Atmospheric Analytical Chemistry

SoSe 2013

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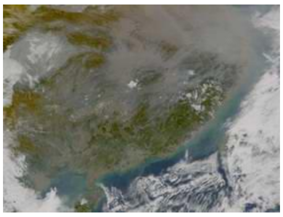

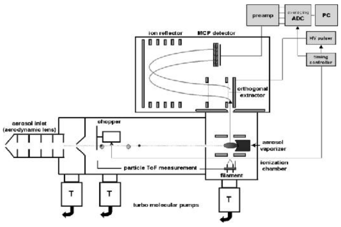

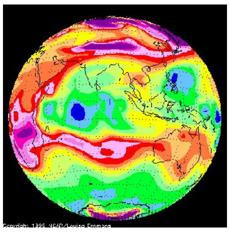

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Die atmosphärische Gasphase

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Teil 1 – Die atmosphärische Gasphase

- Forschungsgebiet des AK Hoffmann
    - Komponenten i.d. Gasphase (Teil 1) und Partikelphase (Teil 2)
    - organische und anorganische Analyten

Einführung in die Chemie und Physik der Atmosphäre

Aufbau der Atmosphäre

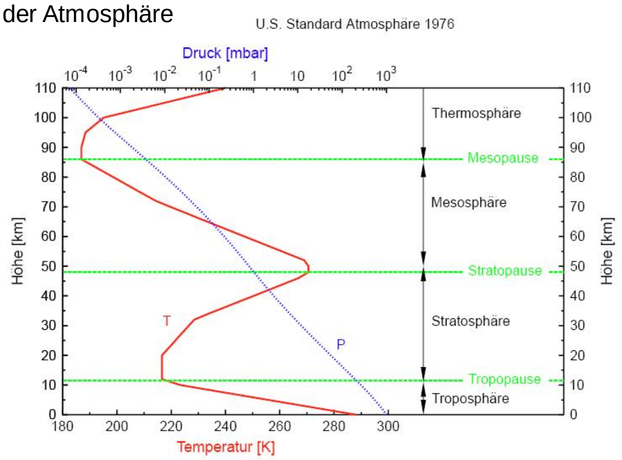


Abbildung 1-1: Aufbau der Atmosphäre. Auf der linken Seite ist der Verlauf von Temperatur (rot durchgezogene Linie) und Druck (blau gepunktete Linie) als Funktion der Höhe für die U.S. Standard Atmosphäre von 1976 aufgetragen. Letztere wird als einheitliche Referenz in vielen Atmosphärenmodellen eingesetzt. Auf der rechten Seite sind die einzelnen Stockwerke der Atmosphäre aufgetragen. Sie werden durch die sogenannten Pausen (grün gestrichelt) getrennt, die durch Minima bzw. Maxima im Temperaturverlauf definiert sind.

