Climate Forcing through Atmospheric Chemistry

- indirect effects on greenhouse gases
- secondary organic aerosols

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

(IPCC TAR Wg1 SPM, adapted Prather May 2002)
Global Mean Radiative Forcing of Climate for year 2000 relative to 1750

IPCC TAR, 2001 - impacted by reactive chemistry & aerosols
"Reactive" Atmospheric Chemistry

- Greenhouse Agents

- Emission of reactive trace gas (NOx, 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 (NOx, CO, VOC)
- fast atmospheric chemistry (O_3, OH, HO_2, RO_2, ...)

produce tropospheric O_3, perturb global CH_4
- emission of reactive trace gas (VOC like terpenes, toluene,...)
- fast atmospheric chemistry ($O_3$, OH, HO$_2$, RO$_2$, ...)

produce secondary organic aerosols (SOA)
Reaction mechanism for the ozonolysis of α-pinene

then lead to cis-pinic acid
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), & CH_4 control

Tropospheric Chemistry (OH, HO_2)

which is the sink for CH_4 & HFCs; the source for O_3
$CH_4$ feedback on its lifetime

Isaksen & Hov, 1987
Prather, 1994
IPCC SAR (multi-model assessment), 1995
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 CH$_4$ feedback effect amplifies the climate forcing of an addition of CH$_4$ to the current atmosphere by lengthening the perturbation lifetime relative to the global atmospheric lifetime of CH$_4$ by a factor of 1.4. This earlier finding is corroborated here by new model studies that also predict only small changes in this CH$_4$ feedback for the different scenarios projected to year 2100. Another feedback has been identified for the addition of N$_2$O to the atmosphere; it is associated with stratospheric O$_3$ chemistry and shortens the perturbation lifetime relative to the global atmospheric lifetime of N$_2$O by about 5%. 

CH$_4$ self-feedback, 2001
Time scales in atmospheric chemistry: Theory, GWPs for CH$_4$ and CO, and runaway growth

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Abstract. Atmospheric CH$_4$ perturbations, caused directly by CH$_4$ 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 CH$_4$; 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 CH$_4$ (decades) 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 CH$_4$ molecule with the same decadal duration as direct CH$_4$ addition. Extrapolating these results, CH$_4$ sources would have to triple before runaway growth when CH$_4$ emissions exceed the oxidizing capacity of the troposphere.
CO becomes an indirect greenhouse gas

- long-term CH₄ increase
- short-term O₃ increase

3D CTM: add CO
- tropical bio-burn
- NH industrial
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 COstimulates 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)

Aerosols affect the global budgets of O$_3$, OH, and CH$_4$ 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 O$_3$ by 0.63 Dobson units and increase tropospheric CH$_4$ 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/m$^2$. ... The predominant impact is due to the aerosols over land; aerosols over the ocean contribute less than a third to globally integrated changes.
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 \textit{(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 ... \textbf{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.

\textit{but}

\textbf{studies focus on total aerosol (primarily dust) not on anthropogenic aerosols}
NOx identified as an indirect greenhouse gas

NOx 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, NOx is indirect greenhouse gas.
NO\textsubscript{X} \quad \text{O}_3 \quad \text{OH} \quad \text{CH}_4 \quad \text{O}_3

regional

(Wild, Prather, Akimoto, 2001)

Global Tracer Mass / Tg

Year of Run

(NOx Emissions Period)

O\textsubscript{3} CO CH\textsubscript{4} global

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

- short-term O₃ increase
- regional heating
- long-term CH₄ decrease
- global cooling
Impact of NOx is strongly depends on location
(Wild, Prather, Akimoto, 2001)

0.5 Tg-N of NOx: tropical, high-altitude emissions have greatest impact
NOx (and O₃ prod.) is highly regional

future NOx increases are projected to be highly regional

Geographic shift in NOx emissions from Y2000 to SRES Y2100 (A2)
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 S12000 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

Greenhouse Gas Mixing Ratios

- CO₂ (ppm)
- CH₄ (ppb)

1950 1975 2000 2025 2050

- ice core
- "alternative scenario"

in situ
non-SRES futures

Atmos. Chem. Phys. Discuss., 4, 1–68, 2004
www.atmos-chem-phys.org/acpd/4/1/
SRref-ID: 1690-7375/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. Derwent⁶
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 NOx, 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 NO$_2$yr$^{-1}$).
CO emissions

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

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John H. Seinfeld
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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 Dabdu,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-toluate 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

