

*IPCC / NGGIP, Expert Meeting
Emission Estimation of Aerosols Relevant to Climate Change
2-4 May 2005, Geneva*

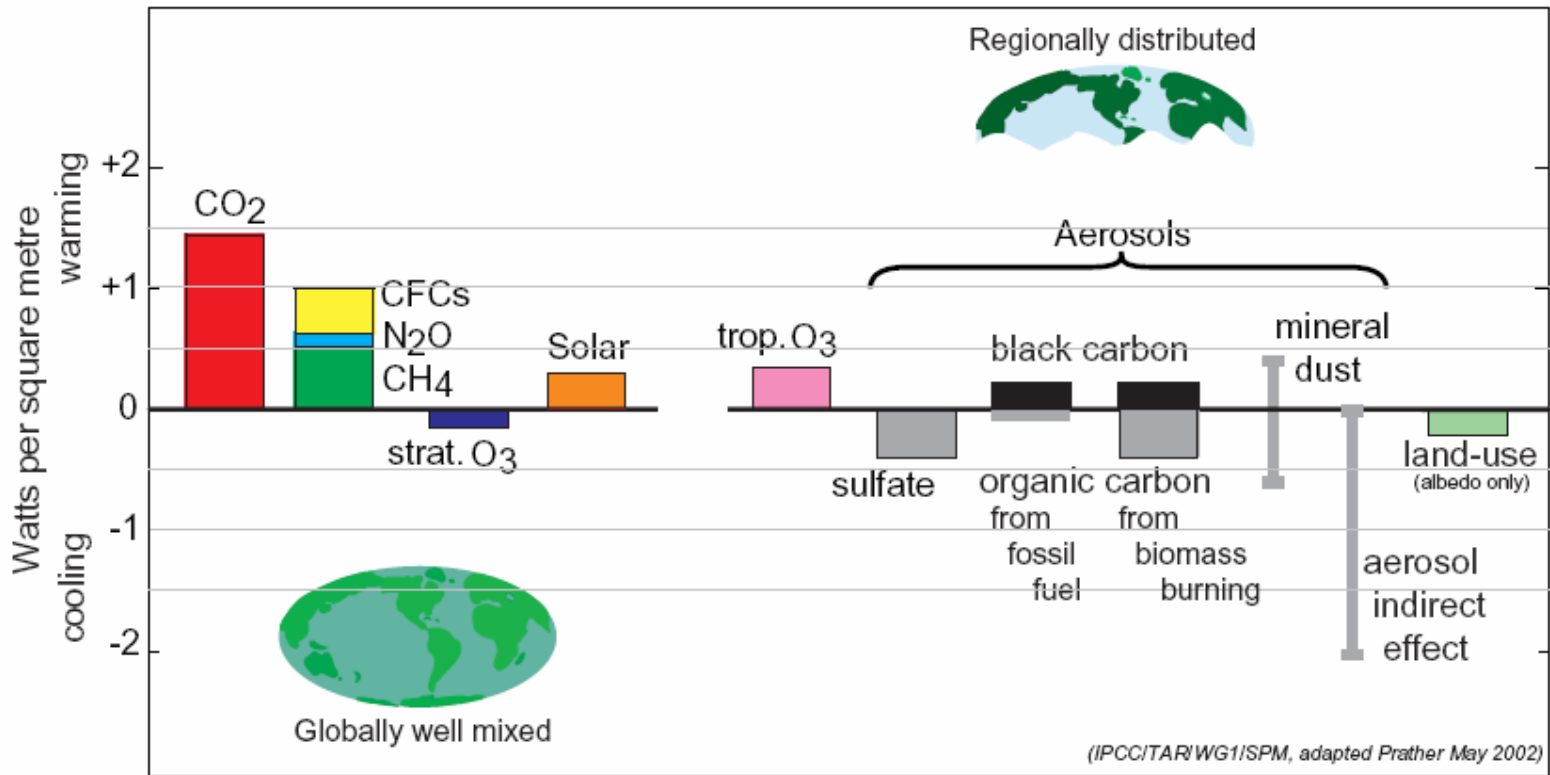
Climate Forcing through Atmospheric Chemistry

- ▶ indirect effects on greenhouse gases
- ▶ secondary organic aerosols

*Michael J. Prather
Earth System Science Dept
University of California at Irvine*

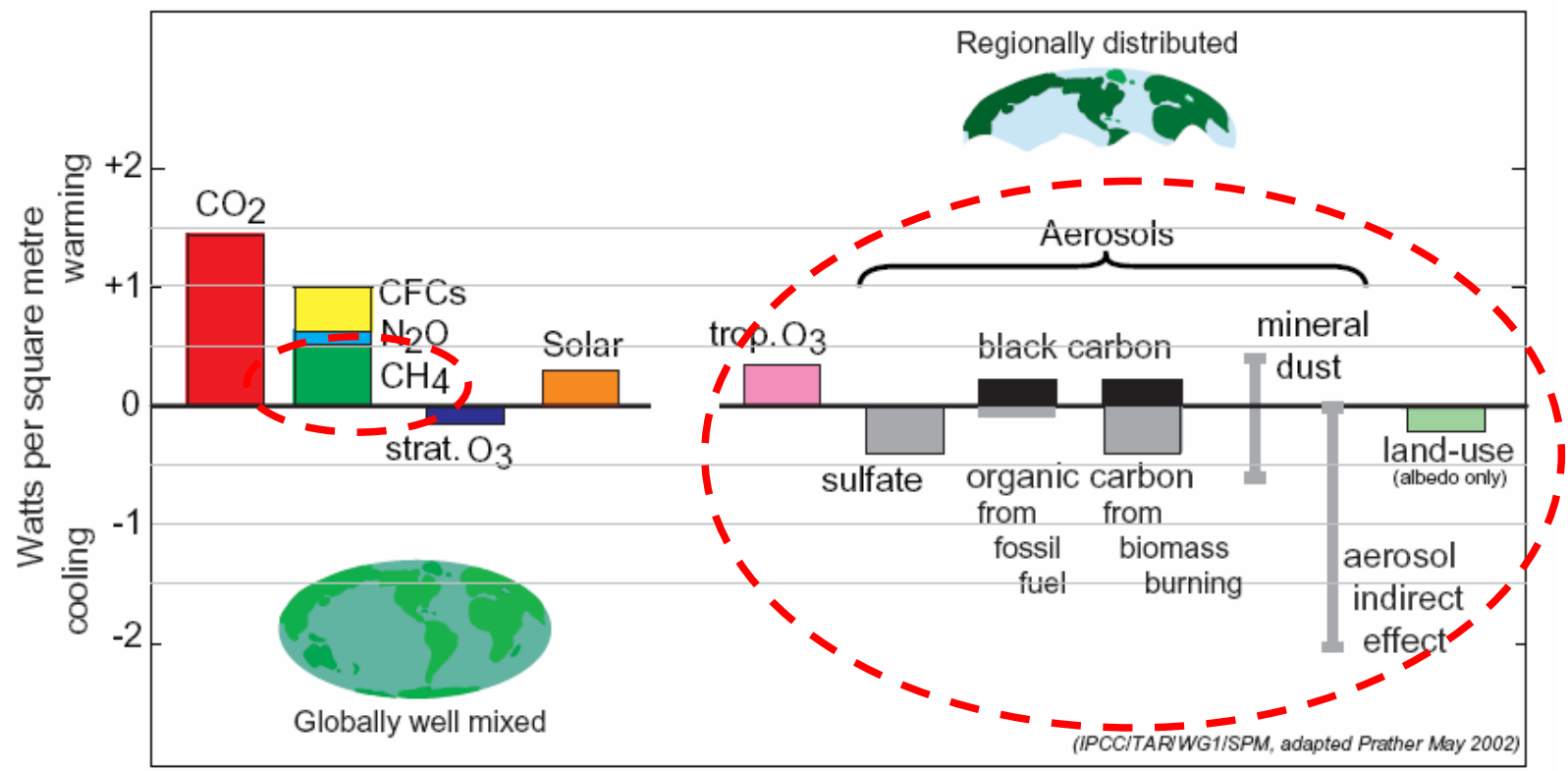
IPCC TAR, 2001

Global Mean Radiative Forcing of Climate for year 2000 relative to 1750



IPCC TAR, 2001 - impacted by reactive chemistry & aerosols

Global Mean Radiative Forcing of Climate for year 2000 relative to 1750

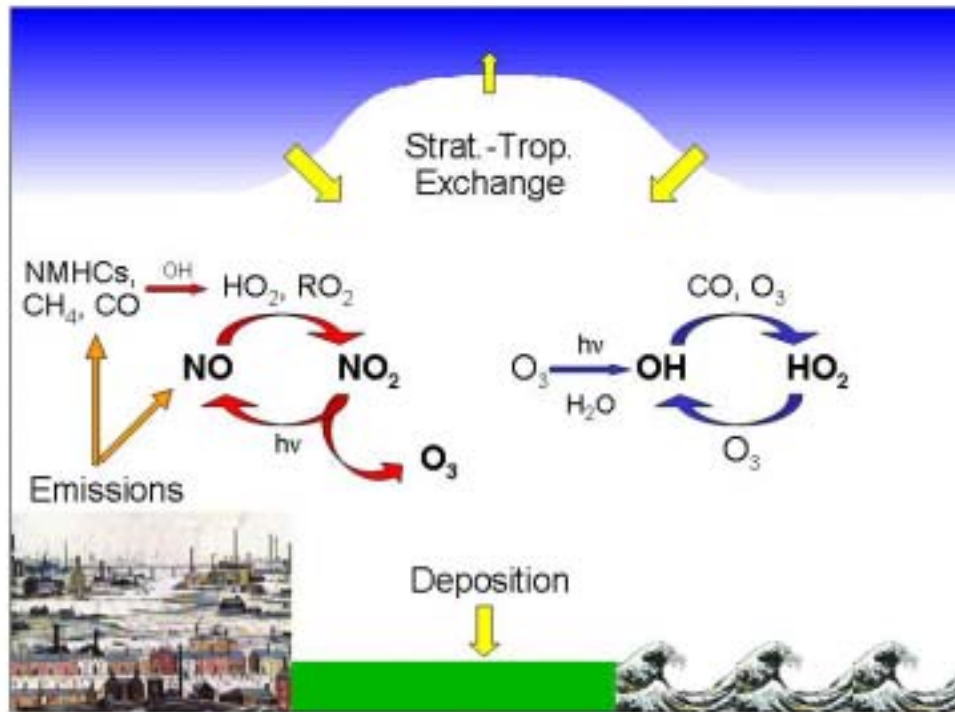


"Reactive" Atmospheric Chemistry

▶ Greenhouse Agents

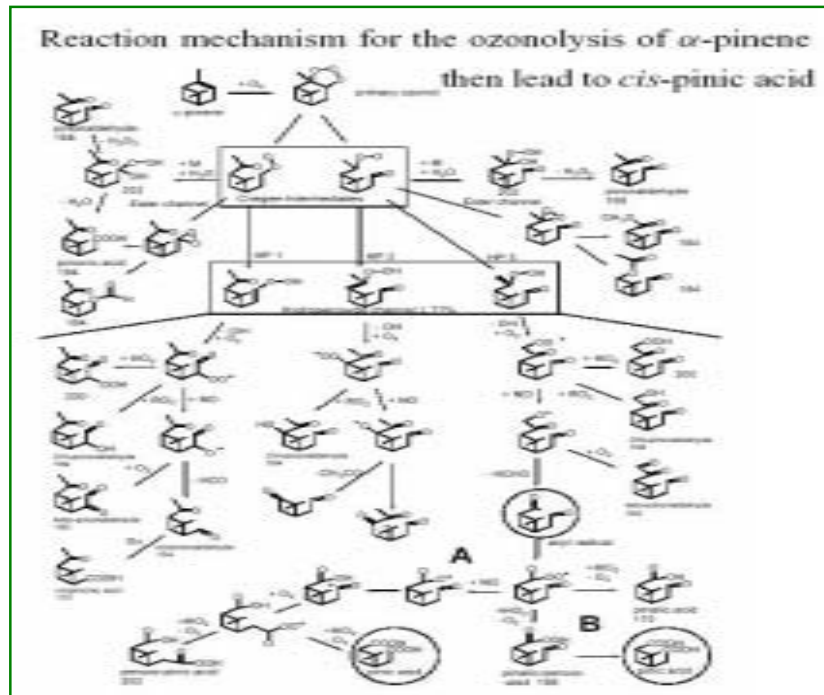
- ▶ emission of reactive trace gas (NO_x, CO, VOC)
 - ▶ fast atmospheric chemistry (O₃, OH, HO₂, RO₂, ...)
 - ▶ produce tropospheric **O₃**, perturb global **CH₄**
- ▶ emission of reactive trace gas (VOC like terpenes, toluene,...)
 - ▶ fast atmospheric chemistry (O₃, OH, HO₂, RO₂, ...)
 - ▶ produce **secondary organic aerosols (SOA)**

- ▶emission of reactive trace gas (NO_x, CO, VOC)
- ▶fast atmospheric chemistry (O₃, OH, HO₂, RO₂, ...)



- ▶produce tropospheric O₃, perturb global CH₄

- ▶emission of reactive trace gas (VOC like terpenes, toluene,...)
- ▶fast atmospheric chemistry (O_3 , OH, HO_2 , RO_2 , ...)



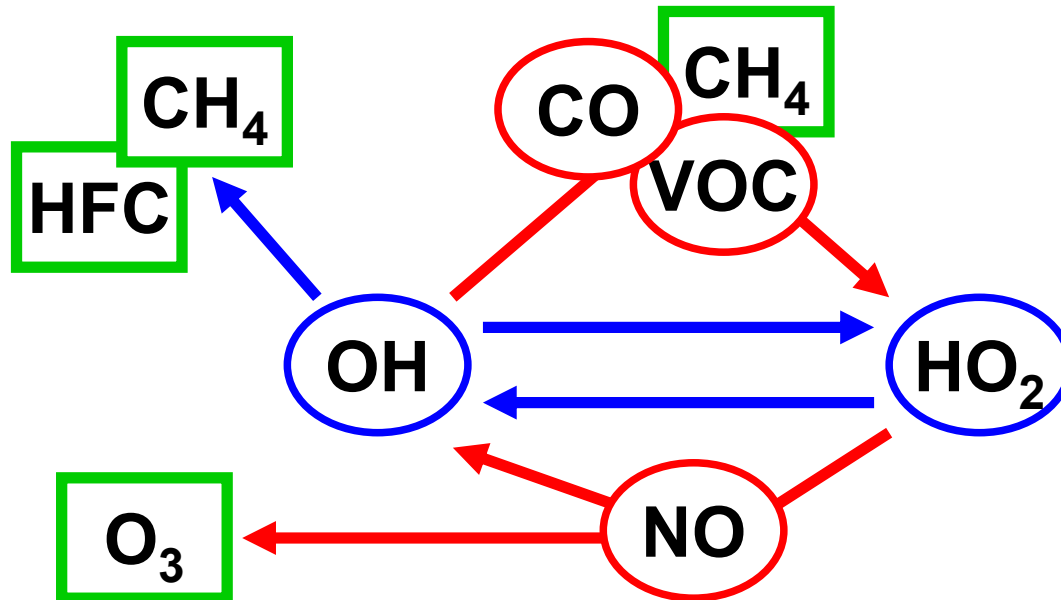
- ▶produce **secondary organic aerosols (SOA)**

*IPCC / NGGIP, Expert Meeting
Emission Estimation of Aerosols Relevant to Climate Change
2-4 May 2005, Geneva*

Climate Forcing through Atmospheric Chemistry

- ▶ **indirect effects on greenhouse gases**
- ▶ secondary organic aerosols

Reactive chemistry and the greenhouse gases ?