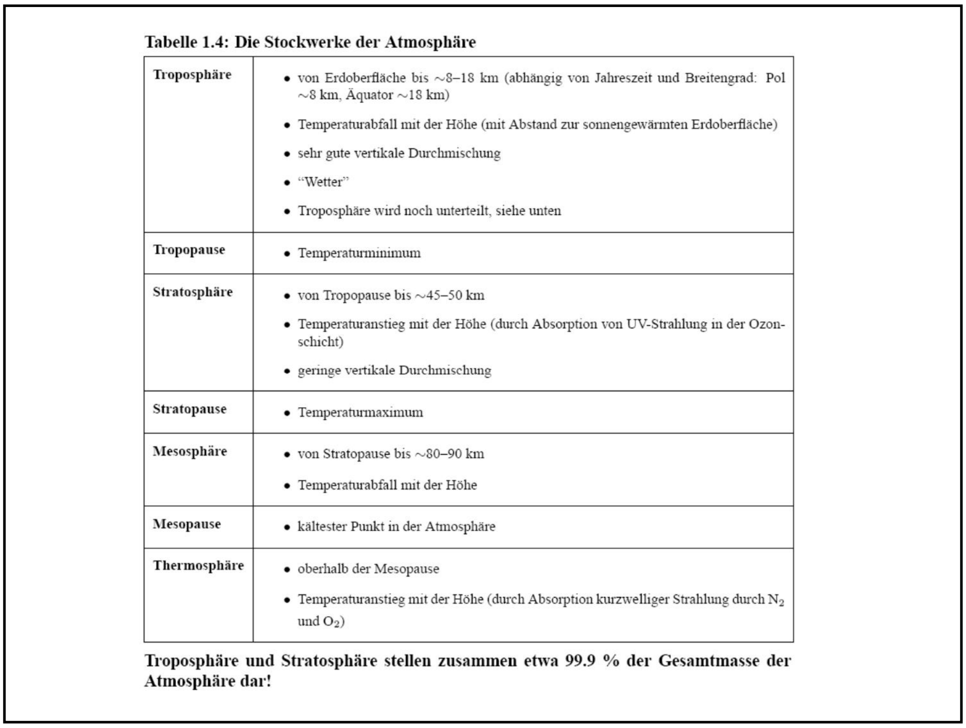


Tabelle 1.4: Die Stockwerke der Atmosphäre

Troposphäre	• von Erdoberfläche bis ∼8–18 km (abhängig von Jahreszeit und Breitengrad: Pol ∼8 km, Äquator ∼18 km) • Temperaturabfall mit der Höhe (mit Abstand zur sonnengewärmten Erdoberfläche) • sehr gute vertikale Durchmischung • “Wetter” • Troposphäre wird noch unterteilt, siehe unten
Tropopause	• Temperaturminimum
Stratosphäre	• von Tropopause bis ∼45–50 km • Temperaturanstieg mit der Höhe (durch Absorption von UV-Strahlung in der Ozonschicht) • geringe vertikale Durchmischung
Stratopause	• Temperaturmaximum
Mesosphäre	• von Stratopause bis ∼80–90 km • Temperaturabfall mit der Höhe
Mesopause	• kältester Punkt in der Atmosphäre
Thermosphäre	• oberhalb der Mesopause • Temperaturanstieg mit der Höhe (durch Absorption kurzwelliger Strahlung durch N_2 und O_2)

Troposphäre und Stratosphäre stellen zusammen etwa 99.9 % der Gesamtmasse der Atmosphäre dar!

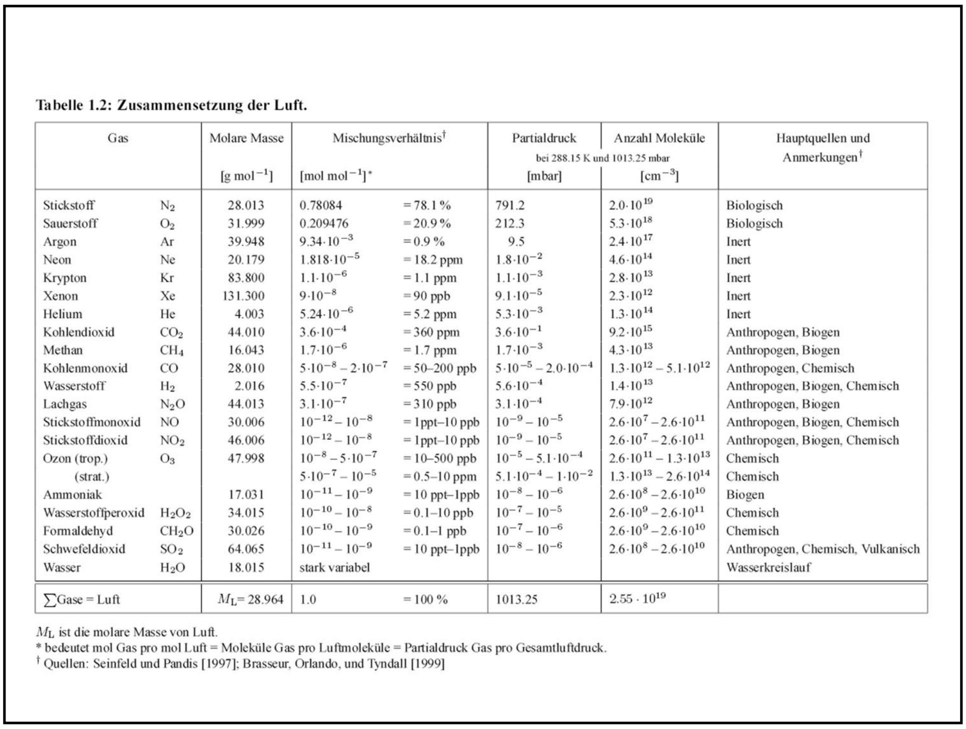


Tabelle 1.2: Zusammensetzung der Luft.