[40] 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

<table>
<thead>
<tr>
<th>Source</th>
<th>Central Los Angeles</th>
<th>Azusa</th>
<th>Claremont</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic</td>
<td>98.3</td>
<td>96.9</td>
<td>92.7</td>
</tr>
<tr>
<td>Biogenic</td>
<td>1.7</td>
<td>3.1</td>
<td>7.3</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>84.0</td>
<td>77.3</td>
<td>64.6</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>16.0</td>
<td>22.7</td>
<td>35.4</td>
</tr>
</tbody>
</table>

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

K. Tsigaridis and M. Kanakidou

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

<table>
<thead>
<tr>
<th>Production (Tg y⁻¹)</th>
<th>Case</th>
<th>VOC precursors (number)</th>
<th>Pre-existing particles</th>
<th>Evaporation</th>
<th>Transport of intermediates</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>13–24</td>
<td>Present day</td>
<td>Biogenic (30)</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Griffin et al. (1999b)</td>
</tr>
<tr>
<td>61–79</td>
<td>Present day</td>
<td>Biogenic (2)</td>
<td>C</td>
<td>No</td>
<td>No</td>
<td>Kanakidou et al. (2000)</td>
</tr>
<tr>
<td>16.5–28</td>
<td>Pre-industrial</td>
<td>Biogenic (2)</td>
<td>C</td>
<td>No</td>
<td>No</td>
<td>Kanakidou et al. (2009)</td>
</tr>
<tr>
<td>11.2</td>
<td>Present day</td>
<td>Biogenic (5)</td>
<td>C</td>
<td>Yes</td>
<td>Yes</td>
<td>Chung and Seinfeld (2002)</td>
</tr>
<tr>
<td>63</td>
<td>Present day</td>
<td>Biogenic (1)</td>
<td>C</td>
<td>Yes</td>
<td>Yes</td>
<td>Derwent et al. (2003)</td>
</tr>
<tr>
<td>7.2 (0.3)ᵇ</td>
<td>Present day</td>
<td>Biogenic (2)</td>
<td>C</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>44.0 (2.0)ᵇ</td>
<td>Present day</td>
<td>Biogenic (2)</td>
<td>C</td>
<td>Yes</td>
<td>Yes</td>
<td>This work – S1</td>
</tr>
<tr>
<td>13.3 (0.7)ᵇ</td>
<td>Present day</td>
<td>Biogenic (2)</td>
<td>C</td>
<td>No</td>
<td>Yes</td>
<td>This work – S2</td>
</tr>
<tr>
<td>44.5 (2.6)ᵇ</td>
<td>Present day</td>
<td>Biogenic (2)</td>
<td>CSN</td>
<td>Yes</td>
<td>Yes</td>
<td>This work – S3</td>
</tr>
</tbody>
</table>

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

Biogenic SOA, August, surface (ug/m3)

Anthropogenic SOA, August, surface (ug/m3)

Biogenic SOA, February, surface (ug/m3)

Anthropogenic SOA, February, surface (ug/m3)
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).
Table 5. Organic Aerosol Oxidation Precursor Volatile Organic Compound Classes Within the AURAMS81 Classification Scheme