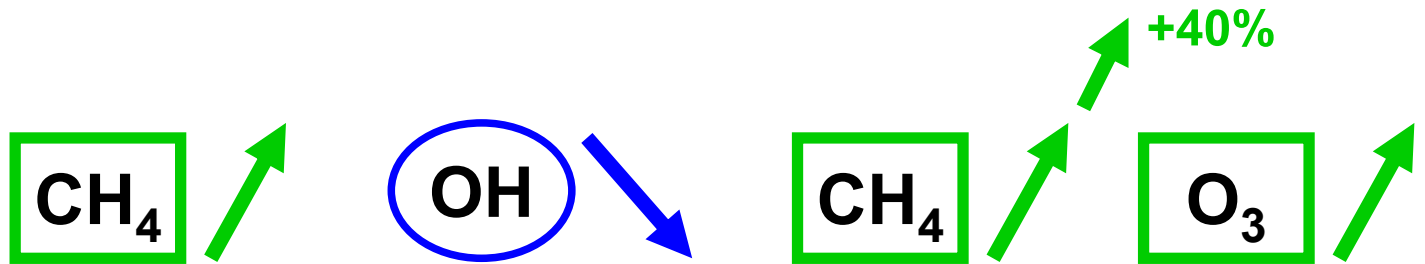


CO, VOC, NO_x (=NO+NO₂), & CH₄ control

Tropospheric Chemistry (OH, HO₂)

which is the sink for CH₄ & HFCs; the source for O₃

CH₄ feedback on its lifetime



Isaksen & Hov, 1987

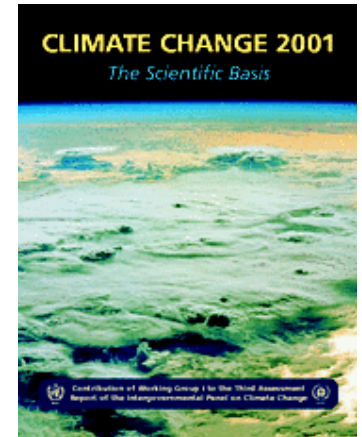
Prather, 1994

IPCC SAR (multi-model assessment), 1995

CH₄ self-feedback, 2001

Changes in atmospheric composition and chemistry over the past century have affected, and those projected into the future will affect, the lifetimes of many greenhouse gases and thus alter the climate forcing of anthropogenic emissions:

The atmospheric lifetime relates emissions of a component to its atmospheric burden. In some cases, for instance for methane, a change in emissions perturbs the chemistry and thus the corresponding lifetime. The CH₄ feedback effect amplifies the climate forcing of an addition of CH₄ to the current atmosphere by lengthening the perturbation lifetime relative to the global atmospheric lifetime of CH₄ by a factor of 1.4. This earlier finding is corroborated here by new model studies that also predict only small changes in this CH₄ feedback for the different scenarios projected to year 2100. Another feedback has been identified for the addition of N₂O to the atmosphere; it is associated with stratospheric O₃ chemistry and shortens the perturbation lifetime relative to the global atmospheric lifetime of N₂O by about 5%.



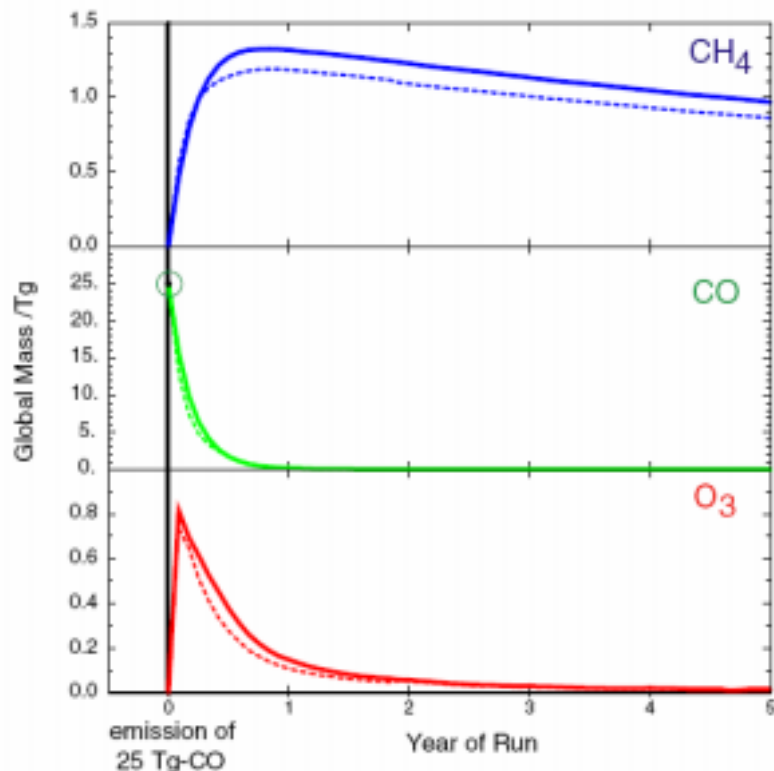
Time scales in atmospheric chemistry: Theory, GWPs for CH₄ and CO, and runaway growth

Michael J. Prather

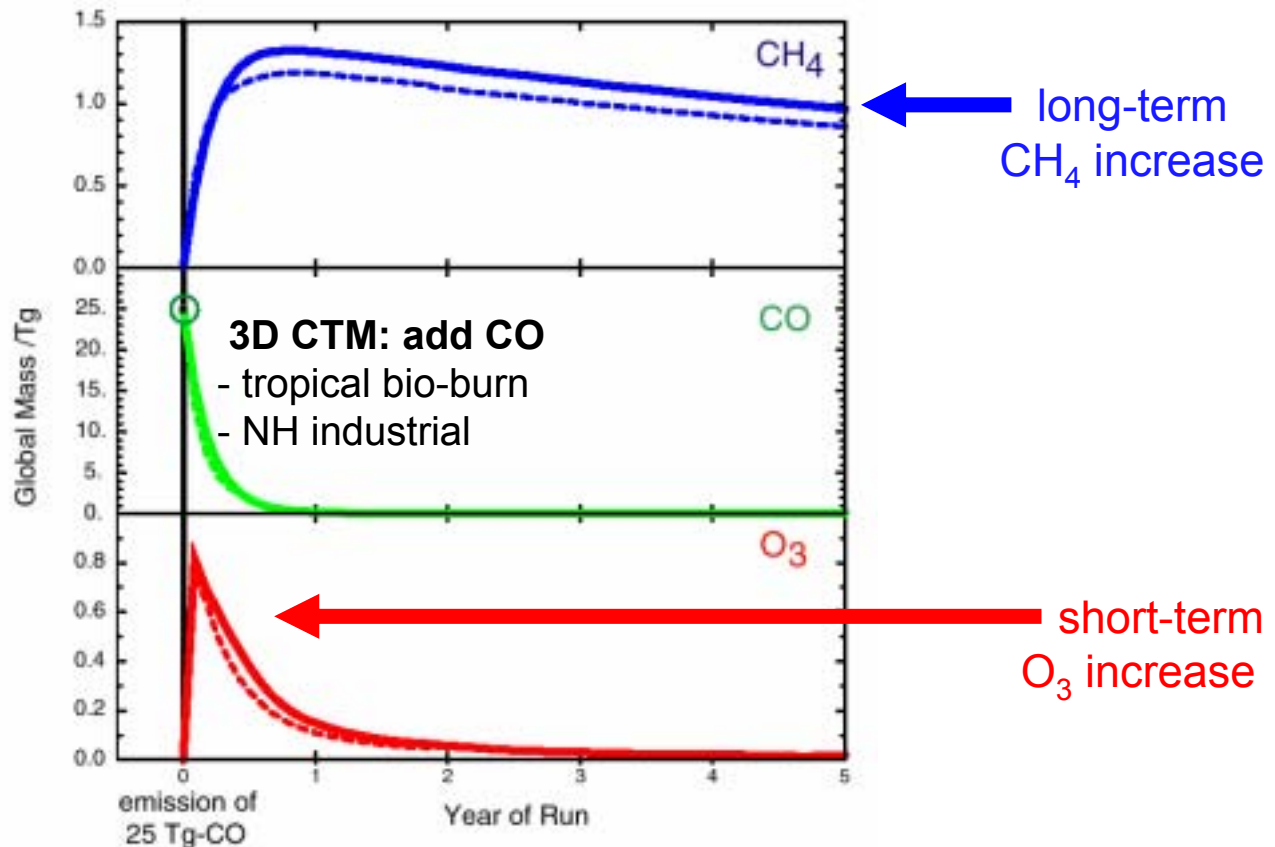
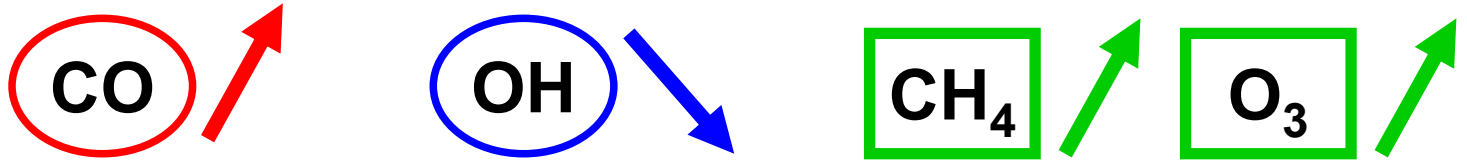
Earth System Science, University of California at Irvine

Abstract. Atmospheric CH₄ perturbations, caused directly by CH₄ emissions or indirectly by those of CO are enhanced by chemical feedbacks. They can be diagnosed in terms of the natural modes of atmospheric chemistry that are general solutions of the continuity equations. Each mode is a pattern in the global distribution of all chemical species, and each has a single time-constant that accurately describes its exponential decay about a given atmospheric state. This mathematical theory extends earlier work and is general for 2-D and 3-D chemistry-transport models. A formal proof relates the steady-state distribution and its lifetime to the integral of the true time-dependent response (properly included in the recent IPCC assessment). Changes in CO are also known to perturb CH₄; however, the impact of CO emissions on climate has not been formally assessed in part because the short lifetime of CO (months) relative to that of CH₄ (decade) was believed to limit the integrated impact. Using the IPCC model studies, this theory predicts that adding 5 CO molecules to today's atmosphere is equivalent to adding 1 CH₄ molecule with the same decadal duration as direct CH₄ addition. Extrapolating these results, CH₄ sources would have to triple before runaway growth, where in CH₄ emissions exceed the oxidizing capacity of the troposphere.

Long-lived increases in CH₄ and trop O₃ follow a pulse of CO
(African biomass burn / European industrial)



CO becomes an indirect greenhouse gas



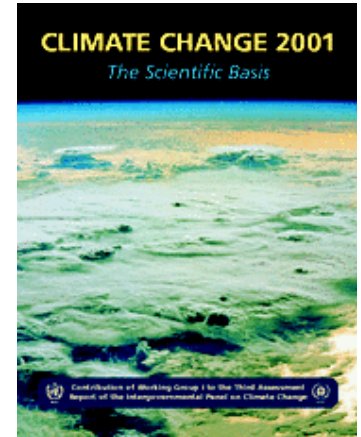
CO indirect

Executive Summary

Two important new findings since the IPCC WGI Second Assessment Report (IPCC, 1996) (hereafter SAR) demonstrate the importance of atmospheric chemistry in controlling greenhouse gases:

Currently, tropospheric ozone (O_3) is the third most important greenhouse gas after carbon dioxide (CO_2) and methane (CH_4). It is a product of photochemistry, and its future abundance is controlled primarily by emissions of CH_4 , carbon monoxide (CO), nitrogen oxides (NO_x), and volatile organic compounds (VOC). There is now greater confidence in the model assessment of the increase in tropospheric O_3 since the pre-industrial period, which amounts to 30% when globally averaged, as well as the response to future emissions. For scenarios in which the CH_4 abundance doubles and anthropogenic CO and NO_x emissions triple, the tropospheric O_3 abundance is predicted to increase by an additional 50% above today's abundance.

CO is identified as an important indirect greenhouse gas. An addition of CO to the atmosphere perturbs the OH- CH_4 - O_3 chemistry. Model calculations indicate that the emission of 100 Mt of CO stimulates an atmospheric chemistry perturbation that is equivalent to direct emission of about 5 Mt of CH_4 .



Clouds & Aerosols impact photochemistry by changing photolytic rates (J-values)



Bian H., M. J. Prather, and T. Takemura,

Tropospheric aerosol impacts on trace gas budgets through photolysis,

J. Geophys. Res. 108 (D8), 4242, doi:10.1029/2002JD002743, 2003.

Aerosols affect the global budgets of O₃, OH, and CH₄ in part through their alteration of photolysis rates and in part through their direct chemical interactions with gases (i.e., “heterogeneous chemistry”). ... **Globally averaged, the impact of aerosols on photolysis alone is to increase tropospheric O₃ by 0.63 Dobson units and increase tropospheric CH₄ by 130 ppb (via tropospheric OH decreases of 8%).**

These greenhouse gas increases lead to an aerosol indirect effect (counting both natural and anthropogenic aerosols) of +0.08 W/m². ... The predominant impact is due to the aerosols over land; aerosols over the ocean contribute less than a third to globally integrated changes.

Martin R. V., D. J. Jacob, R. M. Yantosca, M. Chin, and P. Ginoux,
Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, J. Geophys. Res., 108 (D3), 4097, 2003.

