

Regional Scale Air Quality Modelling Concepts & Challenges

Stephan Henne, Dominik Brunner

- Motivation and applications
- Air pollutants lifecycle
- Modelling framework and requirements
- Simulated processes
 - Gas phase chemistry
 - Aerosols
 - Wet phase chemistry
 - Transport

Background Stephan Henne



Position

- PhD in Environmental Sciences
- Senior Scientist
- Group for Atmospheric Modelling and Remote Sensing, Empa (Lead by Dominik Brunner)
- Lecturer, ETH, Zürich



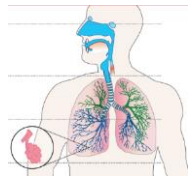
Expertise

- Atmospheric transport of air pollutants in complex terrain
- Atmospheric transport, dispersion and chemistry modeling in the Eulerian and Lagrangian framework
- Regional scale chemistry transport model: COSMO-ART
- Inverse emission modeling techniques for the use with trace gas observations and Lagrangian transport simulations
- Laboratory for Air Pollution/Environmental Technology runs the national air quality network (NABEL) in Switzerland

Motivation & Applications

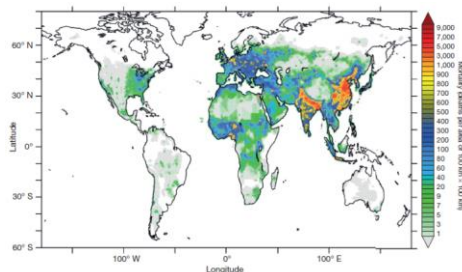
- Regulatory support
 - Sensitivity simulations to study effect of emission past and future reduction measures
 - Additional understand of observed trends
- Impact assessment: Long-term exposure of humans and ecosystems
- Air pollution forecasts (few days)

- Regional scale
 - Secondary pollutants (ozone, particulate matter)
 - Deposition (acidification, eutrophication)



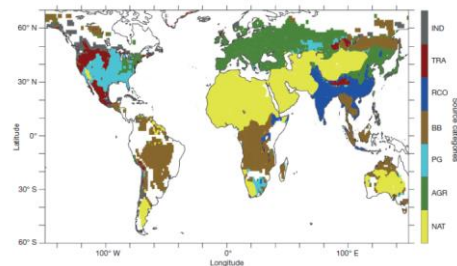
Motivation & Applications

- Global Scale Health Effects of Outdoor Air Pollution
- Assessed with global scale atmospheric chemistry and transport model (ECHAM5/MESSY)
- Impact of PM_{2.5} and surface ozone
- Globally 3.3 million deaths in 2010

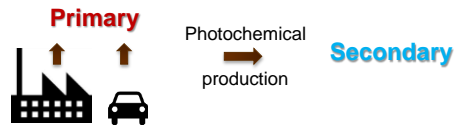


Mortality

Source: Lelieveld et al., 2015, Nature



Most important source: Industry (IND), Traffic (TRA), Residential and commercial energy use (RCO), biomass burning (BB), power generation (PG), Agriculture (AGR), Natural (NAT).

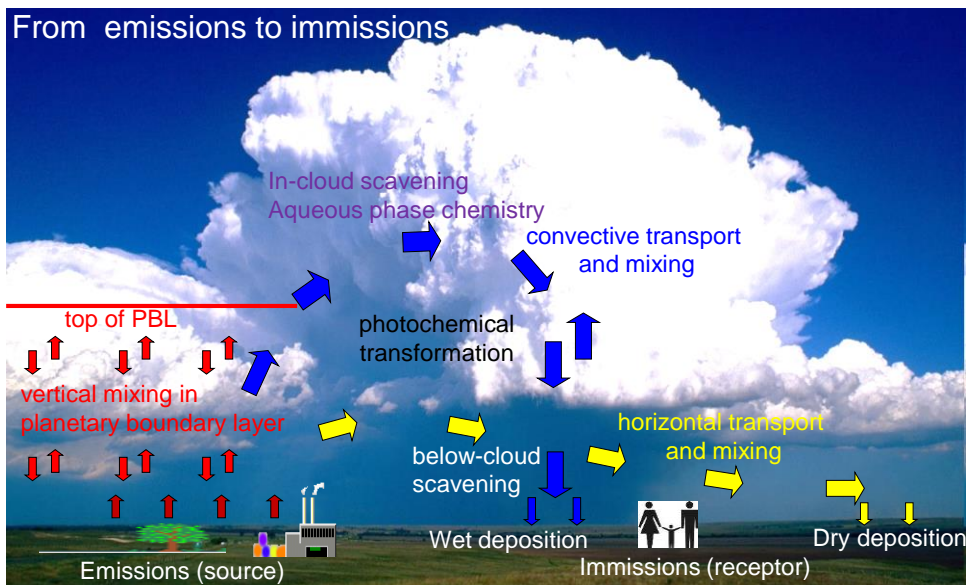


Primary air pollutants

- Directly produced and emitted at source
- Primary gases: Nitrogen oxides NO_x , sulfur dioxide SO_2 , ammonia NH_3
- Primary particulate matter/aerosols:
 - Natural: mineral dust, sea salt, pollen, biomass burning smoke
 - Anthropogenic: soot, primary organic aerosols (POA), abrasion

Secondary air pollutions

- Produced in atmosphere through photochemistry
- Secondary gases: Ozone O_3 , nitric acid HNO_3 , sulfuric acid H_2SO_4 , PAN
- Secondary particulate matter/aerosols:
 - Natural: secondary organic aerosols (SOA) from plant & BB emissions
 - Anthropogenic: secondary inorganic (SIA) and organic (SOA) aerosols

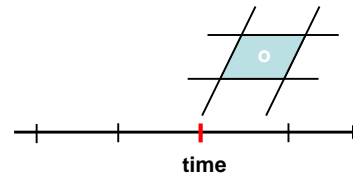


Regional Chemistry Transport Models

- Describe the state of the atmosphere by means of numerical solutions to prognostic equations
- State variables
 - Temperature (T), pressure (p), density (ρ)
 - Wind speed (3D vector) (u, v, w)
 - Composition (gases, liquid and solid particles, including water vapor) (c)

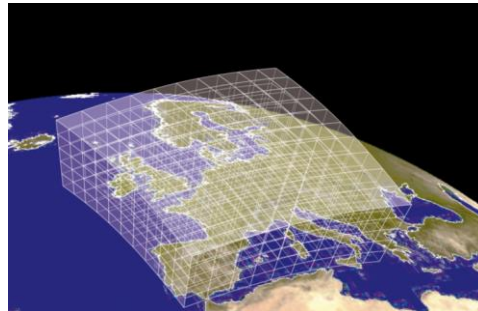
$$\frac{\partial \rho_i}{\partial t} = \underbrace{\mathbf{v} \nabla \rho_i + K \sum_j \frac{\partial^2 \rho_i}{\partial x_j^2}}_{\text{transport}} + \underbrace{\left[\frac{\partial \rho_i}{\partial t} \right]_{\text{conv}}}_{\text{chemistry}} + \underbrace{\left[\frac{\partial \rho_i}{\partial t} \right]_{\text{chem}}}_{\text{chemistry}} + \underbrace{\left[\frac{\partial \rho_i}{\partial t} \right]_{\text{scav}}}_{\text{scavenging}} + \underbrace{\left[\frac{\partial \rho_i}{\partial t} \right]_{\text{dep}}}_{\text{deposition}} + \underbrace{\left[\frac{\partial \rho_i}{\partial t} \right]_{\text{em}}}_{\text{emissions}}$$