<table>
<thead>
<tr>
<th>Organic Compound Species or Class</th>
<th>Partitioning Parameter Reference(^a)</th>
<th>Partitioning Comment(^b)</th>
<th>Rate Constant References (OH, O(_3))(^c)</th>
<th>Rate Constant Comment(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha-Pinene</td>
<td>1</td>
<td></td>
<td>4, 4</td>
<td></td>
</tr>
<tr>
<td>Beta-Pinene</td>
<td>1</td>
<td></td>
<td>4, 4</td>
<td></td>
</tr>
<tr>
<td>D-Limonene</td>
<td>1</td>
<td></td>
<td>4, 4</td>
<td></td>
</tr>
<tr>
<td>D-3-Carene</td>
<td>1</td>
<td></td>
<td>4, 4</td>
<td></td>
</tr>
<tr>
<td>End C(_{9-19}) Alkenes</td>
<td>2</td>
<td></td>
<td>5, 4</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>3</td>
<td></td>
<td>6, 7</td>
<td></td>
</tr>
<tr>
<td>Monoalkyl Aromatics</td>
<td>3</td>
<td></td>
<td>8, – D</td>
<td></td>
</tr>
<tr>
<td>Dialkyl Aromatics</td>
<td>3</td>
<td></td>
<td>9, 7</td>
<td></td>
</tr>
<tr>
<td>Trialkyl Aromatics</td>
<td>3</td>
<td></td>
<td>9, 10</td>
<td></td>
</tr>
<tr>
<td>Alkene Aromatics</td>
<td>3</td>
<td>A</td>
<td>11, 12</td>
<td></td>
</tr>
<tr>
<td>Cresol</td>
<td>3</td>
<td>A</td>
<td>13, 14</td>
<td></td>
</tr>
<tr>
<td>C(_{9-10}) Alkanes</td>
<td>2</td>
<td>B</td>
<td>4, – E</td>
<td></td>
</tr>
<tr>
<td>C(_{11-19}) Alkanes</td>
<td>2</td>
<td>B</td>
<td>4, – E</td>
<td></td>
</tr>
<tr>
<td>End C(_{6-8}) Alkenes</td>
<td>2</td>
<td>B</td>
<td>5, 15</td>
<td></td>
</tr>
<tr>
<td>Internal C(_{6-8}) Alkenes</td>
<td>2</td>
<td>B</td>
<td>16, 17</td>
<td></td>
</tr>
<tr>
<td>Internal C(_{9-19}) Alkenes</td>
<td>2</td>
<td>B</td>
<td>16, 17</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1</td>
<td>C</td>
<td>18, 19</td>
<td></td>
</tr>
<tr>
<td>Aromatic Aldehydes</td>
<td>3</td>
<td>A</td>
<td>13, – E</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>3</td>
<td>A</td>
<td>13, – E</td>
<td></td>
</tr>
</tbody>
</table>
inventory issues !!!

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 speciation 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
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

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

<table>
<thead>
<tr>
<th>Emission Category</th>
<th>Winter Day</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emitted</td>
<td>Condensed</td>
<td></td>
</tr>
<tr>
<td>Total Organic Compound Emissions</td>
<td>37,714</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>34,291</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>Biogenic</td>
<td>3423</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Total Primary Nonvolatile and Semivolatile Emissions</td>
<td>7188</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>6,012</td>
<td>269</td>
<td></td>
</tr>
<tr>
<td>Biogenic</td>
<td>1,176</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>Total Volatile Precursors to Nonvolatile and Semivolatile Oxidation Products</strong></td>
<td>14,801</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>12,650</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Biogenic</td>
<td>2151</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Total Emissions Associated With Organic Aerosol Formation</td>
<td>21,988</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>18,662</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>Biogenic</td>
<td>3326</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

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M. T. Scholt
Canadian Ortech

Partitioned Organic Matter Constituents at Selected Cities, Summer

Parkersburg:
Total: 88 μg/m³
Diacids: 51%
Di-Alkyl Aromatic SOA: 14%
C11-C19 Alkane SOA: 9%
Mono-Alkyl Aromatic SOA: 5%

Toronto
Pittsburgh
New_York_City
Parkersburg W.Va.
Ottawa
Washington D.C.
Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

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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 9).
Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone

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Canadian O
Predicting secondary organic aerosol formation rates in southeast Texas

Matthew Russell and David T. Allen
Center for Energy and Environmental Resou

[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

<table>
<thead>
<tr>
<th>Aromatic Category</th>
<th>Texas Anthropogenic Emissions, Typical Day, $10^3$ kg (%)</th>
<th>Example Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>High SOA yield, low reactivity</td>
<td>241 (55.1)</td>
<td>toluene</td>
</tr>
<tr>
<td>Low SOA yield, high reactivity</td>
<td>128 (29.3)</td>
<td>1,2,4 trimethylbenzene</td>
</tr>
<tr>
<td>High SOA yield, high reactivity</td>
<td>38 (8.6)</td>
<td>1,2 diethylbenzene</td>
</tr>
<tr>
<td>No SOA yield, high reactivity</td>
<td>21 (4.9)</td>
<td>indane</td>
</tr>
<tr>
<td>No SOA yield, low reactivity</td>
<td>9 (2.1)</td>
<td>butylisopropylphthalate</td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th></th>
<th>High-SOA-Yield Aromatics</th>
<th>Low-SOA-Yield Aromatics</th>
<th>α-Pinene</th>
<th>β-Pinene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-level anthropogenic</td>
<td>80.5</td>
<td>46.8</td>
<td>2.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Elevated anthropogenic</td>
<td>3.2</td>
<td>1.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Biogenic</td>
<td>0.0</td>
<td>0.0</td>
<td>634.9</td>
<td>339.2</td>
</tr>
<tr>
<td>Total</td>
<td>83.7</td>
<td>48.0</td>
<td>637.9</td>
<td>341.2</td>
</tr>
</tbody>
</table>