We evaluate the sensitivity of tropospheric OH, O₃, and O₃ precursors to photochemical effects of aerosols not usually included in global models: (1) aerosol scattering and absorption of ultraviolet radiation (*via Fast-J*), and (2) reactive uptake of HO₂, NO₂, and NO₃. ... Aerosols decrease the O₃→O(¹D) photolysis frequency by 5-20% at the surface throughout the Northern Hemisphere (largely due to mineral dust) and by a factor of 2 in biomass burning regions (largely due to black carbon). Aerosol uptake of HO₂ ... **Annual mean OH concentrations decrease by 9% globally and by 5-35% in the boundary layer over the Northern Hemisphere. Simulated CO increases by 5-15 ppbv in the remote Northern Hemisphere**, improving agreement with observations. Simulated boundary-layer O₃ decreases by 15-45 ppbv over India during the biomass burning season in March, and by 5-9 ppbv over northern Europe in August, again improving comparison with observations. We find that particulate matter controls would increase surface O₃ over Europe and other industrial regions.

but

**studies focus on total aerosol
(primarily dust)
not on anthropogenic aerosols**

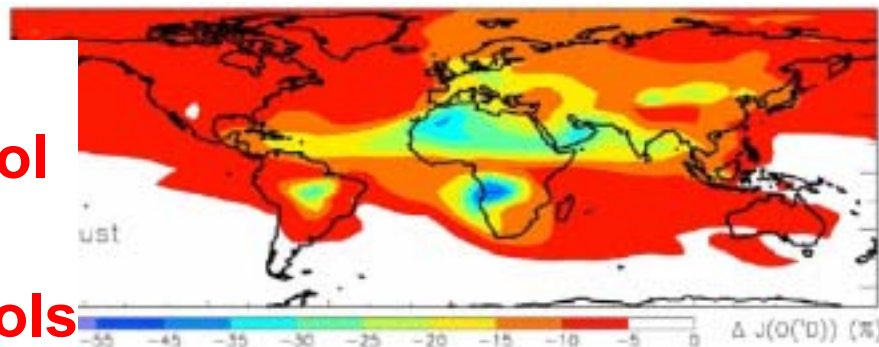
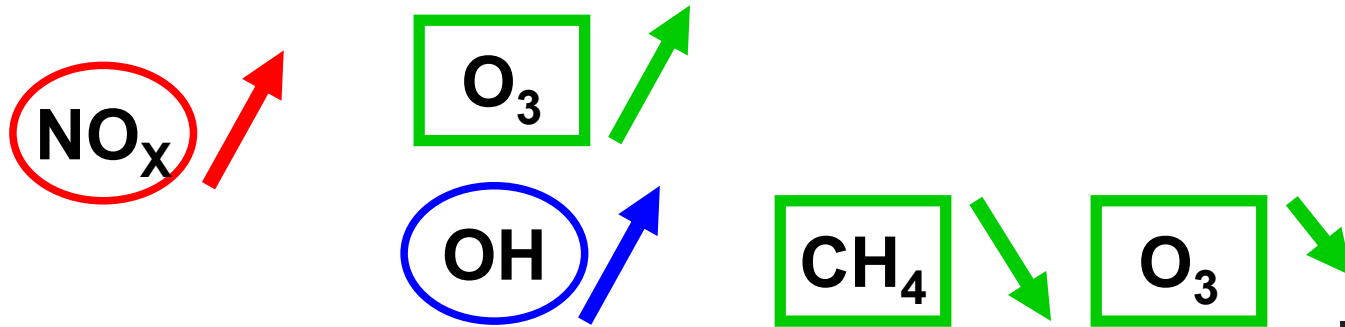


Figure 3: Sensitivity to aerosols of the O₃ → O(¹D) photolysis frequency ($J(O(^1D))$) in surface air. Values are monthly-mean model results for March and August 1997.

NO_x identified as an indirect greenhouse gas



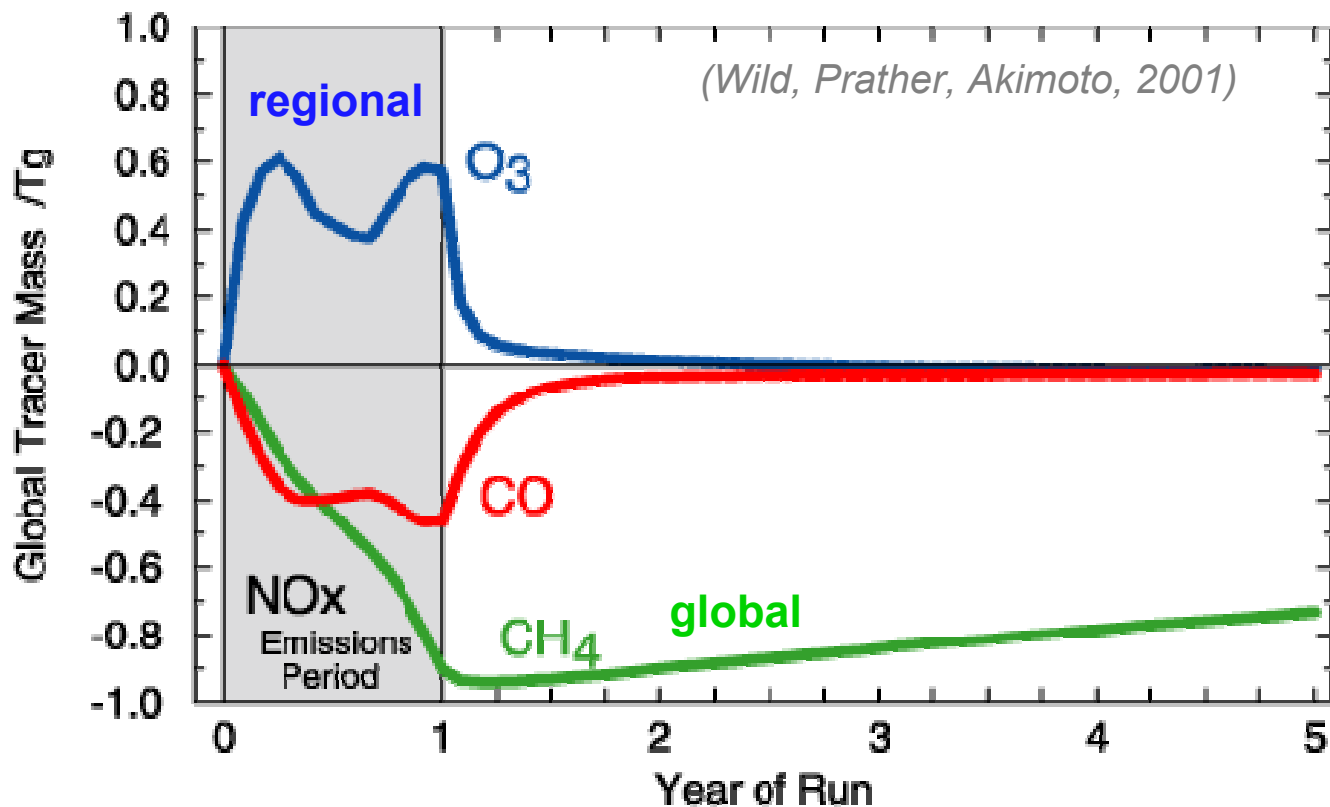
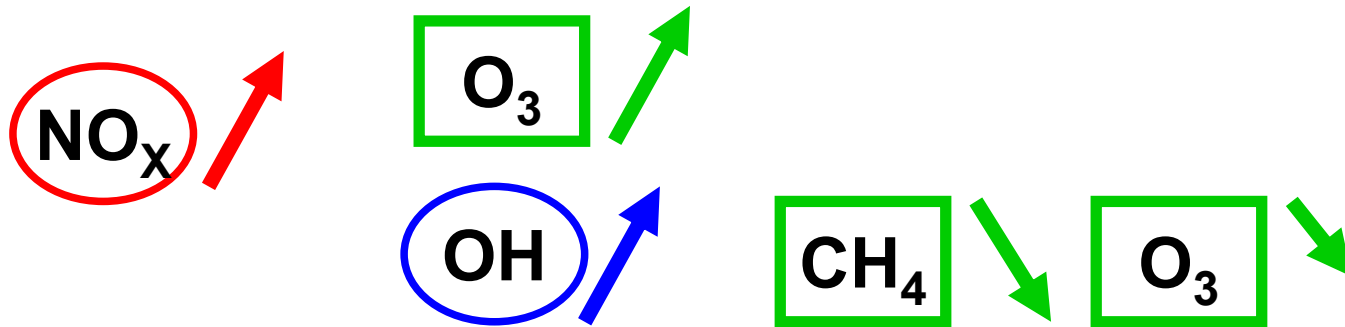
NO_x proposed as indirect greenhouse gas
(Shine, Derwent, et al, 1st IPCC Assessment Report)



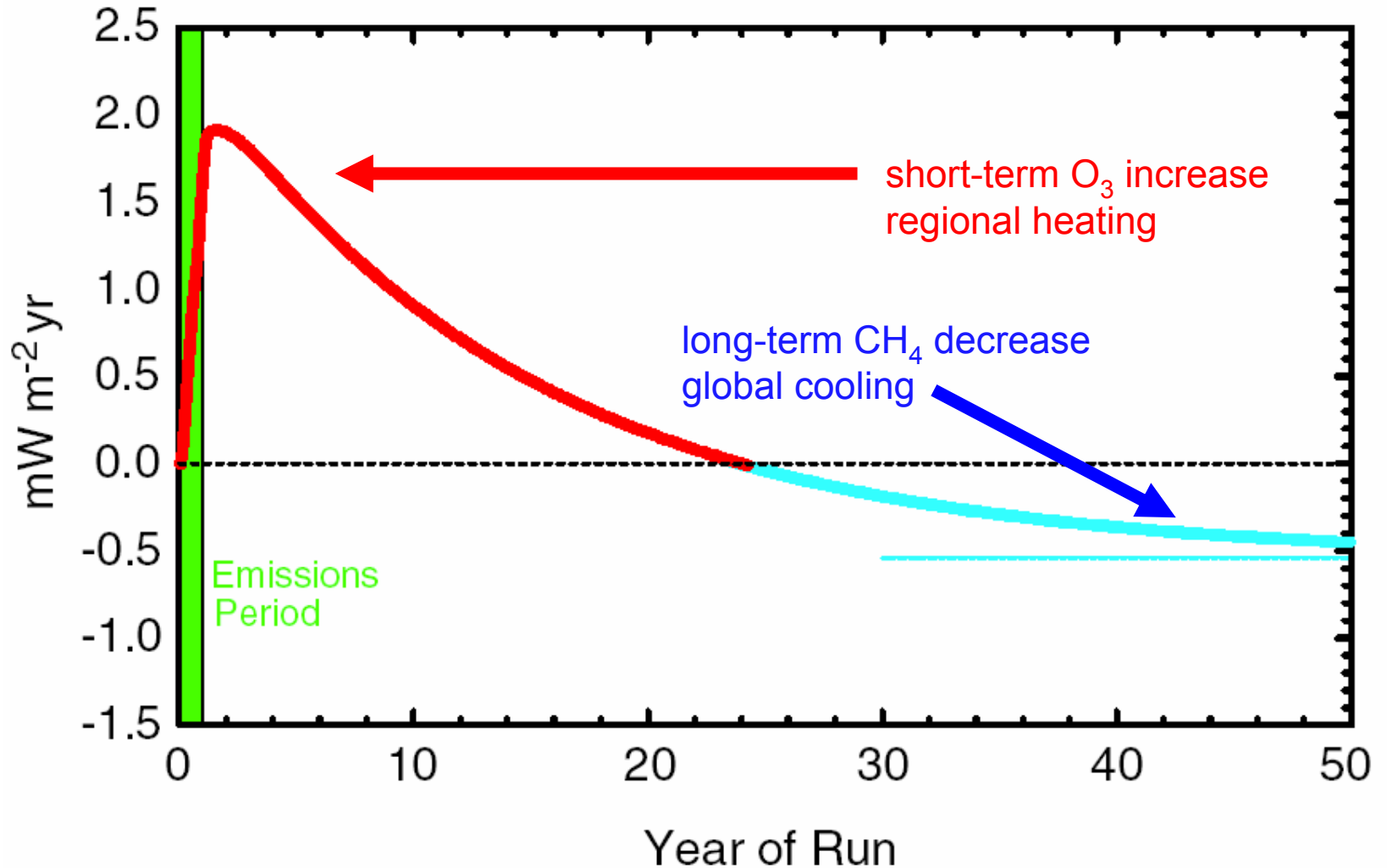
Rejected as too far ahead of its time
(1992 IPCC Interim Report)



Post SAR, explicit in IPCC Aviation Assessment, NO_x is indirect greenhouse gas.



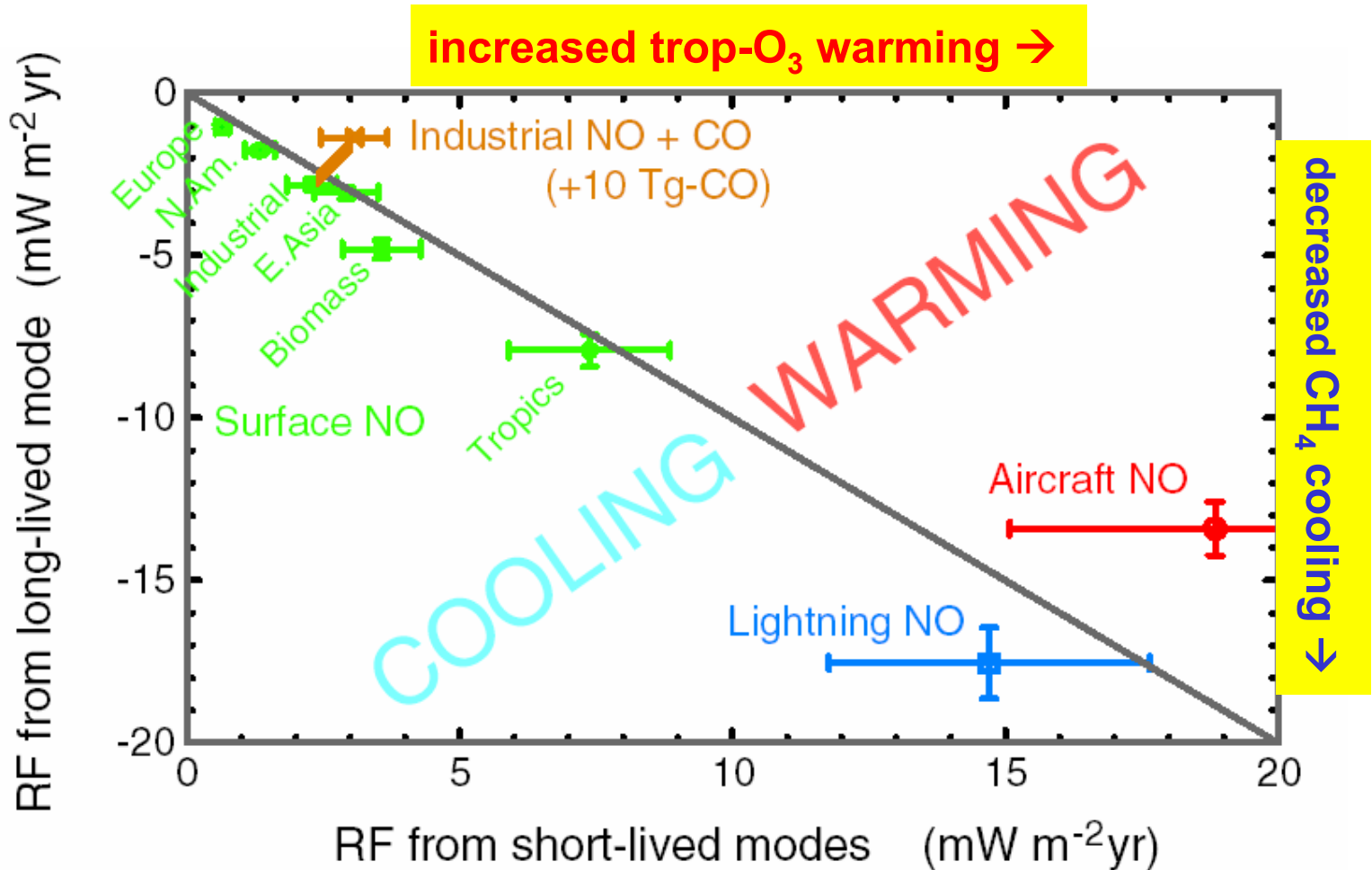
Integrated Radiative Forcing (CH₄ & trop O₃)
from 0.5 Tg-N as global fossil fuel



