CCl_4 pollution episodes maximum 4-5 ppt
- where does the CCl_4 come from?

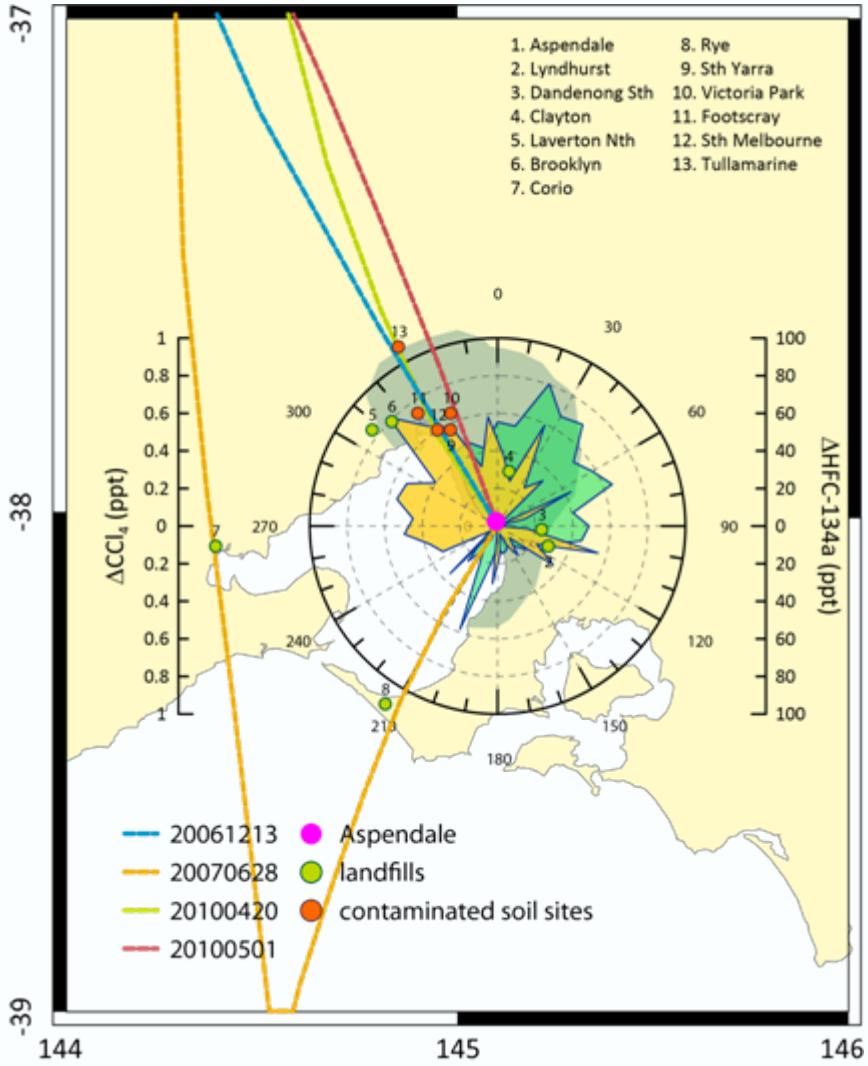
Aspendale CCl_4 & HFC-134a pollution 'roses'





- HFC-134a: NE of Aspendale (demographic centre of Melbourne)
- CCl_4: NW of Aspendale: industrial complex west of Melbourne CBD