- Discretization in time and space (3-dimensional grid, adequate time step)
- Requires initial and boundary conditions



Typical Configuration of Regional Scale Models

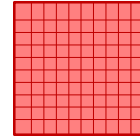
- Eulerian model framework:
 - 3-D mesh of grid cells
 - Grid size: 200 x 300 x 40 = 2.4 mio grid cells
 - Horizontal resolution: 5 to 100 km
 - 200 3-D variables (gases, aerosols, meteo)
 - ~3.5 GB per time (if stored as 8 Byte float)
- Requires parallel implementations
- Run on high performance computers (e.g. linux clusters, Cray)
- Scientific data formats: e.g. netcdf, grib
- Focus on short simulation periods, esp. for sensitivity runs, or short forecasts



Initial and Boundary Conditions

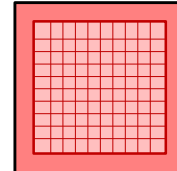
Initial conditions

- Knowledge of all prognostic variables (composition and meteorology) at $t=0$ and all grid points



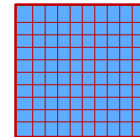
Boundary conditions

- Knowledge of all prognostic variables at the lateral domain boundaries



Offline coupling

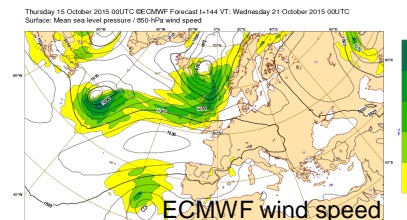
- Knowledge of all driving meteorology at all times and all grid points



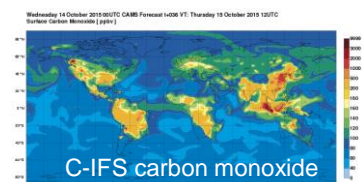
Initial and Boundary Conditions

Available global scale products

- Meteorology: e.g. ECMWF IFS, NCEP GFS, DWD GEM

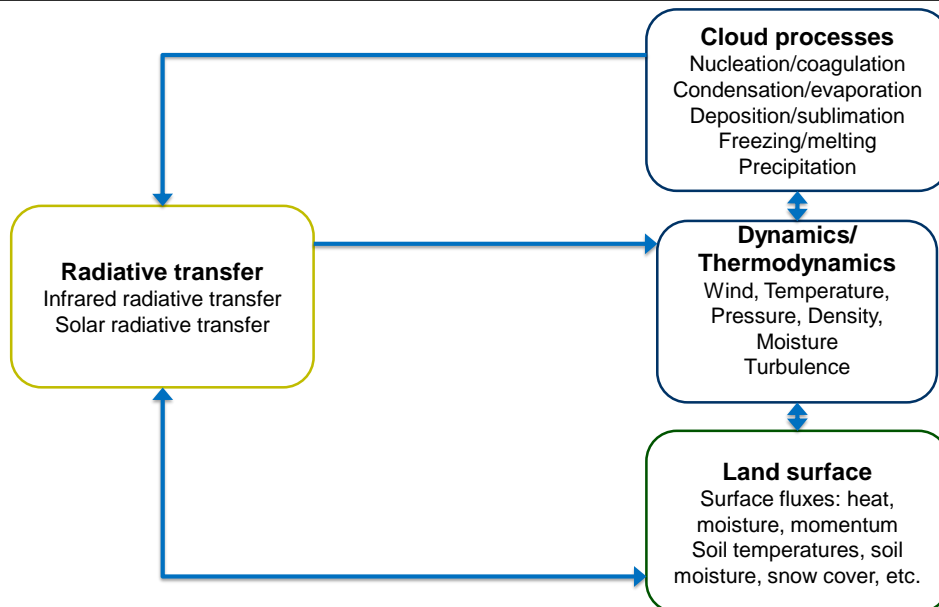
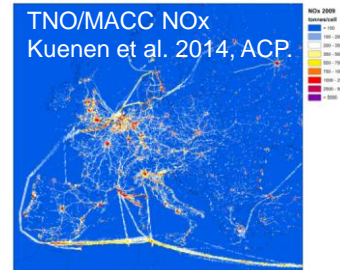


- Chemistry: e.g. IFS-MOZART (C-IFS, trace gases), IFS-LMD (aerosols), MOZART-NCEP

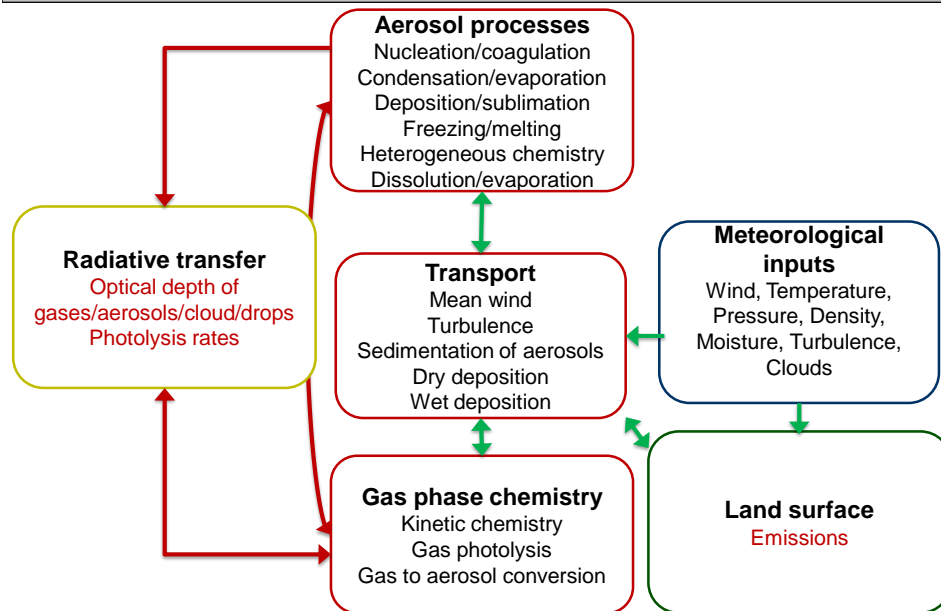


- Interpolation to regional model grid
- May require mapping of organic species and aerosol representation
- Alternativ: climatological vertical profiles