Impact of NO_x is strongly depends on location

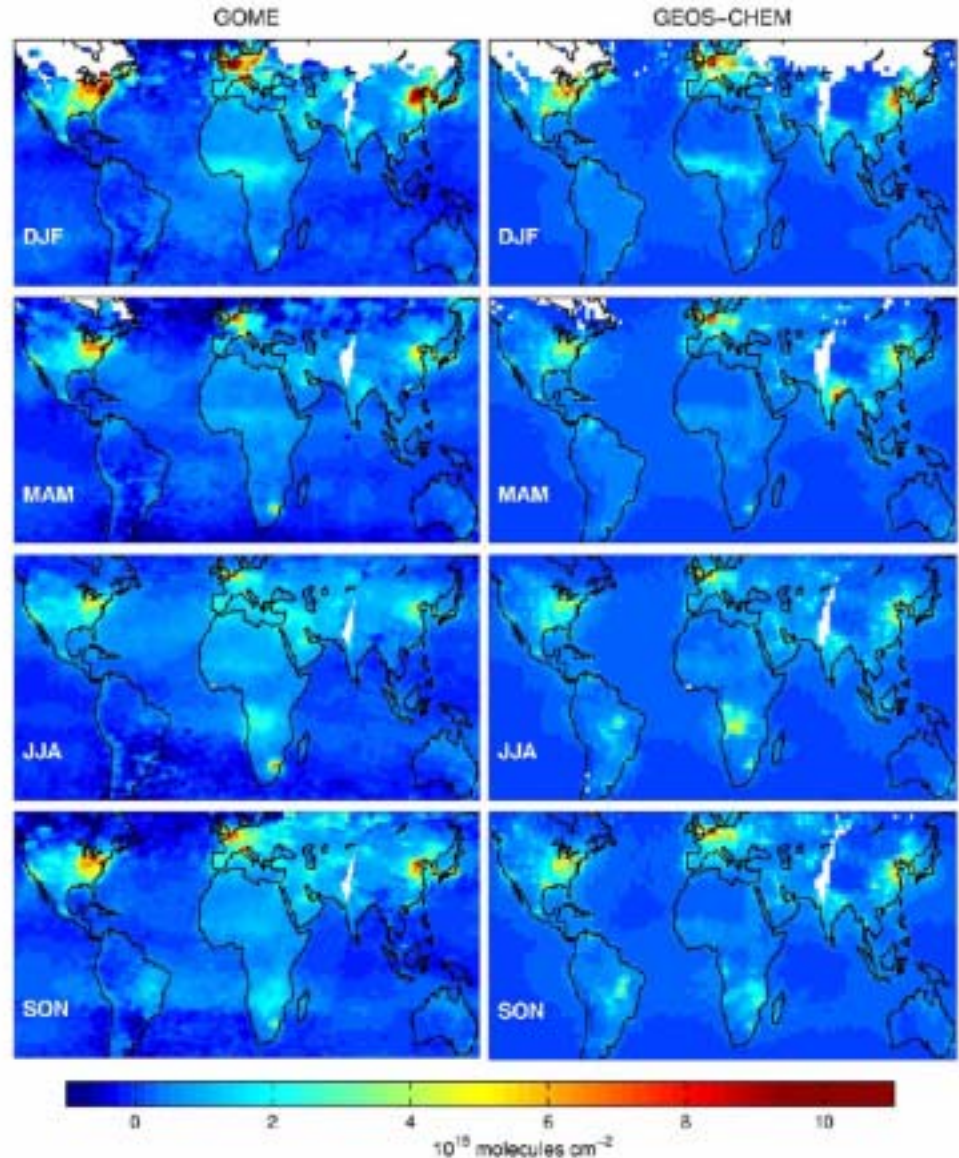
(Wild, Prather, Akimoto, 2001)

0.5 Tg-N of NO_x: tropical, high-altitude emissions have greatest impact



NO_x (and O₃ prod.) is highly regional

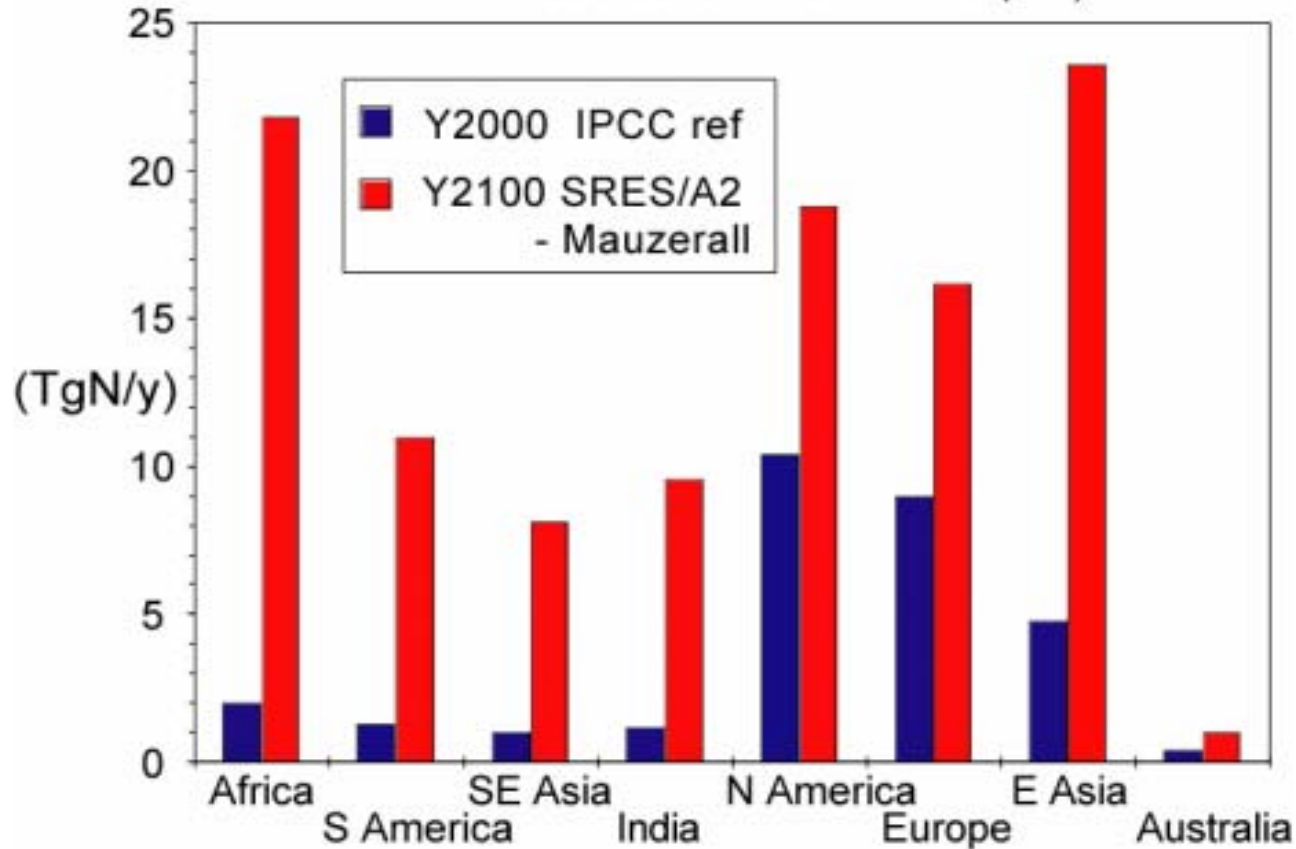
Global Inventory of Nitrogen
Oxide Emissions Constrained
by Space-based (GOME)
Observations of NO₂ Columns,
*R.V. Martin et al.,
JGR, 2003.*



Seasonal mean tropospheric NO₂ columns for September 1996 – August 1997.

future NOx increases are projected to be highly regional

Geographic shift in NOx emissions
from Y2000 to SRES Y2100 (A2)



Chemical transport model ozone simulations for spring 2001 over the western Pacific: Regional ozone production and its global impacts

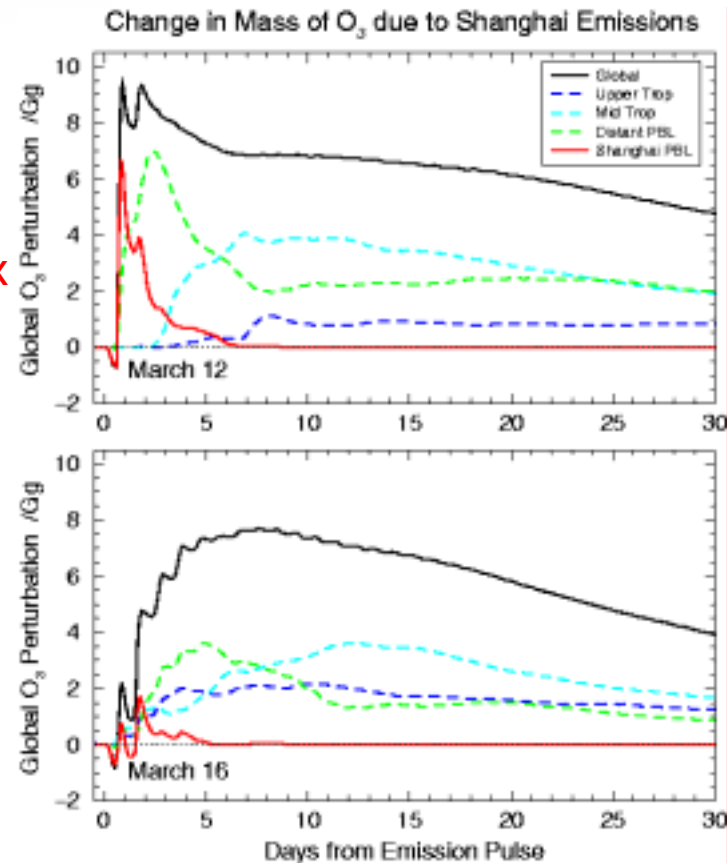
Oliver Wild,¹ Michael J. Prather,² Hajime Akimoto,¹ Jostein K. Sundet,³ Ivar S. A. Isaksen,³ James H. Crawford,⁴ Douglas D. Davis,⁵ Melody A. Aver Yutaka Kondo,⁶ Glen W. Sachse,⁴ and Scott T. Sandholm⁵

Look at regional and global O_3 from a single day's emissions over Shanghai in March 2001

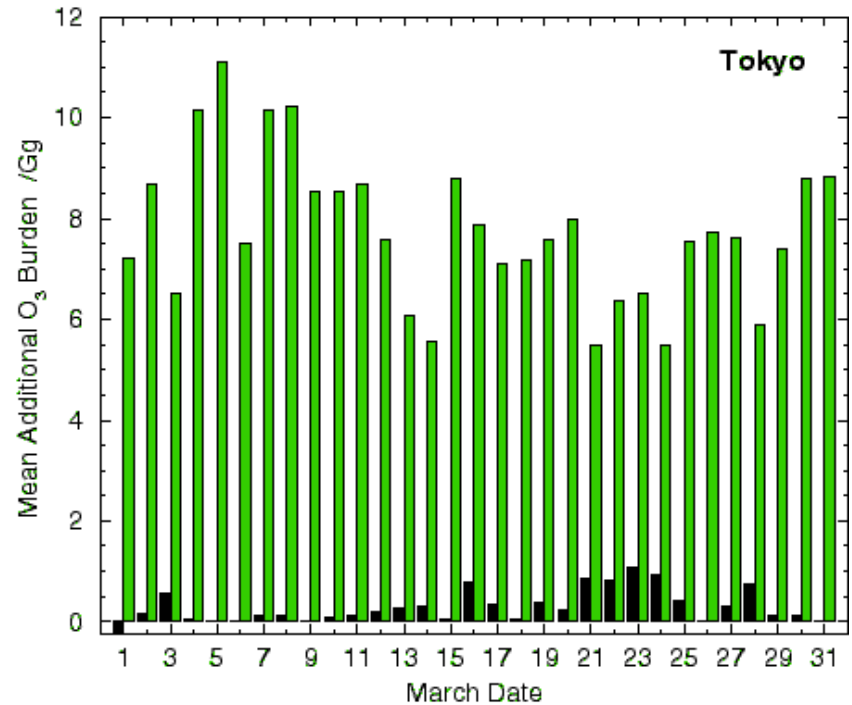
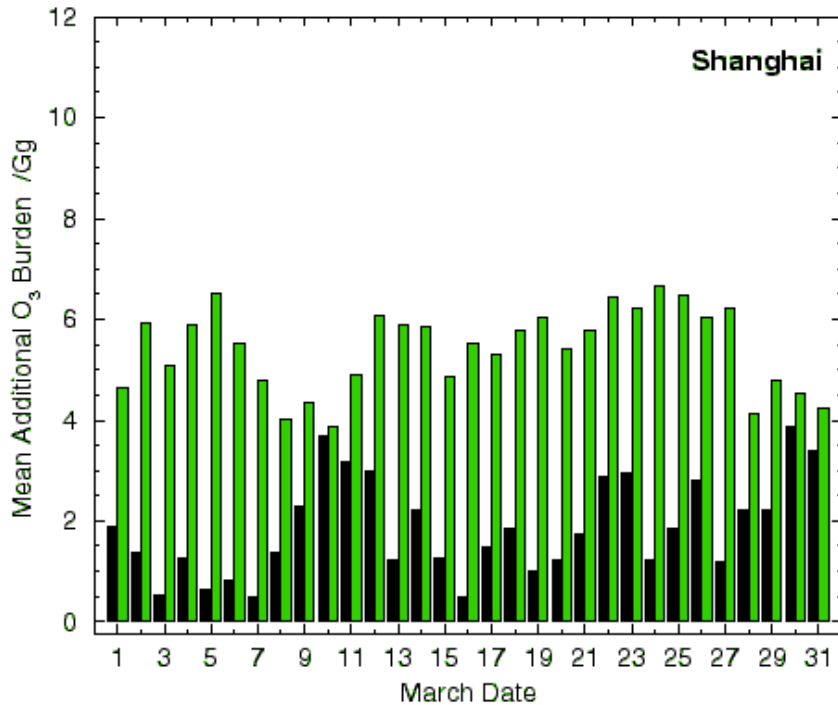
March 12: Sunny, high pressure = Cook-then-mix

March 16: Heavily overcast = Mix-then-cook

Regional production different,
Global production similar, but
Evolution quite different.