Melbourne: potential CCl_4 emission sites



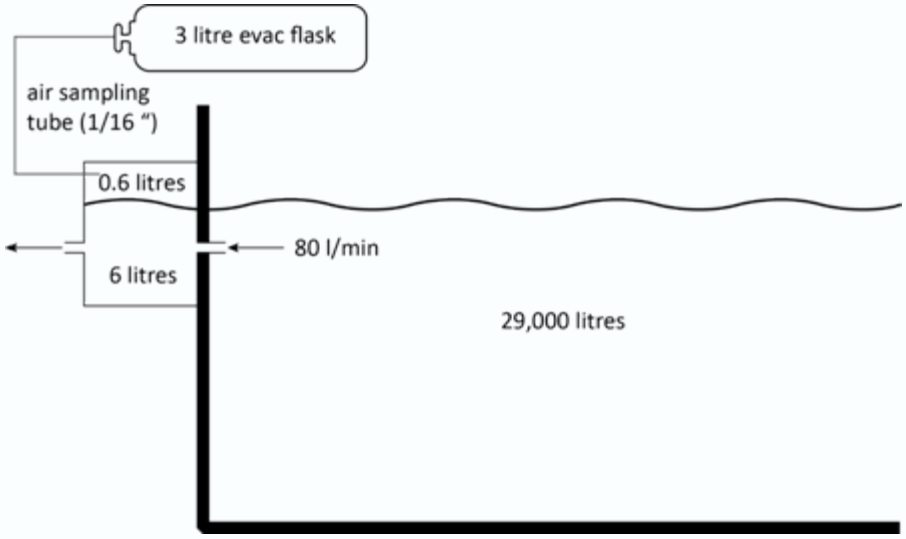
- EPA identified CCl_4 soil contaminated sites
- EPA licensed soil treatment and toxic waste treatment sites
- CCl_4 emissions confirmed at Lyndhurst toxic waste site by up-wind/down wind sampling (2011: 10 ppt difference → 1 tonne/yr)
- currently testing Brooklyn site

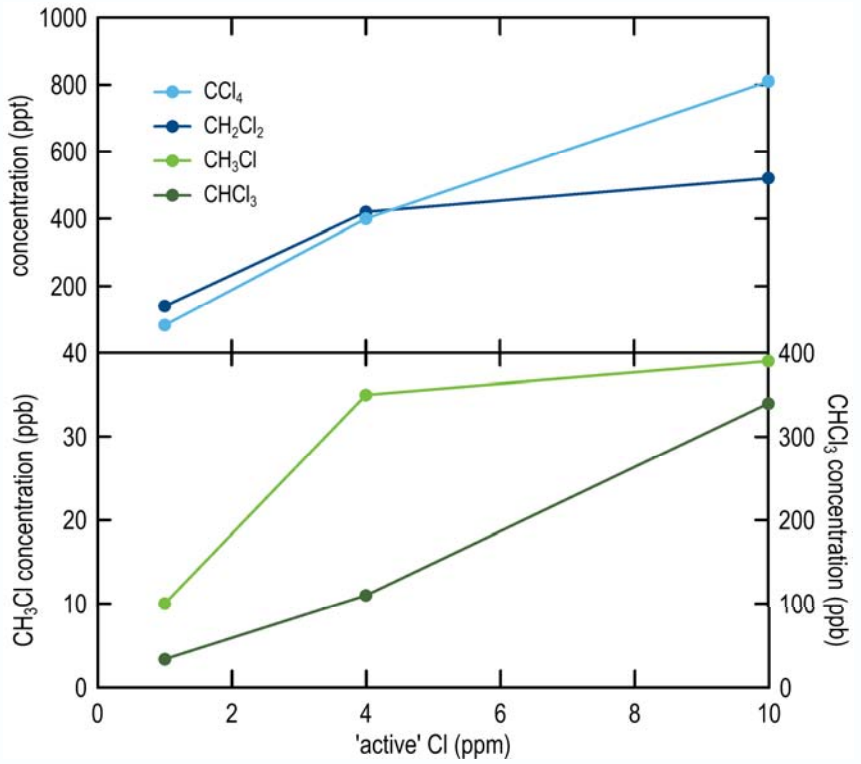
Australian halocarbon emissions: global fraction

Species	Fraction
HFCs	1-3 %
HCFCs, CFCs	0.5-1 %
CH_3CCl_3	1-2 %
CCl_4 (from landfills)	assume 1-2%