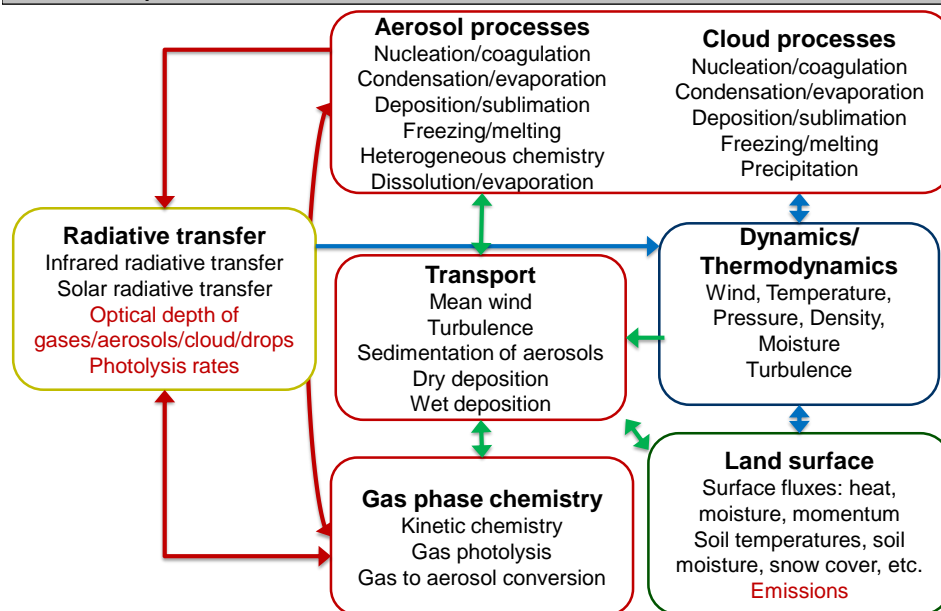
- Emissions
 - Anthropogenic from inventories (e.g. TNO/MACC, EDGAR)
 - mapping of species
 - time functions
 - horizontal resolution and interpolation
 - vertical distribution
 - Wildfires, observation based products (e.g. GFED, GFAS)
- Natural emissions (parameterised in model or provided offline)
 - Dust
 - Biogenic VOC
 - Sea salt
 - Lightning NO_x



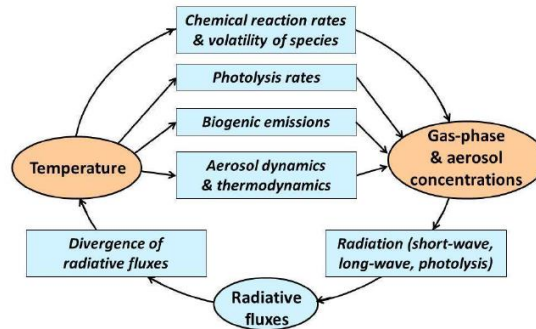
Processes in a Chemistry Transport Model: Offline Coupling



Processes in an Online Coupled Chemistry Transport Model



- Example: Temperature influence on composition and vice versa



Source: Baklanov et al., 2014, ACP

Online (access and integrated)

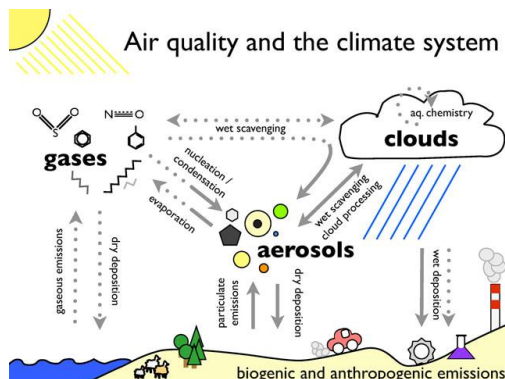
- No interpolation from different grid (only integrated models)
- Meteorology available at each time step
- Same transport mechanism for meteo as composition
- Feedbacks meteo - composition
- Benefits to run with operational meteorological centres

- Computationally more expensive
- Very complex systems

Offline

- Interpolation in time and space
- No feedbacks
- More flexible grid construction
- Computationally cheaper
- Suitable for sensitivity runs

- Limits the lifetime of gases
- Generation of new, potentially harmful species (e.g. ozone, PAN)
- Removal of other harmful species (e.g. NO_2 , benzene)
- Conversion to oxidized and often water soluble species (e.g. HNO_3 , H_2O_2)
- Production of aerosol precursor species



Inorganic chemistry

Available atmospheric gas-phase chemistry schemes are very similar regarding the representation of inorganic chemistry.

The inorganic chemistry typically consists of fewer than 20 species in about 45 inorganic reactions.

The species involved belong to the families

- O_x family (O , O_3)
- HO_x family (HO , HO_2)
- Oxidised nitrogen family (NO , NO_2 , HNO_3)
- Oxidised sulphur family (SO_2 , H_2SO_4)

Adding halogen chemistry (Cl , Br , I) significantly increases the complexity but is usually not required for air quality studies.

Organic chemistry

Explicit mechanisms:

Explicit chemistry of a large range of VOCs

Example: Master chemical mechanism MCM (Jenkin et al., 1997; Saunders et al., 2003):

- ~6700 primary, secondary and radical species
- ~17 000 reactions

For comparison, mechanisms described in 3-D models include at most a few hundred reactions.

Approaches for simplifying organic chemistry:

- **Surrogate mechanisms:** explicit chemistry of a few selected compounds represent the chemistry of all volatile organic compounds (VOCs) (e.g. EKMA with only butane and propene as surrogates)
- **Lumped molecule:** Molecules with similar reactivity are combined (e.g. RADM2)
- **Lumped structure:** Lumping by functional groups (e.g. Carbon Bond mechanisms)