NOx production of **Air Quality O₃** vs. **Greenhouse O₃**



- **Added O₃ burden from a single day's emissions:**
 - over Region (3-day integral: air quality)
 - over **Globe** (1-month integral: climate)
- **Global impact smaller when AQ ozone impact large**
 - Tokyo has greater climate impact than Shanghai

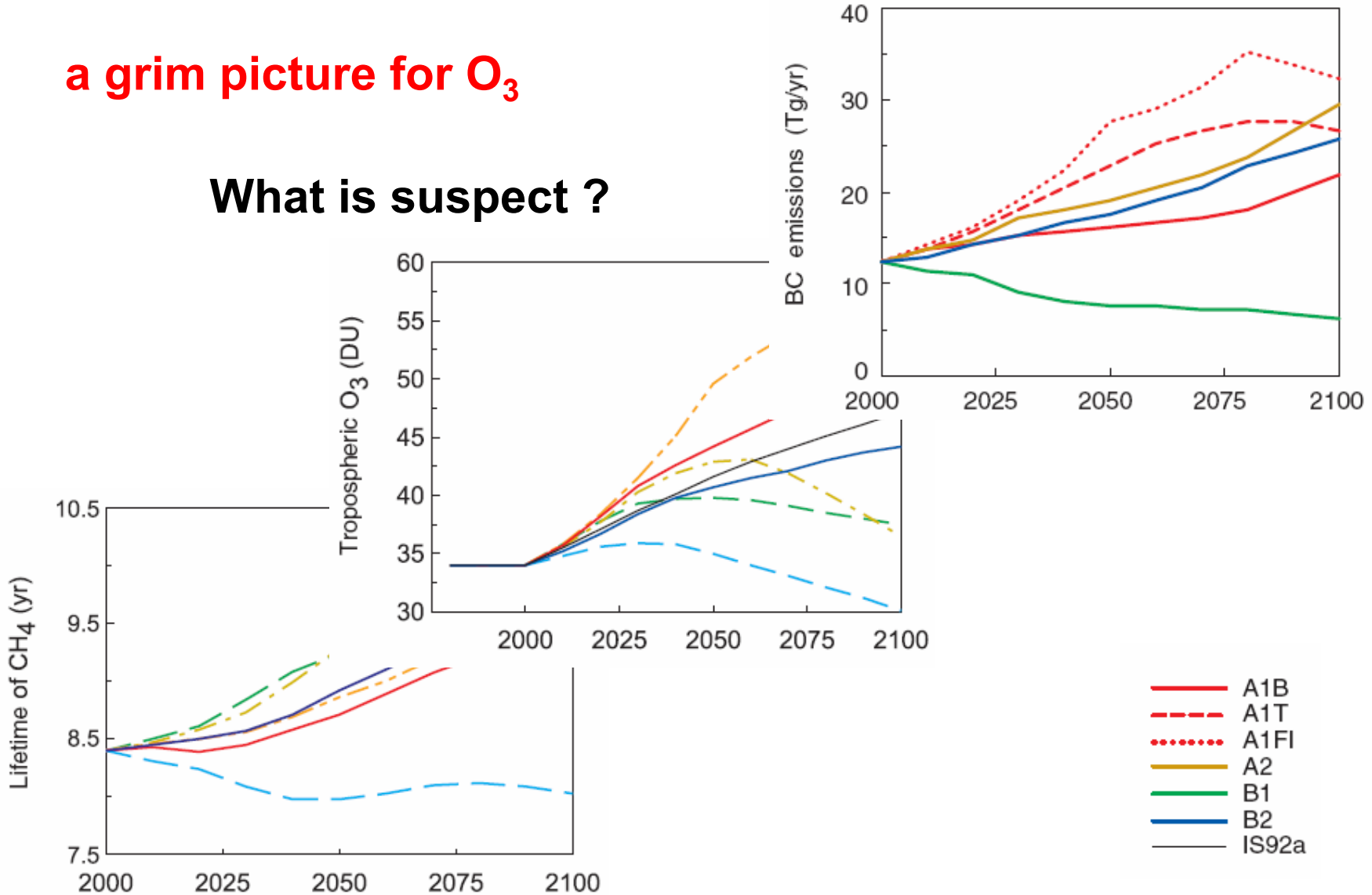
Likewise,

SOA yield from VOC precursors depends on location.

TAR / SRES for reactive chemistry & aerosols:

a grim picture for O_3

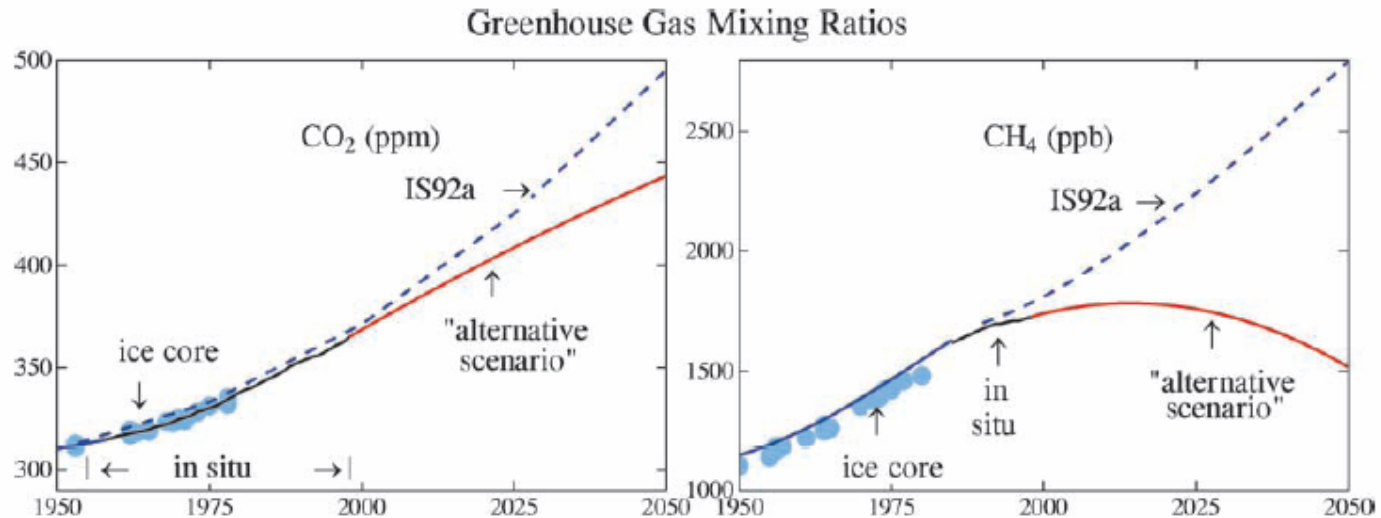
What is suspect ?



non-SRES futures

Climate forcings in Goddard Institute for Space Studies SI2000 simulations

J. Hansen,¹ M. Sato,^{1,2} L. Nazarenko,^{1,2} R. Ruedy,^{1,3} A. Lacis,¹ D. Koch,^{1,4} I. Tegen,⁵ T. Hall,^{1,6} D. Shindell,¹ B. Santer,⁷ P. Stone,⁸ T. Novakov,⁹ L. Thomason,¹⁰ R. Wang,¹¹ Y. Wang,¹² D. Jacob,¹³ S. Hollandsworth,¹⁴ L. Bishop,¹⁵ J. Logan,¹³ A. Thompson,¹⁴ R. Stolarski,¹⁴ J. Lean,¹⁶ R. Willson,² S. Levitus,¹⁷ J. Antonov,¹⁷ N. Rayner,¹⁸ D. Parker,¹⁸ and J. Christy¹⁹



non-SRES futures

Atmos. Chem. Phys. Discuss., 4, 1–68, 2004
www.atmos-chem-phys.org/acpd/4/1/
SRef-ID: 1680-7375/acpd/2004-4-1
European Geosciences Union



The impact of air pollutant and methane emission controls on tropospheric ozone and radiative forcing: CTM calculations for the period 1990–2030

F. Dentener¹, D. Stevenson², J. Cofala³, R. Mechler³, M. Amann³,
P. Bergamaschi¹, F. Raes¹, and R. Derwent⁴

The “Current Legislation” (**CLE**) scenario reflects the current perspectives of individual countries on future economic development and takes the anticipated effects of presently decided emission control legislation in the individual countries into account.

The “Maximum technically Feasible Reduction” (**MFR**) scenario considers emission reductions offered by full implementation of the presently available emission control technologies, while maintaining the projected levels of anthropogenic activities.

Whereas the resulting projections of methane emissions lie within the range suggested by other greenhouse gas projections, the recent pollution control legislation of many Asian countries, requiring introduction of catalytic converters for vehicles, leads to significantly lower growth in emissions of the air pollutants NO_x, NMVOC and CO than in SRES.

These new scenarios form the core the new IPCC AR4 atmospheric chemistry studies (Stevenson and Dentener, ACCENTworkshop, Jan 2005, Oslo).

NO_x emissions

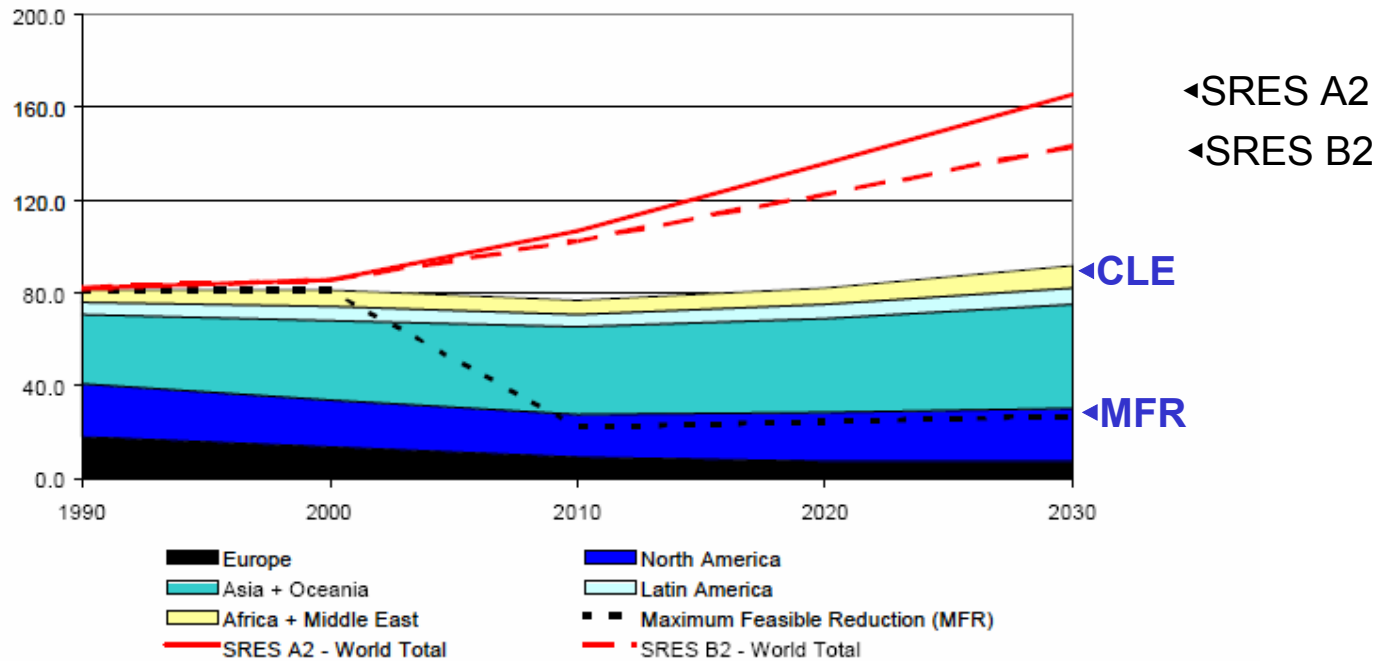


Fig. 1. Projected development of IIASA anthropogenic NO_x emissions by SRES world region (Tg NO₂yr⁻¹).

CO emissions

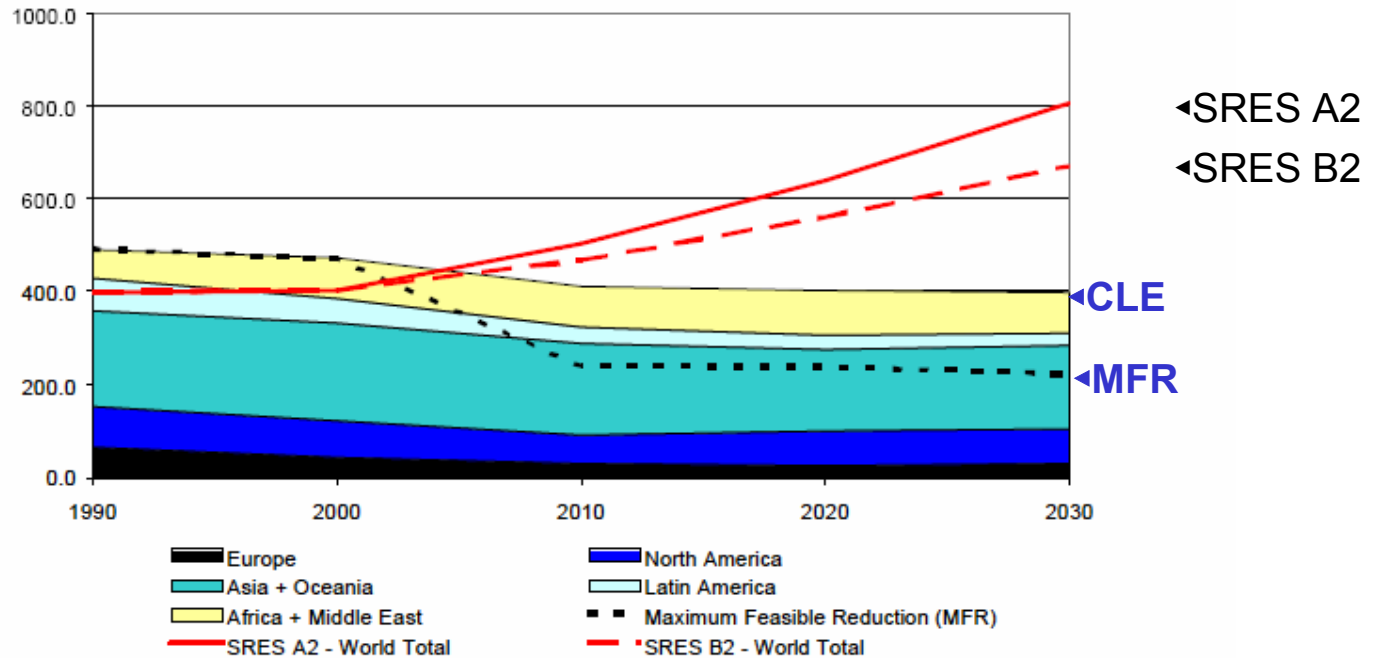


Fig. 2. Projected development of IIASA anthropogenic CO emissions by SRES world region (Tg CO yr⁻¹).

IPCC / NGGIP, Expert Meeting

Emission Estimation of Aerosols Relevant to Climate Change

2-4 May 2005, Geneva

Climate Forcing through Atmospheric Chemistry

- ▶ indirect effects on greenhouse gases
- ▶ **secondary organic aerosols**

Secondary organic aerosol

1. Atmospheric chemical mechanism for production of molecular constituents

Robert J. Griffin¹

Department of Chemical Engineering, California Institute of Technology, Pasadena, California, USA

Donald Dabdub

Department of Mechanical and Aerospace Engineering, University of California at Irvine, Irvine, California, USA

John H. Seinfeld

Department of Chemical Engineering, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. D17, 4333, doi:10.1029/2001JD000542, 2002
Pasadena, California, USA

Secondary organic aerosol

2. Thermodynamic model for gas/particle partitioning of molecular constituents

Betty K. Pun,¹ Robert J. Griffin,^{2,3} Christian Seigneur,¹ and John H. Seinfeld⁴

Secondary organic aerosol

3. Urban/regional scale model of size- and composition-resolved aerosols

Robert J. Griffin,^{1,2} Donald Dabdub,³ Michael J. Kleeman,⁴ Matthew P. Fraser,⁵
Glen R. Cass,^{6,7} and John H. Seinfeld⁸

3.7. Aromatics

[28] Aromatic species comprise a significant portion of the hydrocarbon component of motor vehicle emissions [Harley *et al.*, 1992] and have been identified as the most likely class of anthropogenic SOA precursors [Odum *et al.*, 1996, 1997]. Aromatics are found in relatively high concentrations in the urban atmosphere [Fraser *et al.*, 1999] and come from a variety of sources [Schauer, 1998; Schauer *et al.*, 1999a, 1999b].

