Atmos. Chem. Lecture 20, 11/25/13: Aerosol chemistry (organic)

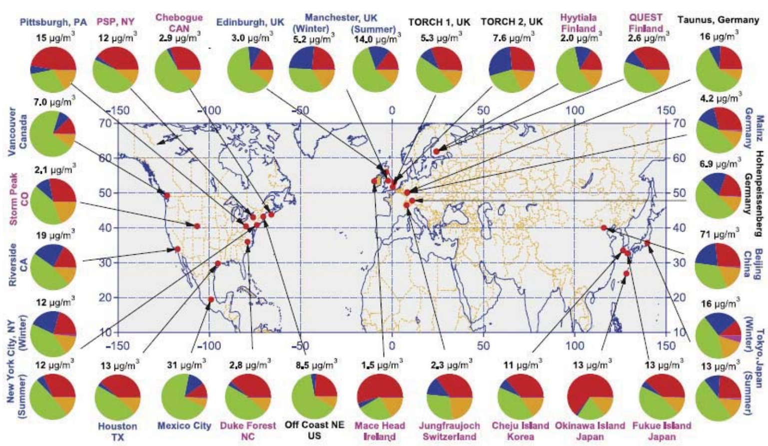
Jessica: Satellite measurements

Intro to organic aerosol

Partitioning, vapor pressures of organics

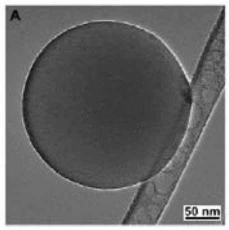
Modeling approaches for organic aerosol

Chemical composition of fine particulate matter



organic sulfate nitrate ammonium *Zhang et al. 2007*

Climate-relevant properties of organics: Direct effect

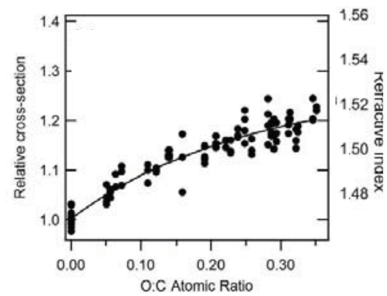


Brown Carbon Spheres in East Asian Outflow and Their Optical Properties

Duncan T. L. Alexander, Peter A. Crozier, James R. Anderson

Science 321:833 (2008)

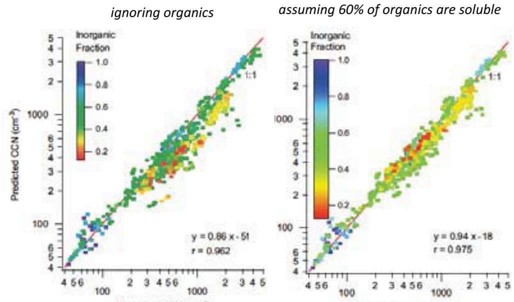
See also Kirchstetter et al., *JGR* 109:D21208 (2004);
Bond and Bergstrom, *AS&T* 40:27 (2006);
Feng et al. *ACP* 13:8607 (2013)



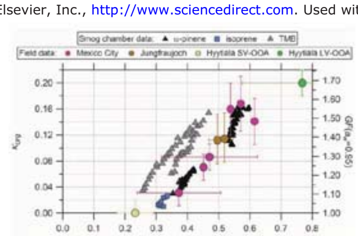
Cappa et al., *JGR* 116:D15204 (2011)

Climate-relevant properties of organics: Indirect effect

ignoring organics *assuming 60% of organics are soluble*



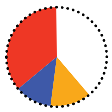
Chang et al., *Atm. Env.* 41:8172 (2007)



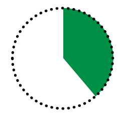
Surface tension lowering: Sareen et al., *PNAS* 110:2723 (2013)

Jimenez et al., *Science* 326:1525 (2009)

Inorganic vs. organic aerosol



Inorganics

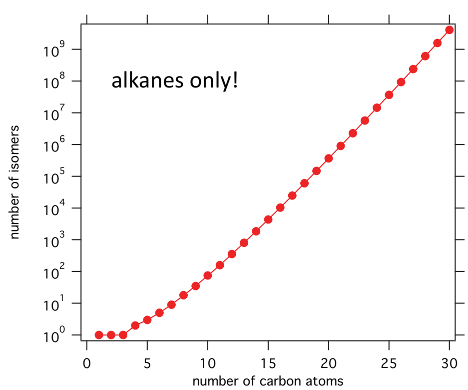


Organics

Inorganics	Organics
Few components (SO_4^{2-}, NO_3^-, NH_4^+...)	1,000's-10,000's of compounds (more?)
Formed by well-established chemistry	Formation chemistry uncertain
Well-characterized properties	Properties highly variable
Relatively inert chemically	Reactive (oxidation reactions)
Generally well-represented in models	Very poorly described by models

e.g., Heald et al., *GRL* 32, L18809 (2005)
Volkamer et al., *GRL* 33, L17811 (2006)