Chemical Mechanisms Used in State-Of-The-Art Regional Models

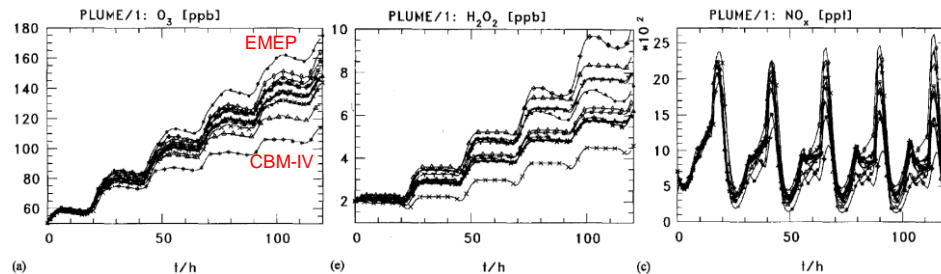
Mechanism	Chem Species	Chem rxns	Photol rxns	Het. rxns	Aq. chem	Model(s)	Reference(s)
ADOM-IIb	50	100	+	NA	NA	GEM	Venkatram et al. (1988)
CACM	189	349	+	NA	NA	Meso-NH	Griffin et al. (2002)
CBM-IV (aka CB4)	33	81	+	NA	NA	NDMB/BSC-CTM, BOLCHEM, RACMO2/LOTOS-EUROS	Gery et al. (1989)
CBM-05 (aka CB05)	52	156	+	NA	NA	NDMB/BSC-CTM, WRF-CMAQ, C-IFS	Sarwar et al. (2008)
CBM-Z	55-66	132	+	NA	NA	RegCM-Chem, Enviro-HIRLAM, WRF-Chem	Zaveri and Peters (1999)
GEOS-CHEM							
CRIMech							
MECCA1							
MOZART2	63	132	32	N ₂ O ₅ and NO ₃ on sulphate	NA	ECHAM5/6-HAMMOZ	Horowitz et al. (2003)
MOZART3	108	218	18	71	NA	IFS-MOZART	Kinnison et al. (2007)
MOZART4	85	157	39	4	NA	ECHAM5/6-HAMMOZ, WRF-Chem	Emmons et al. (2010)
NWP-Chem	17-28	27-32	4	NA	17	Enviro-HIRLAM v1	Korsholm et al. (2008)
RADMK	86	171	22	1	NA	COSMO-ART	Vogel et al. (2009)
RADM2	63	136	21	NA	NA	MCCM, M-SYS, REMO, WRF-Chem, M-SYS	Stockwell et al. (1990)
RACM	77	214	23	NA	NA	COSMO-LM-MUSCAT, MCCM, Meso-NH, RegCM-Chem, MEMO-MARS, WRF-Chem	Stockwell et al. (1997)
RACM-MIM	84	221	23	NA	NA	MCCM, WRF-Chem	Geiger et al. (2003)
RAQ (plus CLASSIC)	61	115	23	NA	Oxidation of SO ₂ by H ₂ O ₂ and O ₃	MetUM	Collins et al. (1997,1999)
ReLACS	37	128	+	NA	NA	Meso-NH	Crassier et al. (2000)
ReLACS2	82	343	+	NA	NA	Meso-NH	Tulet et al. (2006)
ReLACS-AQ	41	128	+	NA	Complete Aq. Phase chemistry	Meso-NH	Crassier et al. (2000), Lenschke et al. (2013)
SAPRC90 SOA	43	131	16	NA	NA	BOLCHEM	Carter (1990)
SAPRC99	72	198	+	NA	NA	RAMS/ICLAMS, WRF-CMAQ, WRF-Chem	Carter (2000)
SAPRC07	44-207	126-640	+	NA	NA	WRF-CMAQ	Carter (2010)
StdTrop (plus CLASSIC)	42	96	25	NA	Oxidation of SO ₂ by H ₂ O ₂ and O ₃	MetUM	Collins et al. (1997,1999)

Number of species varies between 33 (CBM-IV) and 189 (CACM)
Number of reactions varies between 81 (CBM-IV) and 349 (CACM)

Source: Baklanov et al., ACP, 2014

Different mechanisms produce different results

Evolution of O_3 , H_2O_2 and NO_x in different state-of-the-art photochemical mechanisms for a moderate polluted case. Compared are RADM- and CBM-IV type schemes, EMEP, ADOM II and “explicit” schemes and using different chemical solvers.



Source: Kuhn et al., Atmos. Environ., 1998

- Mechanisms were frequently compared in 1-box model setups
- Reference is usually the most complete/explicit mechanism (or the mean)
- Which result is the most accurate? Sometimes evaluated vs. smog chamber data.

Numerical Solution

System of coupled non-linear ordinary differential equations

If we have N different chemical species, we can consider the equation

$$\frac{\partial n_i}{\partial t} = \sum_{j \neq i} \left[J_j \cdot n_j + \sum_{k \neq i} k_{jk} n_j n_k \right] - \left(J_i + \sum_j k_{ij} n_j + k_i \right) n_i$$

Numerical approaches to solve this problem

- **explicit solvers** (e.g. forward Eulerian, Runge-Kutta): source terms calculated based on known concentrations at time t_0 and previous time steps
- **implicit solvers**: source terms calculated based on unknown concentrations at time $t_0 + \Delta t$ (and known concentrations at t_0 and possibly previous time steps)

The problem of stiffness

Longest/shortest lifetimes in atmospheric chemistry

$$\tau_L \approx 1 \cdot 10^7 \text{ (s)}$$

$$\tau_S \approx 1 \cdot 10^0 \text{ (s)}$$

$$stiffness = \frac{\tau_L}{\tau_S}$$

Resolving fast reactions requires a short integration time step which makes the numerical solution extremely expensive!

More advanced schemes used in modern numerical solvers

- Semi-implicit: Linearisation of source term \mathbf{s} around the solution ψ^n
- Quasi steady state approach (QSSA): Numerical method depends on reaction speed
- Gear's method: High order implicit scheme
(Gear, 1971; Hindmarsh, 1974; 1977)
- Runge-Kutta-Rosenbrock methods: High order implicit scheme that is efficient as it does not require iteration
(Rosenbrock, 1963; Verwer et al. 1983; Sandu et al. 1996, Sandu and Sander, 2006)
- TwoStep: Efficient and comparatively accurate explicit scheme
(Verwer and Simpson, 1995)

Gear and Rosenbrock solvers are implemented in the Kinetic Pre-Processor tool **KPP** (Damian et al., 2002; Sandu and Sander, 2006)

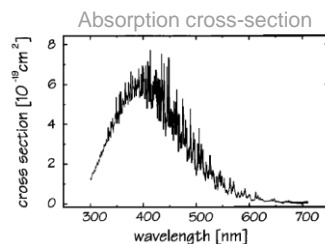
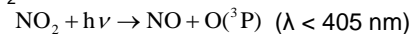
Photolysis

The rate j [s^{-1}] of a photolytic reaction can be computed as

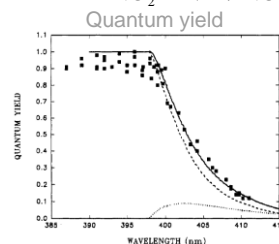
$$j = \int Q_A(\lambda) \sigma_A(\lambda) \Phi(\lambda) d\lambda \quad \text{Integration over wavelength } \lambda$$

quantum yield
absorption cross section
actinic flux

Spectrally dependent quantum yields and absorption cross-sections are obtained from laboratory data. Example: Photolysis of NO_2 :



Source: Kirmse, 1997.