[29] Aromatic species are aggregated depending on their reactivity, their degree and nature of substitution, and their potential for SOA formation, as determined by Odum *et al.*

[1996, 1997]. Low SOA-yield aromatics (AROL, represented by 1,2,3-trimethylbenzene) are those with two or more methyl side groups and no functional side groups (such as phenols, aldehydes, acids, or nitro groups); high SOA-yield aromatics (AROH, represented by *m*-(*n*-propyl)-toluene) have one or no methyl side groups and no functional side groups. Phenolic species (AROO, represented by 2,6-dimethyl-phenol) may have one or more alkyl side groups and one or more phenolic substituents. Aldehydic aromatics (ARAL, represented by *p*-tolualdehyde) have one aldehydic functional group; acidic aromatics (ARAC, represented by *p*-toluic acid) have one carboxylic functional group. Gas-phase polycyclic aromatic hydrocarbons (PAHs, represented by 1,2-dimethyl-naphthalene) have multiple aromatic rings. Generally, only PAHs with two aromatic rings remain in the gas-phase; those with more partition between the gas- and aerosol-phases [Fraser *et al.*, 1999]. The chemistry of aromatics proceeds typically via OH addition to the ring or H-atom abstraction from alkyl side chains. Any deviations are explained appropriately in the sections below.

4.3. Total Semivolatile Species

[46] A principal goal of the gas-phase mechanism CACM is to predict concentrations of those surrogate organic products that have the potential to partition to the aerosol phase. Based on available or estimated vapor pressures or solubility, a product is considered to have the potential to partition to the aerosol phase if it meets one or more of the following criteria: (1) it is known to be partially soluble; (2) it is an aromatic acid; (3) it is an aromatic with two functional groups that are not aldehydes; (4) it has 12 or more carbon atoms (excluding primary gas-phase emission of ALKH and PAH); (5) it has at least 10 carbons and two functional groups; (6) it has at least six carbon atoms and two functional groups, one of which is an acid; or (7) it is trifunctional. The products considered capable of forming SOA based on these criteria are marked with a plus sign in

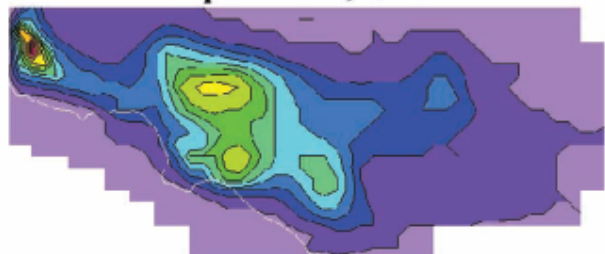
[49] Because aromatics are known to be an important source of anthropogenic SOA [Odum *et al.*, 1996] and because uncertainties in aromatic chemistry have been well documented [Atkinson, 1994], an issue that merits evaluation here is the sensitivity of SOA predicted from aromatic precursors to key aspects of aromatic photooxidation. One

Table 4. Predicted Percent Contribution to SOA Formation of Different Sources and Formation Mechanisms in Three Locations in the SoCAB

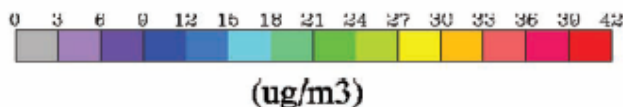
	Central Los Angeles	Azusa	Claremont
Anthropogenic	98.3	96.9	92.7
Biogenic	1.7	3.1	7.3
Hydrophobic	84.0	77.3	64.6
Hydrophilic	16.0	22.7	35.4

emont. Anthropogenic SOA is shown to be the dominant contributor to total SOA in each of these locations (98.3%, 96.9%, and 92.7% by mass, respectively); however, it should be noted that the contribution of anthropogenic species to SOA decreases with downwind location. Biogenically derived SOA is most important in the eastern half of the SoCAB, as plant cover increases in the SoCAB going from upwind to downwind locations. Table 4 also exhibits

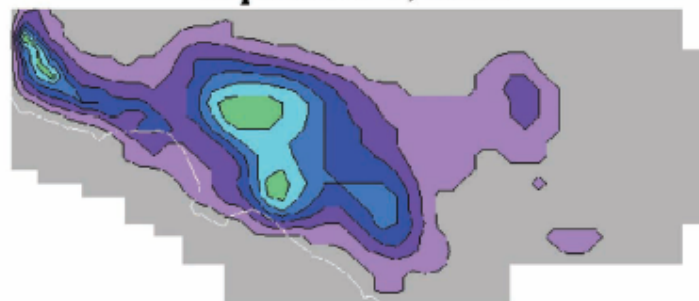
LOS ANGELES
September 8, 1993



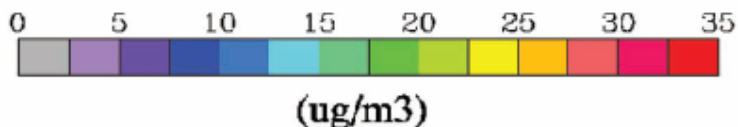
Total Organic Aerosol



LOS ANGELES
September 8, 1993



Secondary Organic Aerosol



Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis

K. Tsigaridis and M. Kanakidou

the global SOA budget. The global annual SOA production from biogenic VOC might range from 2.5 to 44.5 Tg of organic matter per year, whereas that from anthropogenic VOC ranges from 0.05 to 2.62 Tg of organic matter per year. These

Table 5. Global annual SOA production performed using the results of chamber experiments, versus the results of the present 3-D global modelling study

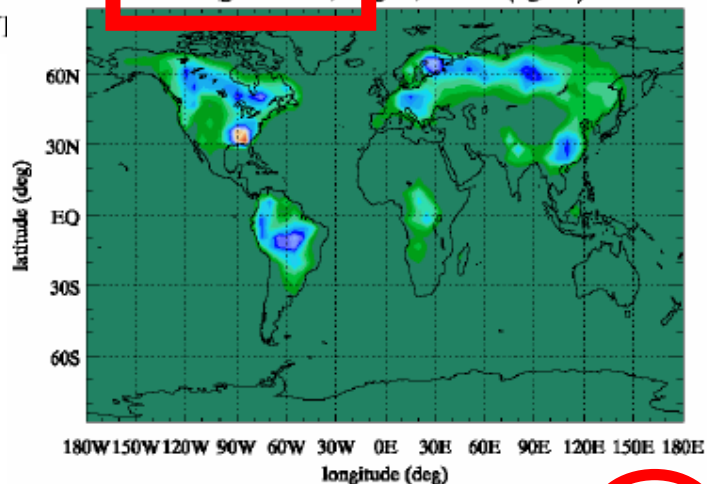
Production (Tg y ⁻¹)	Case	VOC precursors (number)	Pre-existing particles ^a	Evaporation	Transport of intermediates	Reference
13–24	Present day	Biogenic (30)	No	No	No	Griffin et al. (1999b)
61–79	Present day	Biogenic (2)	C	No	No	Kanakidou et al. (2000)
16.5–28	Pre-industrial	Biogenic (2)	C	No	No	Kanakidou et al. (2000)
11.2	Present day	Biogenic (5)	C	Yes	Yes	Chung and Seinfeld (2002)
63	Present day	Biogenic (1)	C	Yes	Yes	Derwent et al. (2003)
7.2 (0.3) ^b	Present day	Biogenic (2) & anthropogenic (2)	C	Yes	Yes	This work – S1
44.0 (2.0) ^b	Present day	Biogenic (2) & anthropogenic (2)	C	No	Yes	This work – S2
13.3 (0.7) ^b	Present day	Biogenic (2) & anthropogenic (2)	CSN	Yes	Yes	This work – S3
44.5 (2.6) ^b	Present day	Biogenic (2) & anthropogenic (2)	CSN	No	Yes	This work – S4

^a C: Carbonaceous aerosols, CSN: Carbonaceous, sulphate, methanesulphonate and ammonium aerosols ^b Read as: Biogenic VOC contribution to SOA (Anthropogenic VOC contribution to SOA)

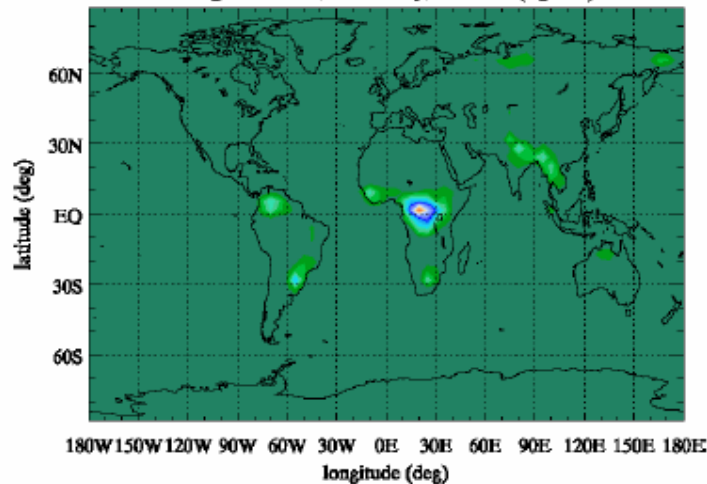
Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis

K. 7

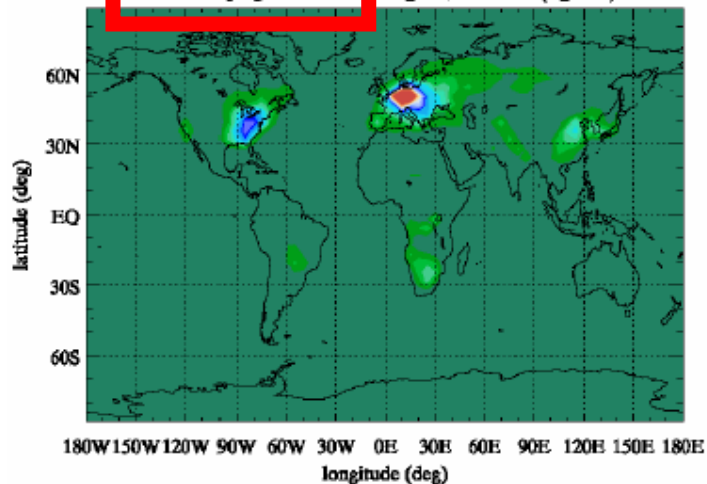
Biogenic SOA, August, surface ($\mu\text{g}/\text{m}^3$)



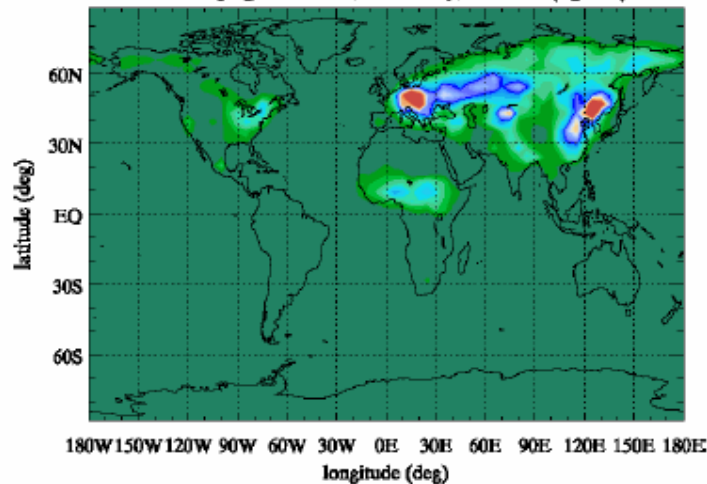
Biogenic SOA, February, surface ($\mu\text{g}/\text{m}^3$)



Anthropogenic SOA, August, surface ($\mu\text{g}/\text{m}^3$)



Anthropogenic SOA, February, surface ($\mu\text{g}/\text{m}^3$)



Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, Canada

M. T. Scholtz and A. Taylor

Canadian Ortech Environmental, Inc., Mississauga, Ontario, Canada

urban areas. Summer anthropogenic organic compound emissions are dominated by a different set of organic compound classes: C_{4-5} *n*-Alkanes and *iso*-Alkanes (largely from On-Road Mobile sources); C_{6-8} *n*-Alkanes and *iso*-Alkanes (Area sources being the largest contributor); Toluene (Area sources outweighing On-Road Mobile sources); Dialkyl Aromatics (sources similar to Toluene); and Ethanol (mostly Area sources in origin).

Speciation of volatile organic compound emissions for regional air quality modeling of part

P. A. Makar and M. D. Moran
Modelling and Integration Division, Air Quality
Service of Canada, Toronto, Ontario, Canada

M. T. Scholtz and A. Taylor
Canadian Ortech Environmental, Inc., Mississauga, Ontario, Canada

Table 5. Organic Aerosol Oxidation Precursor Volatile Organic Compound Classes Within the AURAMS81 Classification Scheme

Organic Compound Species or Class	Partitioning Parameter Reference ^a	Partitioning Comment ^b	Rate Constant References (OH, O ₃) ^c	Rate Constant Comment ^d
Alpha-Pinene	1		4, 4	
Beta-Pinene	1		4, 4	
D-Limonene	1		4, 4	
D-3-Carene	1		4, 4	
End C ₉₋₁₉ Alkenes	2		5, 4	
Toluene	3		6, 7	
Monoalkyl Aromatics	3		8, -	D
Dialkyl Aromatics	3		9, 7	
Trialkyl Aromatics	3		9, 10	
Alkene Aromatics	3	A	11, 12	
Cresol	3	A	13, 14	
C ₉₋₁₀ Alkanes	2	B	4, -	E
C ₁₁₋₁₉ Alkanes	2	B	4, -	E
End C ₆₋₈ Alkenes	2	B	5, 15	
Internal C ₆₋₈ Alkenes	2	B	16, 17	
Internal C ₉₋₁₉ Alkenes	2	B	16, 17	
Naphthalene	1	C	18, 19	
Aromatic Aldehydes	3	A	13, -	E
Phenol	3	A	13, -	E

Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality
Service of Canada, Toronto, Ontario, Canada