Chemical complexity of organics



from http://www.mathe2.uni-bayreuth.de/sascha/oeis/alkane.html

see also
Goldstein and Galbally, *ES&T* 41:1515 (2007);
Kroll et al. *Nat. Chem.* 3:133 (2011)

Example: diesel exhaust

n-butane
n-pentane
n-heptane
n-octane
n-nonane
n-undecane
n-dodecane
n-tridecane
n-tetradecane
n-pentadecane
n-hexadecane
n-heptadecane

isopentane
2,2-dimethylbutane
2,3-dimethylbutane
2-methylpentane
3-methylpentane
2,4-dimethylpentane
2-methylhexane
2,3-dimethylpentane
3-methylhexane
2,2,4-trimethylpentane
2,5-dimethylhexane

ethene
propene
trans-2-butene
cis-2-butene
isobutene
3-methyl-1-butene

2-methyl-1-butene

1,3-butadiene

ethyne

cyclopentane
methylcyclopentane
cyclohexane
methylcyclohexane
pentylcyclohexane
hexylcyclohexane
heptylcyclohexane
octylcyclohexane
nonylcyclohexane
decylcyclohexane

cyclopentene

benzene
toluene
ethylbenzene
m- and p-xylene
o-xylene
n-propylbenzene
p-ethyltoluene
m-ethyltoluene
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
naphthalene
2-methylnaphthalene
1-methylnaphthalene
C_2-naphthalenes
C_3-naphthalenes
C_4-naphthalenes
acenaphthylene
acenaphthene
fluorene

n-octadecane
n-nonadecane
n-eicosane
n-heneicosane
n-docosane
n-tricosane
n-tetracosane
n-pentacosane
n-hexacosane
n-heptacosane
n-octacosane
n-nonacosane

2,4-dimethylhexane
2,3,4-trimethylpentane
2,3-dimethylhexane
2-methylheptane
3-ethylhexane
norfarnesane
farnesane
2,6,10-trimethyltridecane
norpristane
pristane
phytane

trans-2-pentene
trans-2-hexene
cis-2-hexene

2-methyl-2-pentene

undecylcyclohexane
dodecylcyclohexane
tridecylcyclohexane
tetradecylcyclohexane
pentadecylcyclohexane
hexadecylcyclohexane
heptadecylcyclohexane
octadecylcyclohexane
nonadecylcyclohexane

C_1-fluorene
phenanthrene
anthracene
3-methylphenanthrene
2-methylphenathrene
2-methylanthracene
9-methylphenanthrene
1-methylphenanthrene
C_2-MW 178 PAH
C_3-MW 178 PAH
fluoranthene
acephenanthrylene
pyrene
C_1-MW 202 PAH
benzo[ghi]fluoranthene
cyclopenta[cd]pyrene
benz[a]anthracene
chrysene and triphenylene
C_1-MW 228 PAH

8β,13α-dimethyl-14β-n-butylpodocarpane

20S-13β(H),17α(H)-diacholestane

18α(H)-22,29,30-trisnorneohopane
17α(H)-22,29,30-trisnorhopane

20R,5α(H),14β(H),-17β(H)-cholestane
20R,5α(H),14α(H),-17α(H)-cholestane

formaldehyde
acetaldehyde
propanal
butanal
hexanal
heptanal

crotonaldehyde
acrolein

acetone
nonanedioic acid

methylbenzoic acids

dibenzothiophene
dibenzothiazole

benzaldehyde
acetophenone

indanone
fluorenone

glyoxal
methylglyoxal

octanoic acid
nonanoic acid
decanoic acid
undecanoic acid
dodecanoic acid
tridecanoic acid

octanedioic acid

benzoic acid

benzofuran
dibenzofuran
biacetyl

tetradecanoic acid
heptadecanoic acid
octadecanoic acid
nonadecanoic acid
eicosanoic acid

8β,13α-dimethyl-14β-[3'-methylbutyl]-podocarpane

17α(H),21β(H)-29-norhopane
17α(H),21β(H)-hopane

20R&S,5α(H),14β(H),-17β(H)-ergostane
20R&S,5α(H),14β(H),-17β(H)-sitostane

octanal
nonanal
decanal
undecanal
dodecanal
tridecanal

methacrolein

butanone

2,5-dimethylbenzaldehyde

xanthone

→ 170 compounds measured, accounting for ~75% of mass
(there are *many* more: "unresolved complex mixture")

GC-MS measurements from *Schauer et al., ES&T 33:1578 (1999)*

→ diesel exhaust is a relatively simple system!