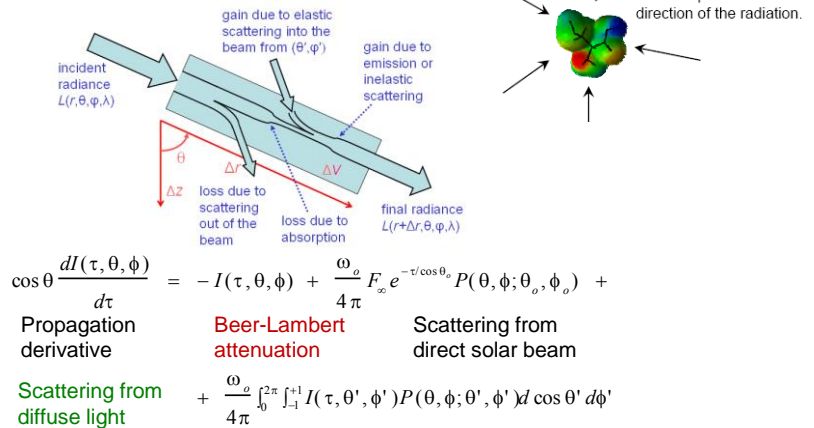
Source: Roehl, 1994.

Solving Radiative Transfer

Computation of the actinic flux

$$\Phi(\lambda) = \int_0^\pi \int_0^{2\pi} I(\theta, \phi, \lambda) \sin \theta d\phi d\theta \quad [\text{photons cm}^{-2} \text{s}^{-1} \text{nm}^{-1}]$$

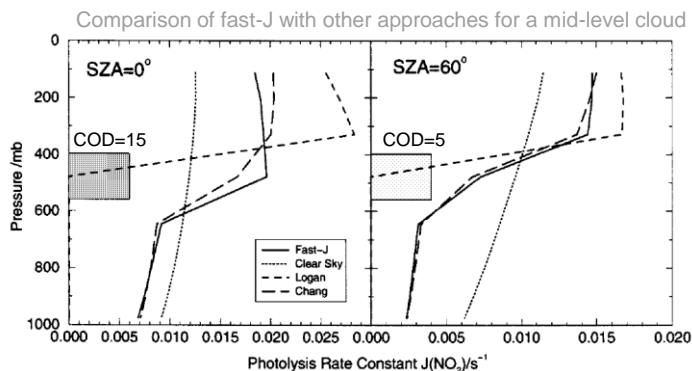
Radiative transfer equation



Solving Radiative Transfer

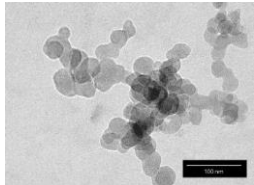
Fast-J photolysis code (Wild, Zhu and Prater, 2000)

- Accounts for effects of clouds and aerosols on radiative transfer
- Optical properties of clouds and aerosols considered: extinction optical depth, single scattering albedo, scattering phase function
- Solves the 8-stream multiple scattering problem
- Fast enough to be included in 3D models & Accurate to mostly better than 3%

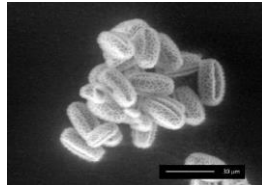


Aerosols = particulate matter (PM): solid or liquid particles suspended in air

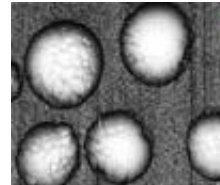
Diesel soot, ca. 0.1 μm



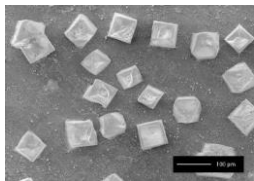
Pollen, 10 – 100 μm



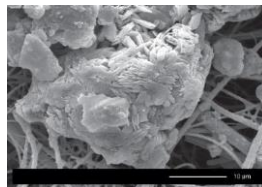
Ammonium sulfate, ca. 0.1 μm



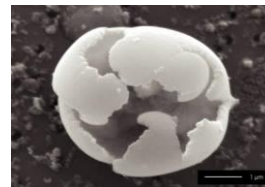
Sea salt, 0.2 – 10 μm



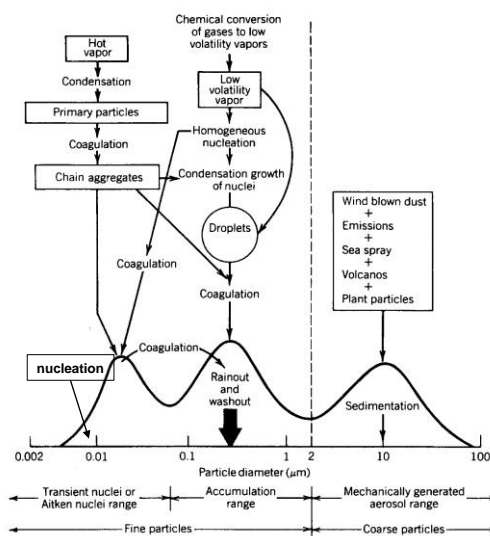
Mineral dust, 0.2 – 10 μm



Railway abrasion, 1 – 10 μm



Aerosols – Size Distribution & Processes



Trimodal size distribution after Withby und Sverdrup (1980)

Aerosol processes

- **Emissions** of primary aerosols
- **Nucleation**: new particles forming out of gas phase
- **Condensation**: gases condensing onto surfaces of existing aerosols
- **Coagulation**: two aerosols merging to one, important for particles < 0.1 μm
- **Sedimentation**: gravitational settling, relevant only for particles > 1 μm
- **Chemical ageing**
- **Dry deposition**: Particles deposited at earth surface
- **Wet deposition**: Particles incorporated into cloud and rain droplets and washed out by precipitation

Secondary Aerosols

Strong need to simulate aerosol formation in the atmosphere in order to describe PM10 and esp. PM 2.5 burdens

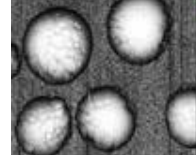
Health impacts depend on size and composition

- About 50% of aerosol mass in Europe (and elsewhere) is secondary
- Secondary inorganic aerosols (SIA): sulfate, nitrate, ammonium

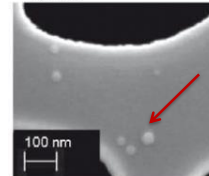
$$\text{H}_2\text{SO}_4 (\text{g}) + 2 \text{NH}_3 (\text{g}) \rightarrow (\text{NH}_4)_2\text{SO}_4 (\text{s})$$

$$\text{HNO}_3 (\text{g}) + \text{NH}_3 (\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3 (\text{s})$$
- Secondary organics aerosols (SOA): oxidized and condensed VOCs (biogenic and anthropogenic)