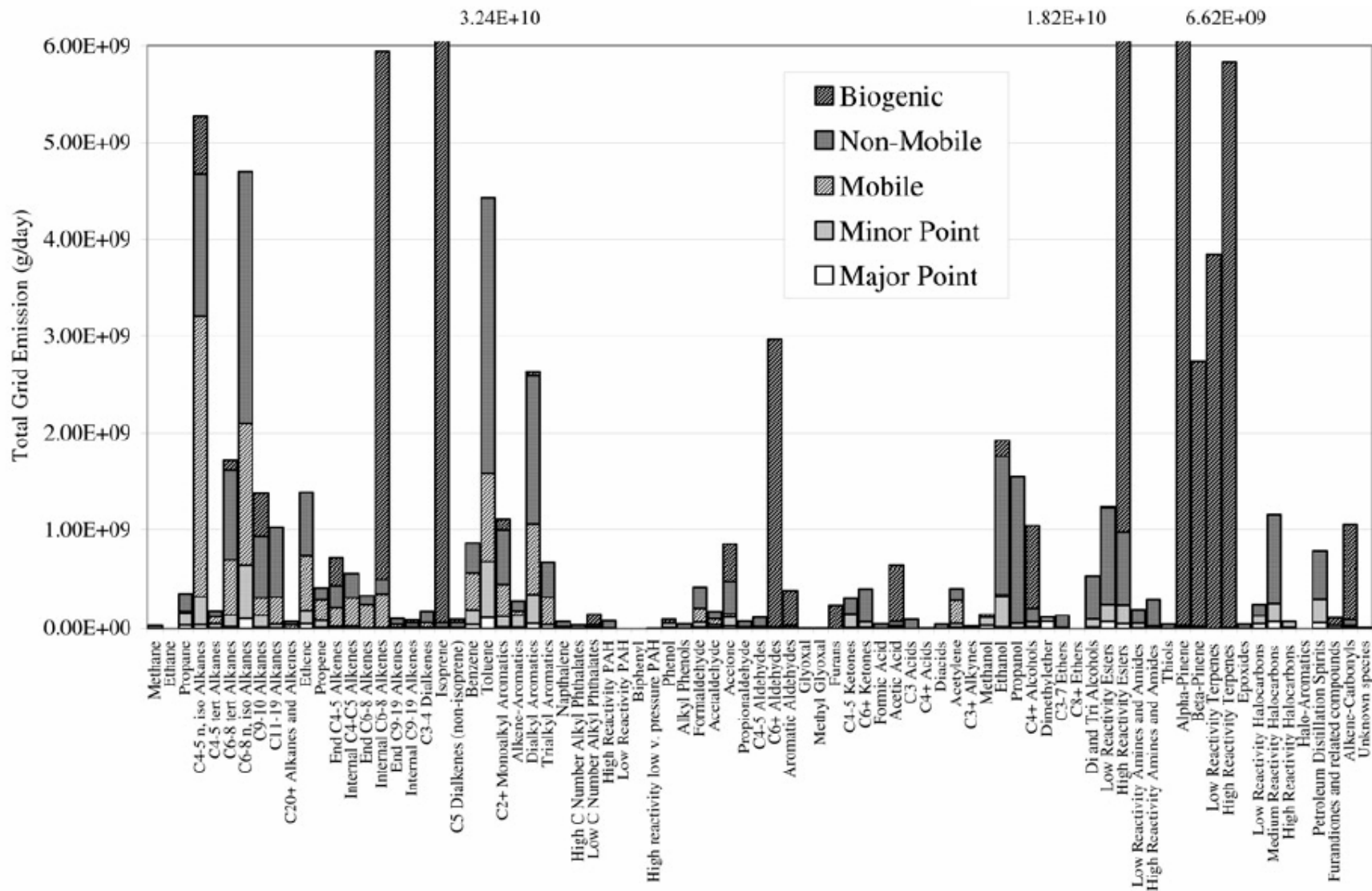
M. T. Scholtz and A. Taylor

Canadian Ortech Environmental, Inc., Mississauga

Total organic compound emissions in each of the three main anthropogenic emissions files (point, area, and on-road mobile: see left-hand side of Figure 2) are reported by source type, where source type is denoted by one of approximately 10,000 process classification codes. Each of these process classification codes is linked in turn to one of approximately 600 organic compound source specification profiles. These profiles split the criteria “VOC” emission into up to 822 individual organic compounds through the use of profile weights (mass fraction of individual compound per unit mass of criteria “VOC”). This disaggregation step from criteria “VOC” emissions to emissions of individual organic compounds is followed by an aggregation or “lumping” step from emissions of these individual species to emissions of model organic compounds. In this step, many of the 822 individual organic compounds are grouped or summed together in order to reduce the number of organics that must be represented in an air quality model. In earlier work during the National

inventory issues !!

Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone



Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, Canada

M. **Table 6.** Eastern North America Organic Compound Emissions (t d^{-1}) and Amount of
Can From These Emissions for a Winter Day and A Summer Day in Base Year 1990^a

Emission Category	Winter Day	
	Emitted	Condensed
Total Organic Compound Emissions	37,714	278
Anthropogenic	34,291	277
Biogenic	3423	1
Total Primary Nonvolatile and Semivolatile Emissions	7188	269
Anthropogenic	6,012	269
Biogenic	1,176	0
Total Volatile Precursors to Nonvolatile and Semivolatile Oxidation Products	14,801	9
Anthropogenic	12,650	8
Biogenic	2151	1
Total Emissions Associated With Organic Aerosol Formation	21,988	278
Anthropogenic	18,662	277
Biogenic	3326	1

Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

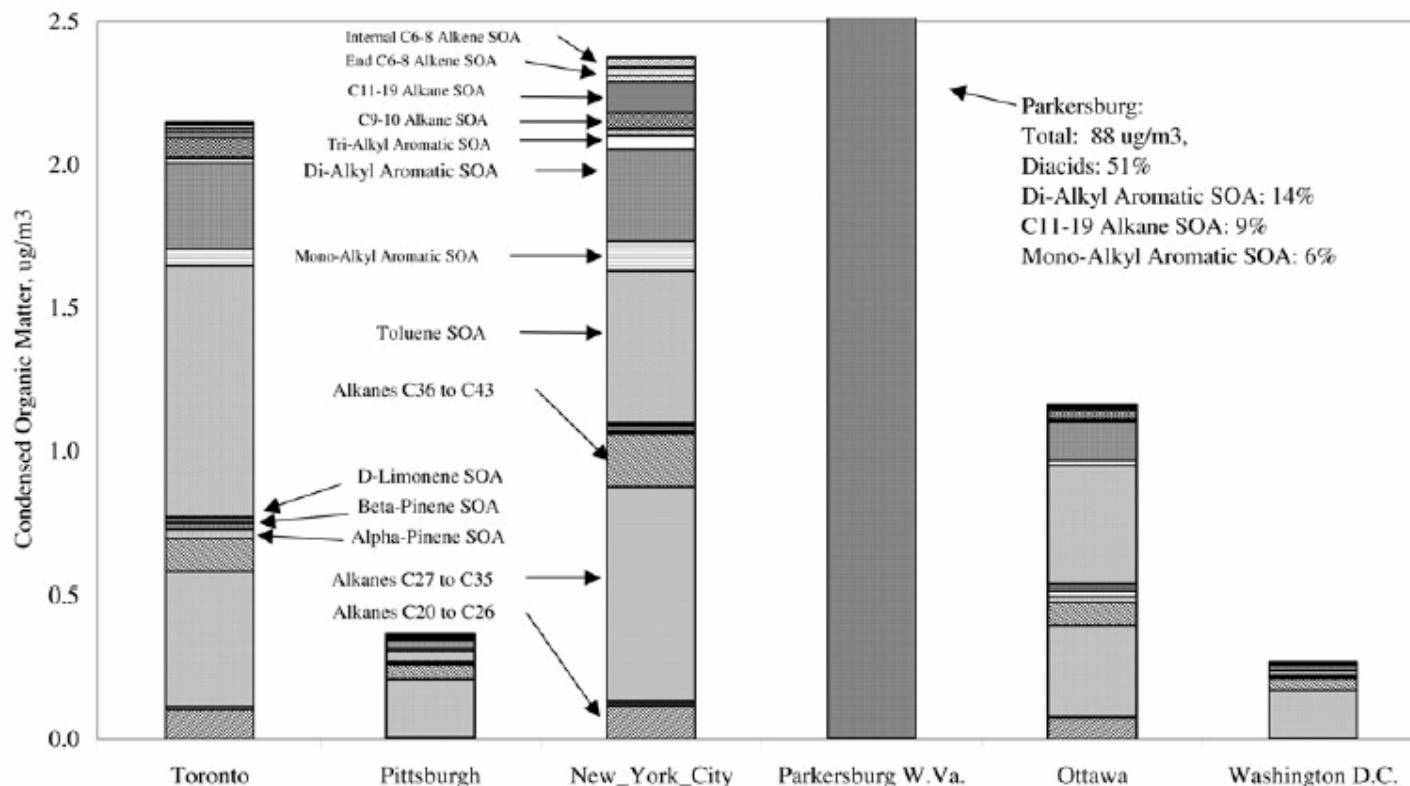
P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, Canada

M. T. Scholt

Canadian Ortech

Partitioned Organic Matter Constituents at Selected Cities, Summer



Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, Canada

M. T. Scholtz and A. Taylor

Canadian Ortech Environmental, Inc., Mississauga, Ontario, Canada

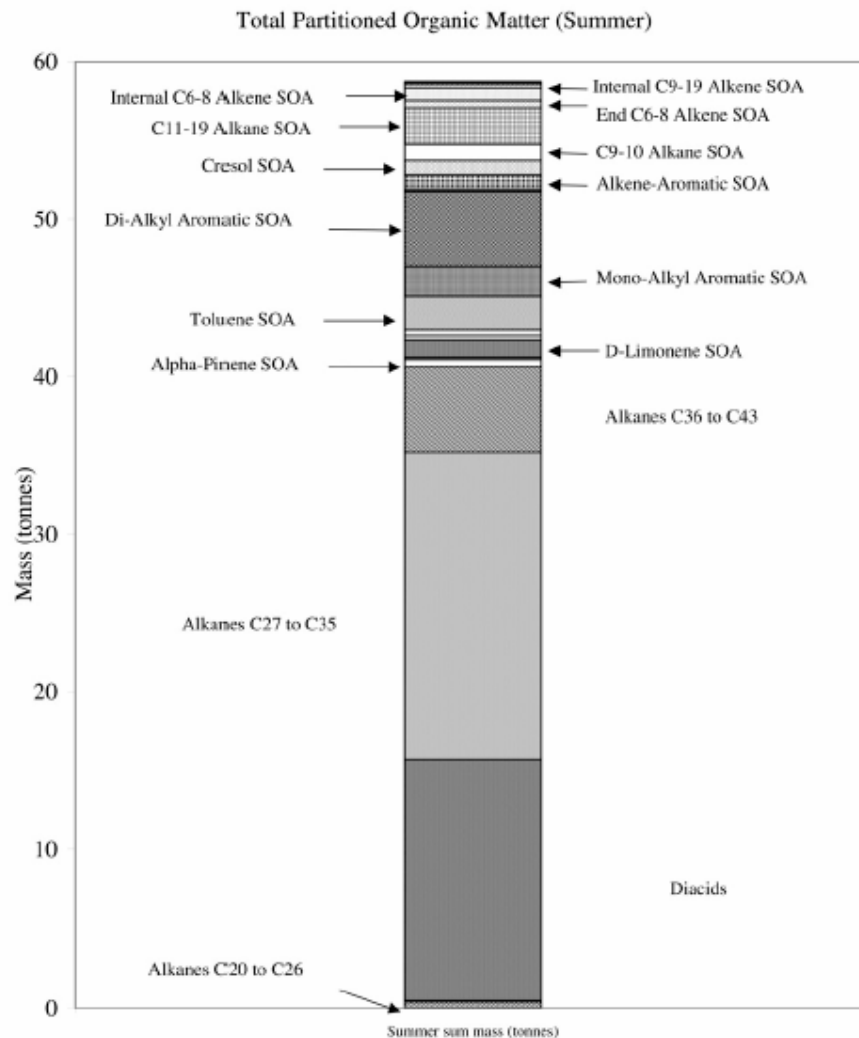


Figure 9. Contribution by organic compound class and source pathway to domain-total partitioned organic matter production (Summer Day, t).

Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

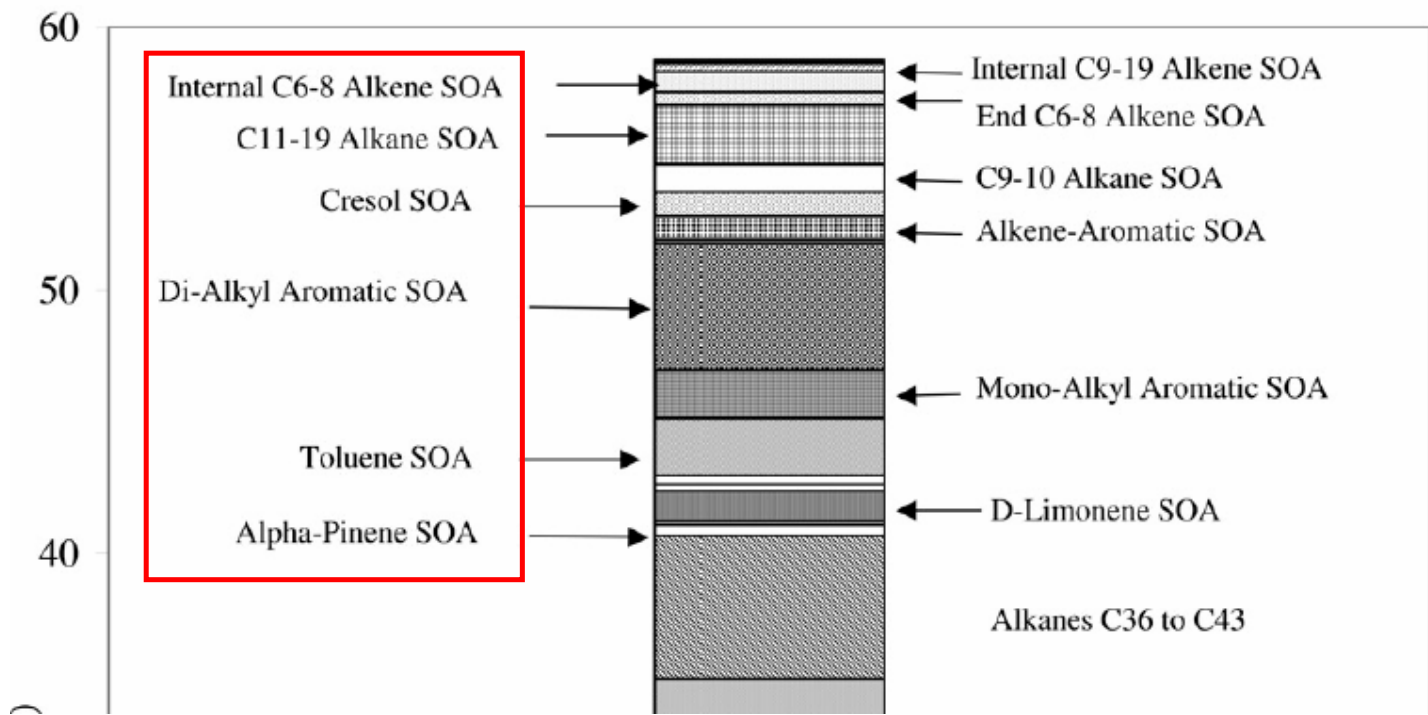
P. A. Makar and M. D. Moran

Modelling and Integration Division, Air Quality Research Branch, Meteorological Service of Canada, Toronto, Ontario, Canada

M. T. Scholtz and A. Taylor

Canadian O

Total Partitioned Organic Matter (Summer)



Predicting secondary organic aerosol formation rates in southeast Texas

Matthew Russell and David T. Allen

Center for Energy and Environmental Resour

[10] A small but growing number of studies have incorporated SOA formation into airshed models and some important insights have been gained. Notably, *Pandis et al.* [1992] modeled SOA formation in the Los Angeles basin and found that both anthropogenic and biogenic precursors were important in forming SOA. *Strader et al.* [1999] improved upon these methods by accounting for gas/particle partitioning and found that SOA formation was a strong function of temperature in the San Joaquin valley in California. Recently, R. J. Griffin and coworkers have reported on the development of a highly detailed model for SOA formation, including chemical mechanism formulation [*Griffin et al.*, 2002b], partitioning of semivolatile organic compounds [*Pun et al.*, 2002a], and application of the model to the Southern California area [*Griffin et al.*, 2002a]. The authors found that SOA from anthropogenic sources dominated aerosol in the urban area and that biogenic precursors contributed more in the rural areas than urban areas. The SOA was

Predicting secondary organic aerosol formation rates in southeast Texas

Matthew Russell and David T. Allen

Center for Energy and Environmental Resources, University of Texas, Austin, Texas, USA

Table 2. Texas Statewide Aromatic Emissions From Different SOA Yield Categories^a

Aromatic Category	Texas Anthropogenic Emissions, Typical Day, 10 ³ kg (%)	Example Compound
High SOA yield, low reactivity	241 (55.1)	toluene
Low SOA yield, high reactivity	128 (29.3)	1,2,4 trimethylbenzene
High SOA yield, high reactivity	38 (8.6)	1,2 diethylbenzene
No SOA yield, high reactivity	21 (4.9)	indane
No SOA yield, low reactivity	9 (2.1)	butylisopropylphthalate

^aCompound-specific emissions were grouped into yield categories on the basis of data given by *Odum et al.* [1997b].