- based on atmospheric data and National GHG Inventory reporting
- Australian landfill emissions ~160 tonnes
- global landfill emissions 8-16 k tonnes
- landfills 20%-40% of global 40 k tonnes 'gap' between emissions and UNEP potential emissions

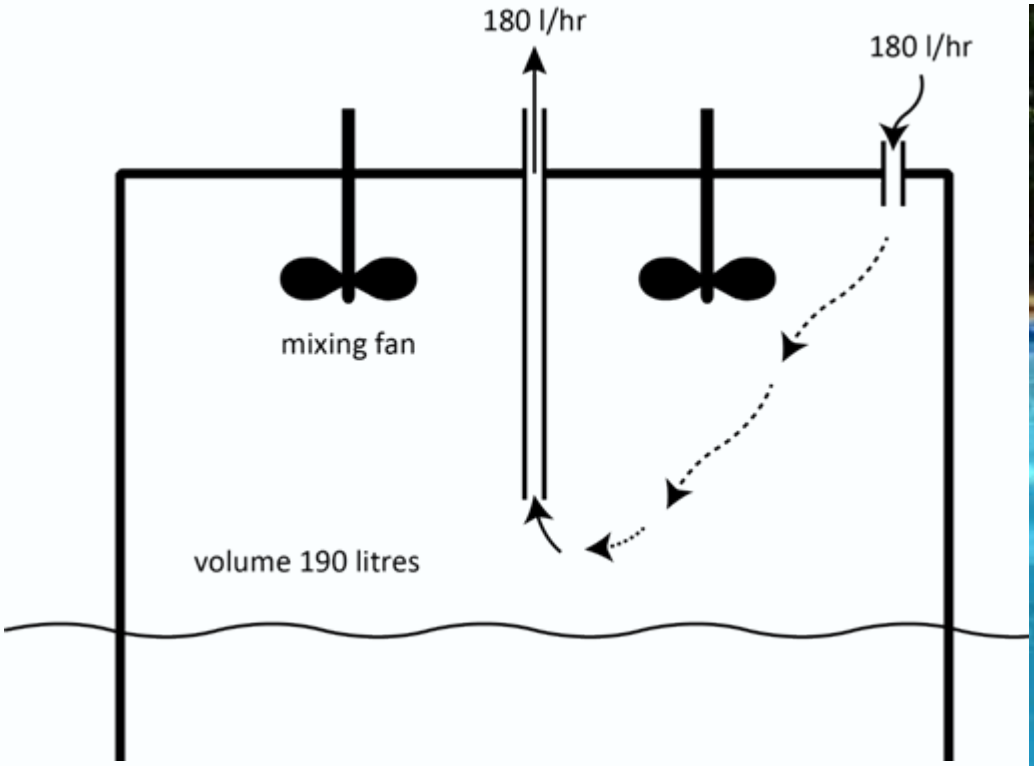
Water chlorination: CCl_4 source?





- $CHCl_3$ > CH_3Cl > CH_2Cl_2, CCl_4:: 1000:100:<1
- What is the significance of this CCl_4 source?
- CCl_4 source ~0.1% of the $CHCl_3$ source
- $OCl^- + Cl^- + 2H^+ \rightleftharpoons Cl_2 + H_2O$
  basic acidic
- Cl_2 + organics $\not\rightarrow$ $CHCl_3$ +……CCl_4?

Water chlorination: CCl_4 source?