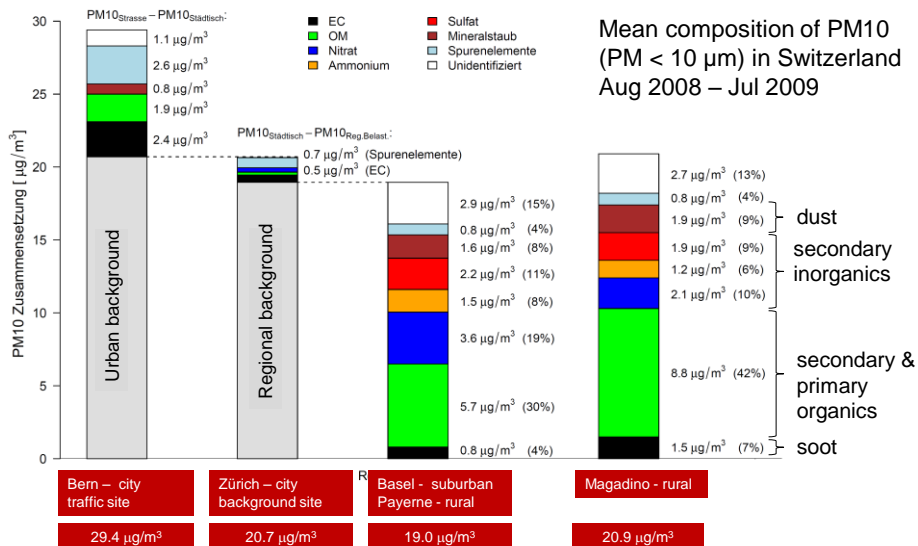
Ammonium sulfate, ca. 0.1 μm

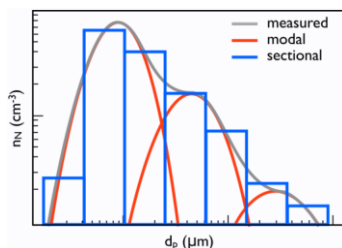


c Hyytiälä 15 May 09
27 nm

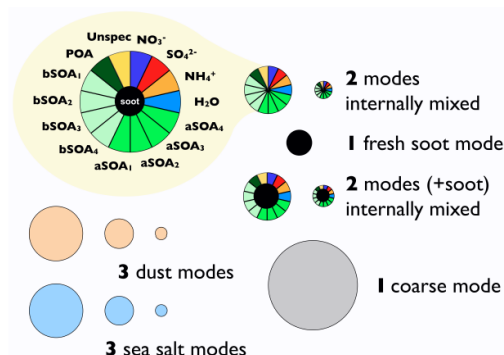


Aerosols – Chemical Composition





Aerosol size distribution



Aerosol representation in
COSMO-ART / MADEsoot

Typical cloud droplet radii:

Cloud droplet: $r = 5 - 50 \mu\text{m}$

Raindrop: $r = 100 - 2000 \mu\text{m}$

Typical cloud liquid water contents:

$$L = 0.05 - 3 \text{ g m}^{-3}$$

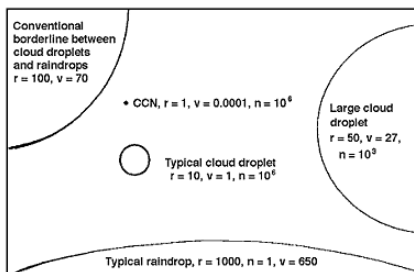
The liquid water volume mixing ratio w_L is defined as

$$w_L (\text{vol water/vol air}) = 10^{-6} L (\text{g m}^{-3})$$

The cloud water mixing ratio w_L is thus in the range

$$w_L = 5 \times 10^{-8} \text{ to } 3 \times 10^{-6} \text{ g m}^{-3}$$

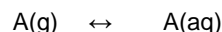
Typical droplet radii $r [\mu\text{m}]$, settling velocities $v [\text{cm s}^{-1}]$, and droplet number densities $n [\text{litre}^{-1}]$



Source: Wallace & Hobbs 1977

Only a tiny fraction ($\sim 10^{-6}$) of the volume of a cloud is occupied by droplets!

The equilibrium of a species A between gas and aqueous phase



is usually expressed in terms of the so-called **Henry's law coefficient H_A** :

$$H_A = \frac{[A(aq)]}{p_A}$$

where p_A is the partial pressure [atm] of A in the gas phase and $[A(aq)]$ is the concentration in the aqueous phase [mol L⁻¹].

The units [mol L⁻¹] will be denoted as [M].

The usual units of H_A are thus [M atm⁻¹].

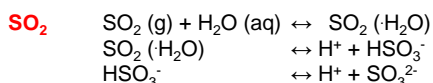
Henry's law coefficients

Species ^a	H (M atm ⁻¹) at 298 K
O ₂	1.3×10^{-3}
NO	1.9×10^{-3}
C ₂ H ₄	4.8×10^{-3}
NO ₂	1.0×10^{-2}
O ₃	1.13×10^{-2}
N ₂ O	2.5×10^{-2}
CO ₂	3.4×10^{-2}
H ₂ S	0.12
DMS	0.56
HCl	1.1
SO ₂	1.23
CH ₃ ONO ₂	2.6
CH ₃ O ₂	6
OH	25
HNO ₂	49
NH ₃	62
CH ₃ OH	220
CH ₃ OOH	227
CH ₃ C(O)OOH	473
HO ₂	2.0×10^3
HCOOH	3.6×10^3
HCHO ^b	2.5
CH ₃ COOH	8.8×10^3
H ₂ O ₃	7.45×10^4
HNO ₃	2.1×10^5
NO ₃	2.1×10^5

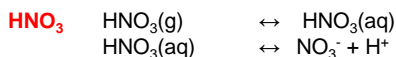
Source: Seinfeld & Pandis 1998

Acid-Base Equilibria

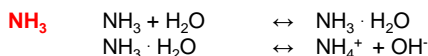
Acids and bases dissociate in cloud water which greatly enhances solubility



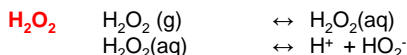
HSO₃⁻ dominating over wide range of pH



HNO₃ exists almost exclusively in the form of nitrate ions



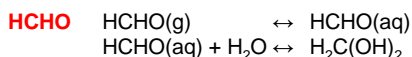
principle basic compound to neutralize acids



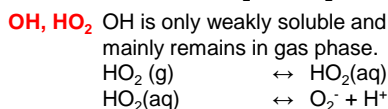
H₂O₂ is only a weak electrolyte and mainly remains in the form of H₂O₂(aq).

O₃ poorly soluble, remains mainly in the gas phase

NO, NO₂ poorly soluble, remain mainly in the gas phase



Formaldehyde undergoes hydrolysis to form methylene glycol.