Table 4. Daily Emissions of SOA Precursors in the 4-km Houston-Beaumont Domain in Figure 1)[†] ^aUnits are 10³ kg/d.

	High-SOA- Yield Aromatics	Low-SOA-Yield Aromatics	α -Pinene	β -Pinene
Low-level anthropogenic	80.5	46.8	2.5	1.6
Elevated anthropogenic	3.2	1.3	0.5	0.3
Biogenic	0.0	0.0	634.9	339.2
Total	83.7	48.0	637.9	341.2

▶ **secondary organic aerosols**

complications

Modeling the formation of secondary organic aerosol in coastal areas: Role of the sea-salt aerosol organic layer

Xuyi Cai¹ and Robert J. Griffin²

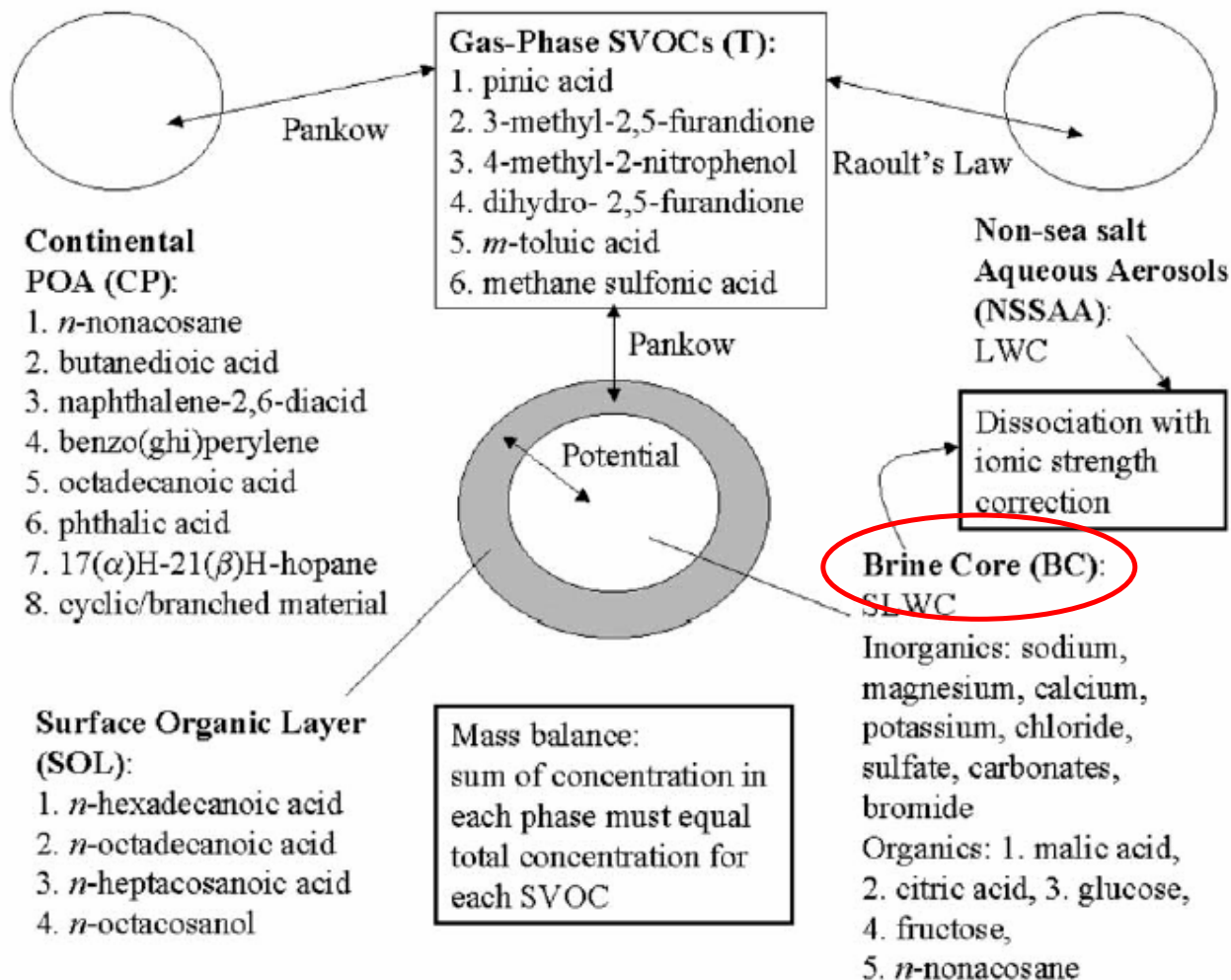
Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina, USA

Received 18 October 2002; revised 24 April 2003; accepted 1 May 2003; published 2 August 2003.

[1] In recent models the formation of secondary organic aerosol has been described by absorption of semivolatile oxidation products to an organic aerosol mixture and/or dissolution into an aerosol aqueous phase. In coastal areas, freshly formed sea-salt aerosol absorbs secondary semivolatile organic oxidation products into its surface organic layer, which consequently allows for the partitioning of the secondary organics to the sea-salt aerosol brine core. This process is modeled in the present study. Equilibrium between the gas phase and a continental primary organic aerosol phase, a sea-salt organic layer, and a continental aqueous aerosol is maintained, as is equilibrium between the organic layer and the brine core. Within aqueous phases, dissociation of acidic species is considered, and charge balance determines pH. Six semivolatile organic oxidation products that have been observed as secondary organic aerosol constituents, eight primary organic aerosol constituents representative of urban aerosols, five sea-salt organic layer species, and four organic components of the brine core are described molecularly. Numerical iteration techniques are used to solve the relevant nonlinear governing equations for the concentrations of each product in each aerosol phase and the gas phase, as well as for the pH of the relevant aqueous phases. Variables of interest include ambient temperature and species concentrations. Results indicate that the aqueous aerosols and the sea-salt aerosol brine core are the most efficient media for absorption under the conditions described, that organic layers enhance the partitioning to the brine core, and that secondary organic acids contribute to the acidification of the sea-salt aerosol brine core. *INDEX*

Modeling the formation of secondary organic aerosol in coastal areas: Role of the sea-salt aerosol organic layer

Xuyi Cai¹ and Robert J. Griffin²



Secondary inorganic aerosol simulations for Europe with special attention to nitrate

M. Schaap^{1,2}, M. van Loon², H. M. ten Brink³, F. J. Dentener⁴, and P. J. H. Builtjes^{1,2}

Abstract. Nitrate is an important component of (secondary inorganic) fine aerosols in Europe. We present a model simulation for the year 1995 in which we account for the formation of secondary inorganic aerosols including ammonium sulphate and ammonium nitrate, a semi volatile component.

▶ **secondary organic aerosols**

a review

Organic aerosol and global climate modelling: a review

M. Kanakidou¹, J. H. Seinfeld², S. N. Pandis³, I. Barnes⁴, F. J. Dentener⁵, M. C. Facchini⁶, R. Van Dingenen⁵, B. Ervens⁷, A. Nenes⁸, C. J. Nielsen⁹, E. Swietlicki¹⁰, J. P. Putaud⁵, Y. Balkanski¹¹, S. Fuzzi⁶, J. Horth⁵, G. K. Moortgat¹², R. Winterhalter¹², C. E. L. Myhre⁹, K. Tsigaridis¹, E. Vignati⁵, E. G. Stephanou¹, and J. Wilson⁵

2.1 Primary carbonaceous emissions: global and regional emission estimates

Sources of primary carbonaceous particles include fossil fuel burning (especially transportation and energy production), domestic burning (cooking and heating), and uncontained burning of vegetation (savannah and deforestation fires) and agricultural waste. There are a number of other types of primary carbonaceous material in the atmosphere such as viruses, bacteria, fungal spores and plant debris (Bauer et

Organic aerosol and global climate modelling: a review

M. Kanakidou¹, J. H. Seinfeld², S. N. Pandis³, I. Barnes⁴, F. J. Dentener⁵, M. C. Facchini⁶, R. Van Dingenen⁵, B. Ervens⁷, A. Nenes⁸, C. J. Nielsen⁹, E. Swietlicki¹⁰, J. P. Putaud⁵, Y. Balkanski¹¹, S. Fuzzi⁶, J. Horth⁵, G. K. Moortgat¹², R. Winterhalter¹², C. E. L. Myhre⁹, K. Tsigaridis¹, E. Vignati⁵, E. G. Stephanou¹, and J. Wilson⁵

2.2 SOA precursor emissions

2.2.1 Mechanism and composition of natural SOA precursor emissions

VOCs are emitted into the atmosphere from natural sources in marine and terrestrial environments, as well as from anthropogenic sources. A key study on global natural emissions was published by Guenther et al. (1995); hereafter called G1995, which is still the basis for later estimates of natural VOC emissions. On a global basis the emissions of biogenic volatile organic compounds (BVOCs), which are emitted mainly by vegetation, are estimated to exceed those from anthropogenic emissions (G1995: Guenther et al.,

Organic aerosol and global climate modelling: a review

Excluding isoprene and methane, VOCs from biogenic sources are often divided (G1995) into the lumped categories i) terpenes, ii) other reactive VOC (ORVOC) and iii) other VOCs (OVOCs). In the widely used GEIA dataset (URL <http://geiacenter.org/>), the latter two are lumped together. ORVOC represent reactive VOCs, with lifetimes <1 day, such as terpenoid alcohols, n-carbonyls, aromatics, sesquiterpenes (C₁₅H₂₄), terpenoid ketones and higher olefins. OVOCs are the less reactive VOCs, with lifetimes longer than 1 day, typically methanol, various aldehydes and ketones. The latter are believed to have little aerosol formation potential, and are not further considered in

ni⁶, R. Van Dingenen⁵,
uzzi⁶, J. Horth⁵,
Stephanou¹, and J. Wilson⁵

Species	Mass % Contribution	
	Class	SP2003 global
Mass percentage of monoterpene, and reactive ORVOC emission		
α -pinene	M	24.8
β -pinene	M	16.4
Sabinene+terpenoid Ketones	M/ORVOC	10.0
Δ^3 -carene	M	3.0
Limonene	M	16.4
α - γ terpinene	M	0.6
Terpinolene	M	1.4
Myrcene	M	3.5
Terpenoid alcohols	ORVOC	14.9
Ocimene	M	1.5
Sesquiterpenes	ORVOC	7.4

Organic aerosol and global climate modelling: a review

M. Kanakidou¹, J. H. Seinfeld², S. N. Pandis³, I. Barnes⁴, F. J. Dentener⁵, M. C. Facchini⁶, R. Van Dingenen⁵, B. Ervens⁷, A. Nenes⁸, C. J. Nielsen⁹, E. Swietlicki¹⁰, J. P. Putaud⁵, Y. Balkanski¹¹, S. Fuzzi⁶, J. Horth⁵, G. K. Moortgat¹², R. Winterhalter¹², C. E. L. Myhre⁹, K. Tsigaridis¹, E. Vignati⁵, E. G. Stephanou¹, and J. Wilson⁵

2.2.2 Anthropogenic SOA precursor emissions

Aromatic components have also the potential to form SOA (Odum et al., 1997). Tsigaridis and Kanakidou (2003) adopted the EDGAR2.0 database (Olivier et al., 1996, 1999a) for the anthropogenic emissions of SOA precursor gases. This database is giving global emissions of 6.7 Tg y^{-1} toluene, 4.5 Tg y^{-1} xylene, 0.8 Tg y^{-1} trimethylbenzene and 3.8 Tg y^{-1} of other aromatics. These emissions add up to about 10–15% of all anthropogenic NMVOC emissions.

Anthropogenic VOC emissions are 5–10 times lower than biogenic VOC emissions (excluding CH_4). When considering the known SOA precursor emissions alone, this ratio increases above 10. Large uncertainties exist also in the anthropogenic emission factors for SOA precursors like aromatics and some oxygenated solvents. Global invento-

Organic aerosol and global climate modelling: a review

M. Kanakidou¹, J.
B. Ervens⁷, A. Nenes⁸,
G. K. Moortgat¹²,

What do we know?

- The major SOA precursors are biogenic VOC. The anthropogenic contribution to the SOA formation is small on a global scale, although it can be important in polluted regions.
- At the global scale chemical formation of SOA could be at least 50% of the primary OA emissions.

- The known chemical mechanisms that form SOA are
 - Gas phase OH, NO₃, O₃ reactions. There is ample evidence that the ozonolysis reactions are major contributors to SOA formation.
 - Heterogeneous reactions that result in the decrease of the volatility of the semi-volatile compounds that are partitioned between aerosol and gas phase.
 - Aqueous phase reactions can be a significant source of dicarboxylic acids.

Organic aerosol and global climate modelling: a review

M. Kanakidou¹, J. H. Seinfeld², S. N. Pandis³, I. Barnes⁴, F. J. Dentener⁵, M. C. Facchini⁶, R. Van Dingenen⁵, B. Ervens⁷, A. Nenes⁸, C. J. Nielsen⁹, E. Swietlicki¹⁰, J. P. Putaud⁵, Y. Balkanski¹¹, S. Fuzzi⁶, J. Horth⁵, G. K. Moortgat¹², R. Winterhalter¹², C. E. L. Myhre⁹, K. Tsigaridis¹, E. Vignati⁵, E. G. Stephanou¹, and J. Wilson⁵

- Large uncertainties exist in the emission inventories of primary carbonaceous aerosols. These uncertainties are mostly due to temporal-regional-sectorial attribution of emission factors to activities, but also due to differences in measurement techniques used to determine these emission factors.
- The emission inventories of the gaseous organics that have been identified as precursors of SOA, are also subject to serious uncertainties dominated by those in the emission rates and the missing pieces of information on chemical speciation of the emissions (e.g. the fast reacting sesquiterpenes).

*IPCC / NGGIP, Expert Meeting
Emission Estimation of Aerosols Relevant to Climate Change
2-4 May 2005, Geneva*

Climate Forcing through Atmospheric Chemistry

- ▶ indirect effects on greenhouse gases
- ▶ secondary organic aerosols

*Michael J. Prather
Earth System Science Dept
University of California at Irvine*

backyard SOA