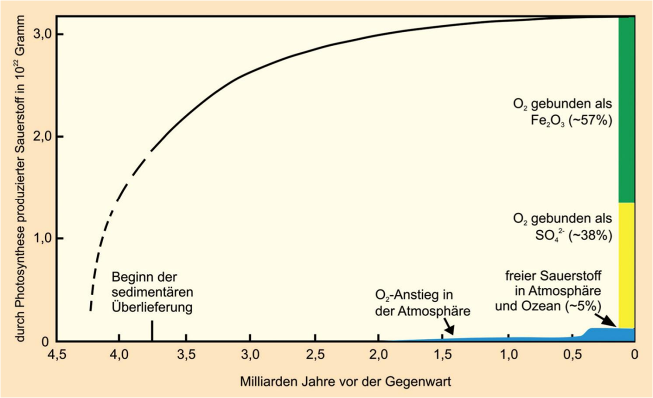
Gas		Molare Masse	Mischungsverhältnis†		Partialdruck	Anzahl Moleküle	Hauptquellen und Anmerkungen†
					bei 288.15 K und 1013.25 mbar		
		[g mol^{-1}]	[mol mol^{-1}]*		[mbar]	[cm^{-3}]	
Stickstoff	N_2	28.013	0.78084	= 78.1 %	791.2	$2.0 \cdot 10^{19}$	Biologisch
Sauerstoff	O_2	31.999	0.209476	= 20.9 %	212.3	$5.3 \cdot 10^{18}$	Biologisch
Argon	Ar	39.948	$9.34 \cdot 10^{-3}$	= 0.9 %	9.5	$2.4 \cdot 10^{17}$	Inert
Neon	Ne	20.179	$1.818 \cdot 10^{-5}$	= 18.2 ppm	$1.8 \cdot 10^{-2}$	$4.6 \cdot 10^{14}$	Inert
Krypton	Kr	83.800	$1.1 \cdot 10^{-6}$	= 1.1 ppm	$1.1 \cdot 10^{-3}$	$2.8 \cdot 10^{13}$	Inert
Xenon	Xe	131.300	$9 \cdot 10^{-8}$	= 90 ppb	$9.1 \cdot 10^{-5}$	$2.3 \cdot 10^{12}$	Inert
Helium	He	4.003	$5.24 \cdot 10^{-6}$	= 5.2 ppm	$5.3 \cdot 10^{-3}$	$1.3 \cdot 10^{14}$	Inert
Kohlendioxid	CO_2	44.010	$3.6 \cdot 10^{-4}$	= 360 ppm	$3.6 \cdot 10^{-1}$	$9.2 \cdot 10^{15}$	Anthropogen, Biogen
Methan	CH_4	16.043	$1.7 \cdot 10^{-6}$	= 1.7 ppm	$1.7 \cdot 10^{-3}$	$4.3 \cdot 10^{13}$	Anthropogen, Biogen
Kohlenmonoxid	CO	28.010	$5 \cdot 10^{-8} - 2 \cdot 10^{-7}$	= 50–200 ppb	$5 \cdot 10^{-5} - 2.0 \cdot 10^{-4}$	$1.3 \cdot 10^{12} - 5.1 \cdot 10^{12}$	Anthropogen, Chemisch
Wasserstoff	H_2	2.016	$5.5 \cdot 10^{-7}$	= 550 ppb	$5.6 \cdot 10^{-4}$	$1.4 \cdot 10^{13}$	Anthropogen, Biogen, Chemisch
Lachgas	N_2O	44.013	$3.1 \cdot 10^{-7}$	= 310 ppb	$3.1 \cdot 10^{-4}$	$7.9 \cdot 10^{12}$	Anthropogen, Biogen
Stickstoffmonoxid	NO	30.006	$10^{-12} - 10^{-8}$	= 1ppt–10 ppb	$10^{-9} - 10^{-5}$	$2.6 \cdot 10^{7} - 2.6 \cdot 10^{11}$	Anthropogen, Biogen, Chemisch
Stickstoffdioxid	NO_2	46.006	$10^{-12} - 10^{-8}$	= 1ppt–10 ppb	$10^{-9} - 10^{-5}$	$2.6 \cdot 10^{7} - 2.6 \cdot 10^{11}$	Anthropogen, Biogen, Chemisch
Ozon (trop.)	O_3	47.998	$10^{-8} - 5 \cdot 10^{-7}$	= 10–500 ppb	$10^{-5} - 5.1 \cdot 10^{-4}$	$2.6 \cdot 10^{11} - 1.3 \cdot 10^{13}$	Chemisch
(strat.)			$5 \cdot 10^{-7} - 10^{-5}$	= 0.5–10 ppm	$5.1 \cdot 10^{-4} - 1 \cdot 10^{-2}$	$1.3 \cdot 10^{13} - 2.6 \cdot 10^{14}$	Chemisch
Ammoniak		17.031	$10^{-11} - 10^{-9}$	= 10 ppt–1ppb	$10^{-8} - 10^{-6}$	$2.6 \cdot 10^{8} - 2.6 \cdot 10^{10}$	Biogen
Wasserstoffperoxid	H_2O_2	34.015	$10^{-10} - 10^{-8}$	= 0.1–10 ppb	$10^{-7} - 10^{-5}$	$2.6 \cdot 10^{9} - 2.6 \cdot 10^{11}$	Chemisch
Formaldehyd	CH_2O	30.026	$10^{-10} - 10^{-9}$	= 0.1–1 ppb	$10^{-7} - 10^{-6}$	$2.6 \cdot 10^{9} - 2.6 \cdot 10^{10}$	Chemisch
Schwefeldioxid	SO_2	64.065	$10^{-11} - 10^{-9}$	= 10 ppt–1ppb	$10^{-8} - 10^{-6}$	$2.6 \cdot 10^{8} - 2.6 \cdot 10^{10}$	Anthropogen, Chemisch, Vulkanisch
Wasser	H_2O	18.015	stark variabel				Wasserkreislauf
$\sum$Gase = Luft		M_L = 28.964	1.0	= 100 %	1013.25	$2.55 \cdot 10^{19}$	