HO₂ is a weak acid. At high pH > 5 HO₂ becomes highly soluble

In addition to acid-base equilibria, chemical reactions in the aqueous phase can **influence the partitioning between gas and liquid phase** and **contribute to the chemical processing of gases and aerosols**

The Chemical Aqueous Phase Radical Mechanism (CAPRAM) v2.4 developed at IfT in Leipzig (Herrmann et al., 2000; Ervens et al. 2003), for example, contains

- 147 chemical species
- 438 reactions



Particularly important reactions:

- oxidation of SO_2 to sulfate: important element in SIA formation
- hydrolysis of N_2O_5 : important pathway for NO_x oxidation to HNO_3

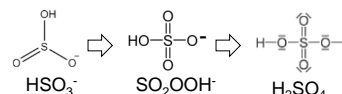
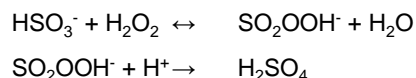
Important Aqueous Phase Reactions

Aqueous phase oxidation of S(IV) to S(VI)

In the gas phase, SO_2 is oxidized to H_2SO_4 by reaction with OH.

Oxidation of S(IV) by dissolved hydrogen peroxide

Main oxidant at low pH (< ~5), very fast:

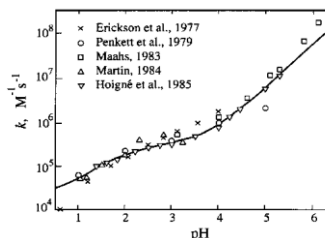


Oxidation of S(IV) by dissolved ozone

Reaction strongly depends on pH, dominates at large pH (>~5)



2nd order reaction rate as function of pH

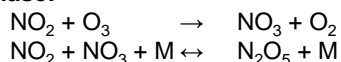


Nitrate formation from NO_3 radicals and N_2O_5

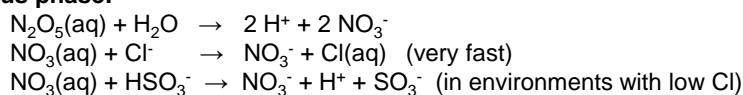
The nitrate radical NO_3 and N_2O_5 are both highly water soluble. Their concentrations are only relevant at night due to rapid photolysis of NO_3 during the day.

Aqueous phase chemistry contributes to the oxidation of NO_x to HNO_3 as follows:

Gas phase:



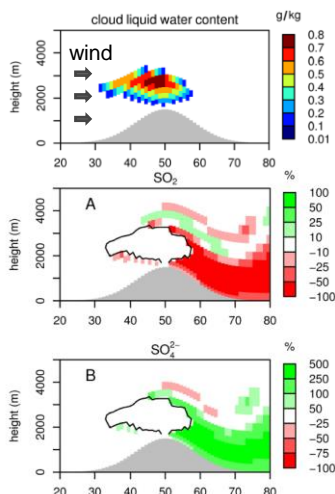
Aqueous phase:



Other important aqueous phase chemistry not mentioned here

- Organic chemistry, e.g. of carbonyls and organic acids
- Oxygen and hydrogen chemistry

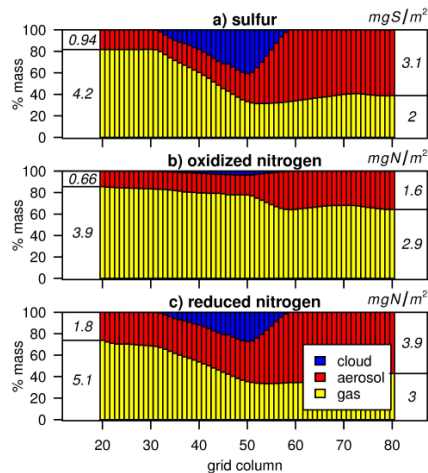
Idealized simulations for an orographically formed cloud



Relative changes in SO_2 and SO_4^{2-} during passage of air through an orographic cloud simulated with COSMO-ART including the SCAV cloud chemistry and aerosol processing module

(Knote and Brunner, 2013)

Idealized simulations for an orographically formed cloud



Change in relative partitioning of sulfur compounds and of oxidized and reduced nitrogen into gas phase, aerosol phase and cloud water phase during passage of the cloud. Shown are column integrated values.

(Knote and Brunner, 2013)

The example demonstrates the important effect of cloud chemistry on the gas – aerosol partitioning mainly due to the production of sulfate.

Numerical Solution of Transport

Desirable properties for transport schemes

- Mass conservation
- Shape preservation (positive definite, monotonic, and non-oscillatory)
- Consistent: avoid mass-wind inconsistency problem
- Preservation of correlations between tracers
- Computationally efficient: i.e. high accuracy for a given computational resource
- Avoiding excessive numerical mixing

Fulfilment of Desirable Properties

Engil Kaas, Nils Bohr Institute, Copenhagen

Model	Scheme	"Category"	Inherently mass-conserving	Strictly shape preserving	Filter category
ATTILA		Fully Lagrangian	Yes	yes	parcel mixing
BOLCHEM	3D-WAF	Flux-form finite volume	Yes	No	minmod
COSMO-ART (B)	Bott	Flux-form finite volume	Yes	(yes)	mon. centred
COSMO-ART (SL)	SL tri-cubic	semi-Lagrangian	No	(yes)	clipping etc.
C-IFS / IFS-MOZART	SL tri-cubic	semi-Lagrangian	No/Fixer	Yes	a posteriori
ECHAM-HAM	Lin and Rood	Flux-form finite volume	Yes	No	1-D limiter
Enviro-HIRLAM / Enviro-HARMONIE	LMCSL-M	semi-Lagrangian	Yes	Yes	a posteriori
ICON-ART	ICON-FFSL	Flux-form finite volume	Yes	Yes	FCT
MCCM	MM5	Flux-form finite volume	No?	Yes	FCT

- No model fulfils all desirable properties
- Many models are not formally wind-mass consistent
- Most models are inherently and locally mass conserving
- Except for Attila all models have issues with numerical diffusion

RegCM-Chem4	~MM5 (hydrost)	Flux-form finite volume	Yes	No?	
SOCOL (MA-ECHAM)	Lin and Rood	Flux-form finite volume	Yes	No	1-D limiter
WRF-Chem	5th order flux (RK3)	Flux-form finite volume	(Yes)	(6 th order filter)	

Summary

- Regional scale air quality models represent processes required to simulate secondary pollutants (ozone, PM)
- Models are complex in terms of described processes (although different degrees of details exist)
- Computationally and I/O intensive: high performance computing
- Require initial and boundary conditions and emissions
- Processes contained in models:
 - Natural emissions (biogenic VOC, sea salt, dust)
 - Gas phase chemistry
 - Radiative transfer (photolysis rates)
 - Wet scavenging of gases and aerosols in clouds and rain (wet deposition)
 - Aqueous phase chemistry
 - Dry deposition
- Aqueous chemistry important for secondary inorganic aerosols
- Feedbacks between different parts of model make evaluation difficult
- Validation and applications in part 2

Reduced Chemical Mechanisms

Carbon bond approach

- Model species represent *concentrations of functional groups* regardless of molecules to which they are attached. Surrogate species
 - PAR: single-bonded carbon atom (C-..), i.e. PAR represents only 1 C atom
 - OLE: carbon-carbon double bond (C=C), i.e. OLE represents 2 C atoms
 - ARO: aromatic rings
 - CAR: C=O bonds (carbonyls)