Conclusions

- Cape Grim data suggest that Australian CCl_4 emissions are about 160 tonnes/yr
  - based on UNEP data, Australian CCl_4 emissions should be zero
- Aspendale CCl_4 data suggest that these emissions possibly originate from contaminated soils and toxic waste treatment plants
- Global CCl_4 emissions from contaminated soils/toxic waste treatment could be 50-100 times the Australian emissions (as are many other chemical emissions)
- Global emissions from this source could be 8-16 k tonnes/yr, 20-40% of the 'gap' between 'top-down' and 'bottom-up' emission identified in WMO 2010
- Water chlorination (potable, waste, pools) may be a source of CCl_4
- How large? – pool flux chamber experiment pending

Thank you

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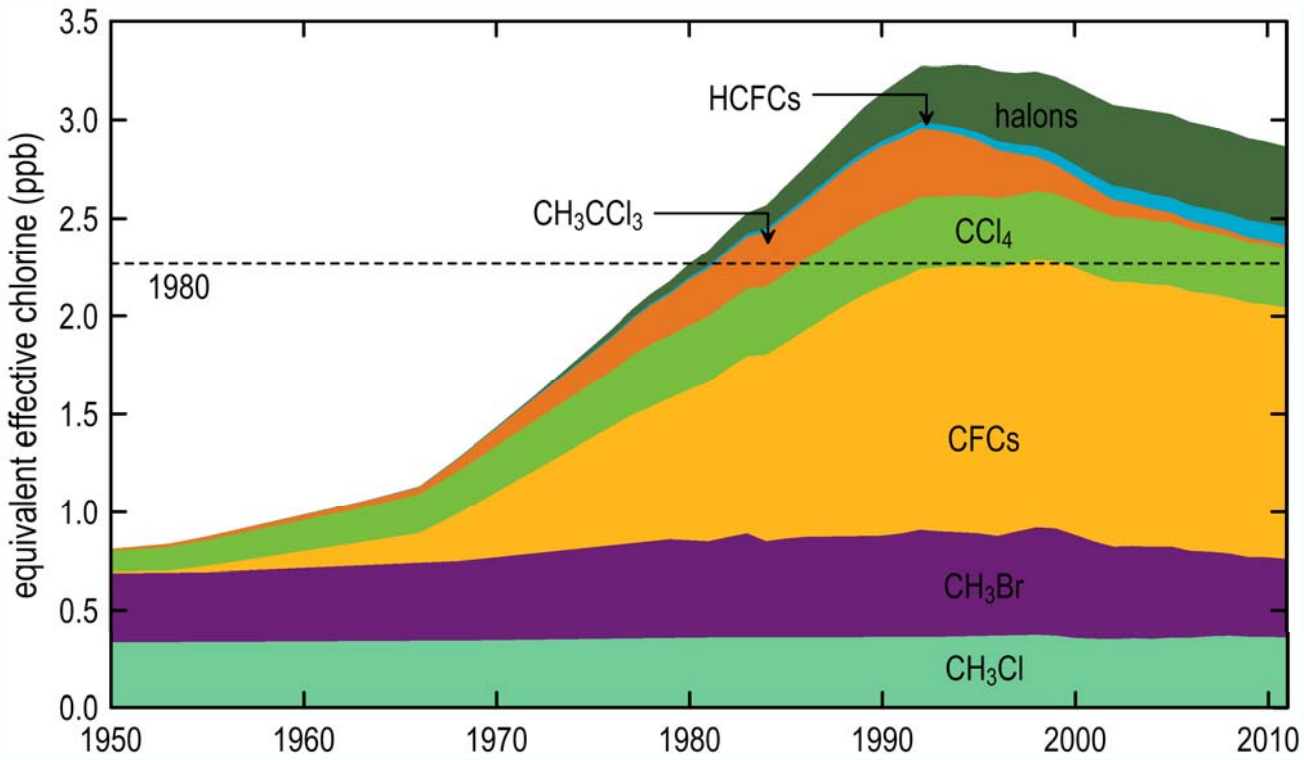
Equivalent effective stratospheric chlorine



- CCl_4: chemical feedstock (CFCs), solvent, refrigerant, fire extinguishers
- AGAGE global data (α = 60), not lagged
- dominated by CFCs: 45% (2011); CCl_4: 11% (2011)
- 1960: CFCs - 9%; CCl_4 - 16%