Sources of organic aerosol

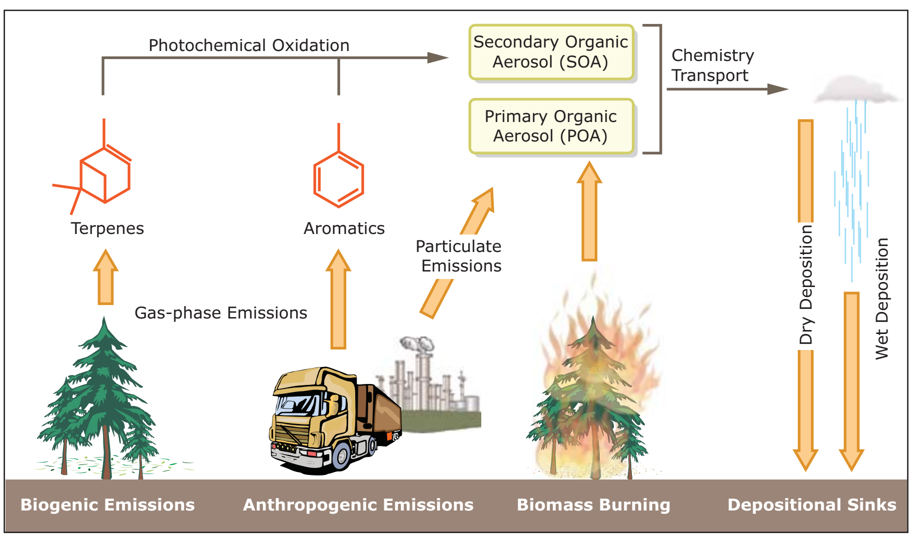


Image by MIT OpenCourseWare.

SOA reviews: Kroll and Seinfeld, *Atmos. Environ.* 42:3593 (2008)
Hallquist et al., *ACP* 9:5155 (2009)

Types of organic aerosol

Primary vs. secondary OA

Molecular markers: mostly POA
e.g. Cass et al.

OC/EC: high levels (~50%) in SOA
e.g., Lim and Turpin, *ES&T* 36:4489 (2002)

O/C ratios: mostly SOA, esp. rural areas
e.g., Zhang et al., *GRL* 34, L13801 (2007)

Anthropogenic vs. "natural" OA

Consideration of VOC emissions: Biogenic
e.g., Goldstein and Galbally *ES&T* 41:1515 (2007)

^{14}C ratios of OA: High modern fraction
e.g., Lemire et al., *JGR* 107:4613 (2002)

Correlation with tracers: Anthropogenic
e.g., De Gouw et al., 110:D16305 (2005)

Blurring these distinctions

see Robinson et al., *Science* 315:1259 (2007)

see Carlton et al., *ES&T* 44:3376 (2010)

Gas-particle partitioning of organics

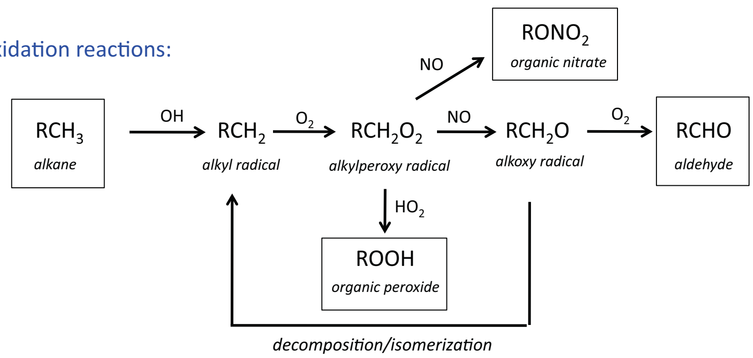
$X (g) \leftrightarrows X (p)$

Absorptive partitioning: Pankow, *Atm. Env.* 28:185 (1994), 28:189 (1994)

[Note: Additional material is discussed here during lecture.]

Changes to saturation vapor pressure

1) oxidation reactions:



2) acid-base reactions
3) oligomerization/accretion reactions
4) temperature

Calculating saturation vapor pressures

Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007) ← SIMPOL.1: *ACP* 8:2773 (2008)

Functional group	Structure	Change in vapor pressure (298 K)[a]
Ketone	–C(O)–	0.10
Aldehyde	–C(O)H	0.085
Hydroxyl	–OH	5.7×10^{-3}
Hydroperoxyl	–OOH	2.5×10^{-3}
Nitrate	$-ONO_2$	6.8×10^{-3}
Carboxylic acid	–C(O)OH	3.1×10^{-4}
Peroxyacid	–C(O)OOH	3.2×10^{-3}
Acyl peroxynitrate	$-C(O)OONO_2$	2.7×10^{-3}
Extra carbon[b]	$-CH_2-$, etc.	0.35[b]

[a] Multiplicative factor.