Suppose there was a mixture of
 1.0 ppmV of butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$)
 1.0 ppmV of propene ($\text{CH}_3\text{HC}=\text{CH}_2$)

These chemical species would be grouped as
 4 PAR from butane + 1 PAR from propene = 5 PAR
 1 OLE from propene

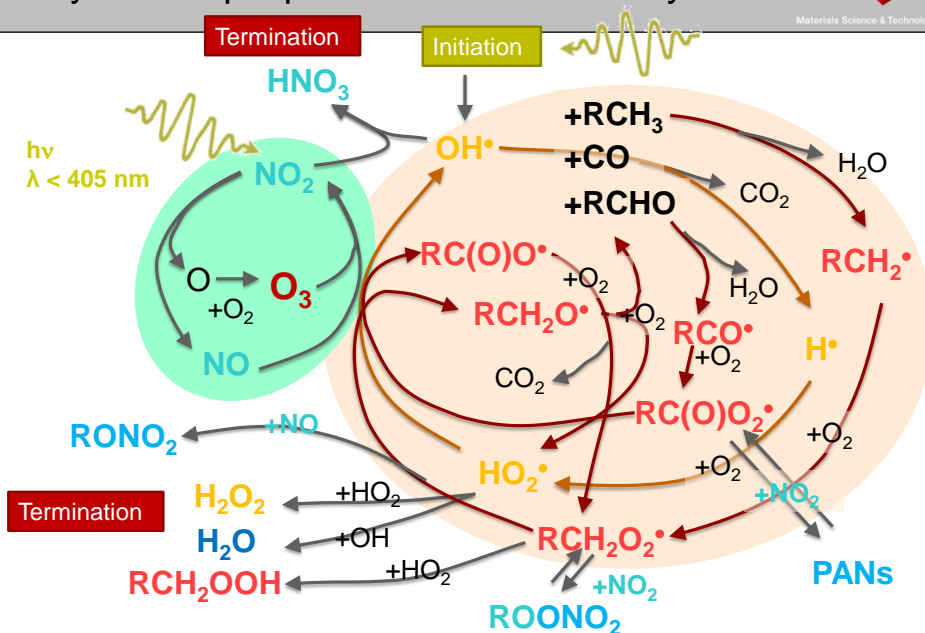
Advantages: total number of C is conserved, only few surrogate species needed, distribution of emitted species onto surrogates straightforward.

Aggregation by molecule

- Model species represent moles of similar molecules. Examples:
 - ALD: all aldehydes (or all aldehydes except HCHO)
 - PRO: propane and all less reactive alkanes
- Individual species are usually assigned to a surrogate species using weighting factors to account for chemical reactivities or carbon mass.
- Examples for this approach are the series of RADM, RACM and SAPRC mechanisms.
- Disadvantages: total number of C not conserved, distribution of emitted species onto surrogates less straightforward (weighting factors).

A challenge for both methods (lumping by molecule, lumping by functional group) is the selection of representative reaction rates

Daytime Tropospheric Ozone Chemistry



Comparing oxidation by H_2O_2 and O_3

As illustrated by the righthand figure, the oxidation by O_3 becomes equally important as the oxidation by H_2O_2 at a pH of about 5. O_3 is much less water soluble than H_2O_2 , but it can be supplied from the gas phase in much higher amounts.

Other oxidation pathways:

- Oxidation by organic peroxides ROOH
- Oxidation by O_2 catalyzed by transition metals like Fe(III) and Mn(II)
- Oxidation by the OH radical
- Oxidation by NO_2

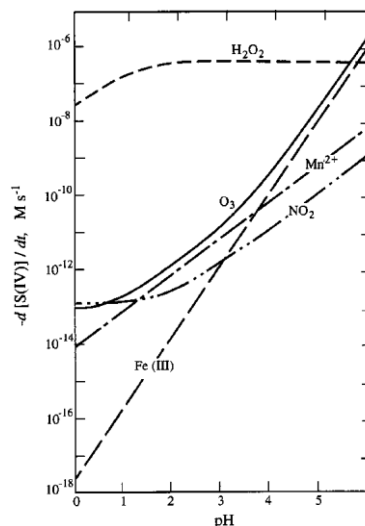


Figure: Comparison of S(IV) to S(VI) conversion rates for conditions: $[\text{SO}_2(\text{g})]=5\text{ppb}$, $[\text{NO}_2(\text{g})]=1\text{ppb}$, $[\text{H}_2\text{O}_2(\text{g})]=1\text{ppb}$, $[\text{O}_3(\text{g})]=50\text{ppb}$, $[\text{Fe(III)}]=0.3\text{ }\mu\text{M}$; $[\text{Mn(II)}]=0.03\text{ }\mu\text{M}$

Oxidation of S(IV) by dissolved ozone

In the gas phase, the reaction of O_3 with SO_2 , is very slow. The aqueous phase oxidation of S(IV), mainly through



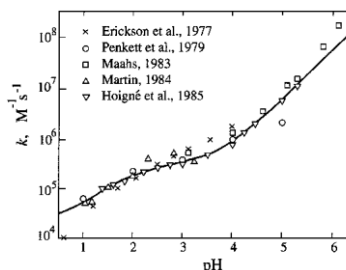
is fast. The second reaction is much faster and since the equilibrium concentration $[\text{SO}_3^{2-}]$ depends on $[\text{H}^+]^{-2}$, this reaction is strongly dependent on pH.

The overall reaction rate can be expressed as

$$\begin{aligned}-d[\text{S(IV)}]/dt &= (k_0[\text{SO}_2 \cdot \text{H}_2\text{O}] + k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}]) [\text{O}_3] \\ &= k [\text{S(IV)}][\text{O}_3]\end{aligned}$$

with $k_0=2.4 \times 10^4$, $k_1=3.7 \times 10^5$, $k_2=1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
The more SO_3^{2-} available, the faster is k .

2nd order reaction rate as function of pH



- Focus on COSMO-ART applications
 - Knoten aerosol paper
 - BAFU Study to PM10 trends
 - Pollen forecast (MeteoSwiss)
 - Dust? Something from KIT
- Evaluation
 - AQMEII exercise

- Baklanov, A., K. Schlünzen, P. Suppan, J. Baldasano, D. Brunner, S. Aksoyoglu, G. Carmichael, J. Douros, J. Flemming, R. Forkel, et al., Online coupled regional meteorology chemistry models in Europe: current status and prospects, *Atmos. Chem. Phys.*, **14**, 317-398, doi: 10.5194/acp-14-317-2014, 2014.
- Lelieveld, J., J. S. Evans, M. Fnais, D. Giannadaki, and A. Pozzer, The contribution of outdoor air pollution sources to premature mortality on a global scale, *Nature*, **525**, 367-371, doi: 10.1038/nature15371, 2015.