*aUnits are $10^3$ kg/d.
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
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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 Cai\(^1\) and Robert J. Griffin\(^2\)

**Continental POA (CP):**
1. \(n\)-nonacosane
2. butanedioic acid
3. naphthalene-2,6-diacid
4. benzo(ghi)perylenes
5. octadecanoic acid
6. phthalic acid
7. 17(\(\alpha\))-H-21(\(\beta\))-H-hopane
8. cyclic/branched material

**Surface Organic Layer (SOL):**
1. \(n\)-hexadecanoic acid
2. \(n\)-octadecanoic acid
3. \(n\)-heptadecanoic acid
4. \(n\)-octacosanol

**Gas-Phase SVOCs (T):**
1. pinic acid
2. 3-methyl-2,5-furandione
3. 4-methyl-2-nitrophenol
4. dihydro-2,5-furandione
5. \(m\)-tolic acid
6. methane sulfonic acid

**Non-sea salt Aqueous Aerosols (NSSAA):**
- LWC
- Dissociation with ionic strength correction

**Brine Core (BC):**
- Inorganics: sodium, magnesium, calcium, potassium, chloride, sulfate, carbonates, bromide
- Organics: 1. malic acid, 2. citric acid, 3. glucose, 4. fructose, 5. \(n\)-nonacosane

Mass balance: sum of concentration in each phase must equal total concentration for each SVOC.
Secondary inorganic aerosol simulations for Europe with special attention to nitrate

M. Schaap¹,², M. van Loon², H. M. ten Brink³, F. J. Dentener⁴, and P. J. H. Builtjes¹,²

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


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 Dingenen⁷, B. Ervens⁸, A. Nenes⁹, C. J. Nielsen¹⁰, E. Swietlicki¹¹, J. P. Pautaud¹², Y. Balkanski¹¹, S. Fuzzi⁶, J. Horth⁵, G. K. Moortgat¹², R. Winterhalter¹², C. E. L. Myhre⁹, K. Tsigaridis¹, E. Vignati¹², 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 (C_{15}H_{24}), terpenoid ketones and higher olefins. OVOCs are the less reactive VOCs, with lifetimes longer than 1 day, typically methanol, various aldehydes, ketones. The latter are believed to have little aerosol formation potential, and are not further considered in

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass % Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class SP2003 global</td>
<td></td>
</tr>
<tr>
<td>Mass percentage of monoterpene, and reactive ORVOC emission</td>
<td></td>
</tr>
<tr>
<td>α-pinene</td>
<td>M</td>
</tr>
<tr>
<td>β-pinene</td>
<td>M</td>
</tr>
<tr>
<td>Sabinene+terpenoid Ketones</td>
<td>M/ORVOC</td>
</tr>
<tr>
<td>Δ3-carene</td>
<td>M</td>
</tr>
<tr>
<td>Limonene</td>
<td>M</td>
</tr>
<tr>
<td>α-γ terpinene</td>
<td>M</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>M</td>
</tr>
<tr>
<td>Myrcene</td>
<td>M</td>
</tr>
<tr>
<td>Terpenoid alcohols</td>
<td>ORVOC</td>
</tr>
<tr>
<td>Ocimene</td>
<td>M</td>
</tr>
<tr>
<td>Sesquiterpenes</td>
<td>ORVOC</td>
</tr>
</tbody>
</table>
2.2.2 Anthropogenic SOA precursor emissions

Aromatic components have also the potential to form SOA (Odum et al., 1997). Tsigeridis 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

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 portioned between aerosol and gas phase.
  
  - Aqueous phase reactions can be a significant source of dicarboxylic acids.
Organic aerosol and global climate modelling: a review


- 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).
biogenic hydrocarbons. However, our knowledge is far from being complete and many gaps exist in the determination

- of all potential gaseous anthropogenic and biogenic pre-cursor molecules of SOA,

- of the secondary photooxidation processes in the gas phase leading to low volatility compounds and thus to SOA formation,

- of the impact of NOx levels on the final products of the SOA formation chemistry

- of the heterogeneous reactions between particle associated substances and gaseous compounds able to modify the composition and the mass of aerosol,

- of the aerosol chemistry responsible for the recently reported oligomer formation which increases the aerosol mass,

- of the aqueous phase chemistry, which might produce semi-volatile compounds that build up aerosol mass,

- of the complete molecular composition of the aerosol produced from the above mentioned processes.
Climate Forcing through Atmospheric Chemistry

- indirect effects on greenhouse gases
- secondary organic aerosols

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