Kroll and Seinfeld, *Atmos. Environ.* 42:3593 (2008)

Many other structure-activity relationships as well
e.g.,EVAPORATION, Compernolle et al. *ACP* 11:9431 (2011)

Treating chemical complexity: Speciated approaches

(1) Explicit mechanisms

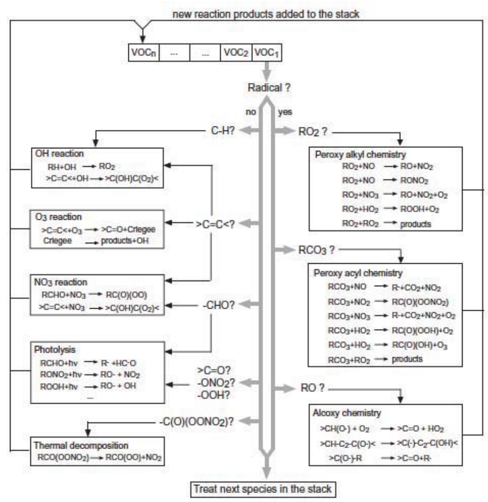
e.g., Master Chemical Mechanism (MCM: *mcm.leeds.ac.uk):* near-explicit description of organic chemistry

(2) Self-generating schemes

e.g., The Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A)

Aumont et al., *ACP* 5:2497 (2005)

Camredon et al., *ACP* 7:5599 (2007)

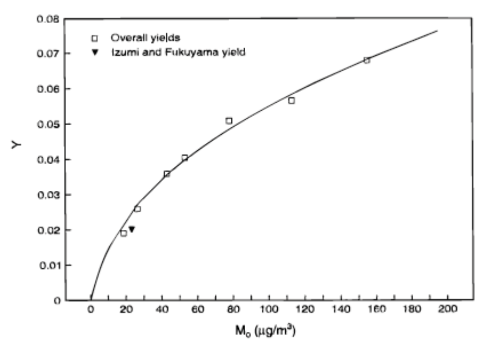


Treating chemical complexity: Ensemble approach

"*n*-product model"

Odum et al., *ES&T* 30:2580 (1996)

$$HC + OH \rightarrow\rightarrow \alpha_1 S_1 + \alpha_2 S_2 + \alpha_3 S_3 + \ldots$$

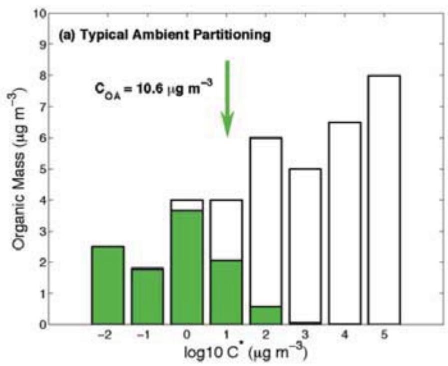


Treating chemical complexity: Ensemble approach

"Volatility basis set"
Donahue et al., *ES&T* 40:2635 (2006)
X_i (g) ⇆ X_i (p)

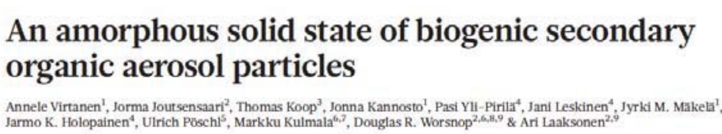
$F_p = K_pM_o/(1+K_pM_o)$

terminology:
$c^* = 1/K_p$
$c_{OA} = M_o$



see also Robinson et al., *Science* 315:1259 (2007)

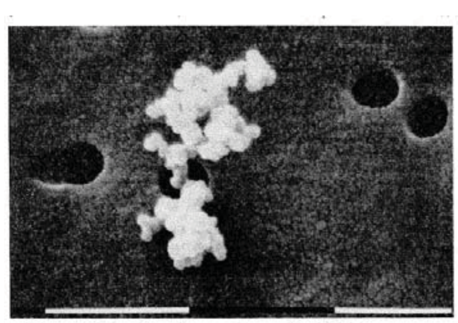
Gas-particle equilibrium?



An amorphous solid state of biogenic secondary organic aerosol particles

Annele Virtanen[1], Jorma Joutsensaari[2], Thomas Koop[3], Jonna Kannosto[1], Pasi Yli-Pirilä[4], Jani Leskinen[4], Jyrki M. Mäkelä[1], Jarmo K. Holopainen[4], Ulrich Pöschl[5], Markku Kulmala[6,7], Douglas R. Worsnop[2,6,8,9] & Ari Laaksonen[2,9]

Nature 467:824 (2010)



Paulson et al., *J. Aerosol Sci.,* 21:S245 (1990)

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013