M_L ist die molare Masse von Luft.

* bedeutet mol Gas pro mol Luft = Moleküle Gas pro Luftmoleküle = Partialdruck Gas pro Gesamtluftdruck.

† Quellen: Seinfeld und Pandis [1997]; Brasseur, Orlando, und Tyndall [1999]

Entwicklung des irdischen Sauerstoffs seit der Entstehung der Erde vor 4,5 Milliarden Jahren



Ursache der Sauerstoffzunahme: biogen durch Photosynthese

Problem: höhere organische Moleküle sowie Biomoleküle wie Aminosäuren und Proteine, wurden in der frühen Atmosphäre durch die energiereiche Sonnenstrahlung (keine Ozonschicht) photolysiert.
Daher entstanden erste Organismen wahrscheinlich im Wasser (photosynthetisierende Purpurbakterien – Schutz vor der kurzwelligen Sonnenstrahlung durch Wasser). Erst nachdem die Erdatmosphäre genügend Sauerstoff angesammelt hatte und das Ozon als UV-Schutzfilter aufgebaut war, konnten sich terrestrische Pflanzen Ausbreiten.

Aus: Chemie über den Wolken. Reinhard Zellner · Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim · ISBN: 978-3-527-32651-8

Atmosphärischer Transport

Temperaturinversion

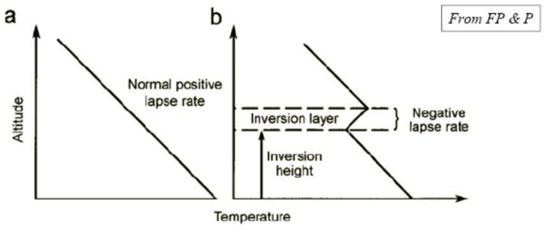


FIGURE 2.18 Variation of temperature with altitude within the troposphere: (a) normal lapse rate; (b) change in lapse rate from positive to negative, characteristic of a thermal inversion.

Atmosphärischer Transport

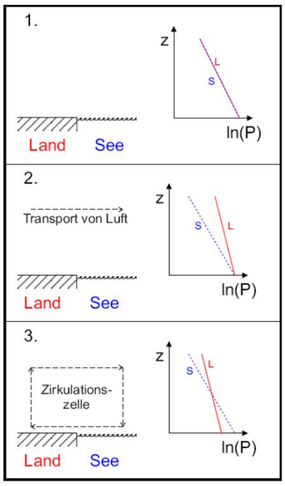


Abbildung 3-1: Entstehung einer lokalen Zirkulationszelle am Beispiel von Land- und Seewind.
1. Über Land und See herrschen die gleichen Bedingungen:

2. An einem sonnigen Tag heizt sich das Land schneller auf als das Meer,,

Atmosphärischer Transport

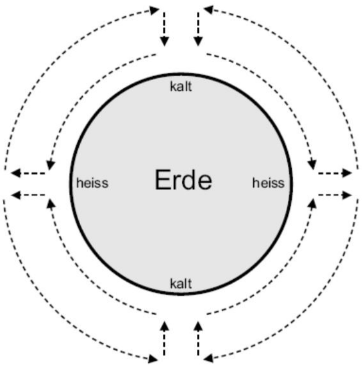


Abbildung 3-2: Modell der globalen Zirkulation nach Hadley. Nach diesem Modell bauen sich Zirkulationszellen wie im Falle des Land-/Seewinds aus, da die Pole kälter und die Tropen wärmer sind. Das Modell vermag das Aufsteigen von Luftmassen in den Tropen und damit das Auftreten der innertropischen Konvergenzzone zu erklären.

Atmosphärischer Transport

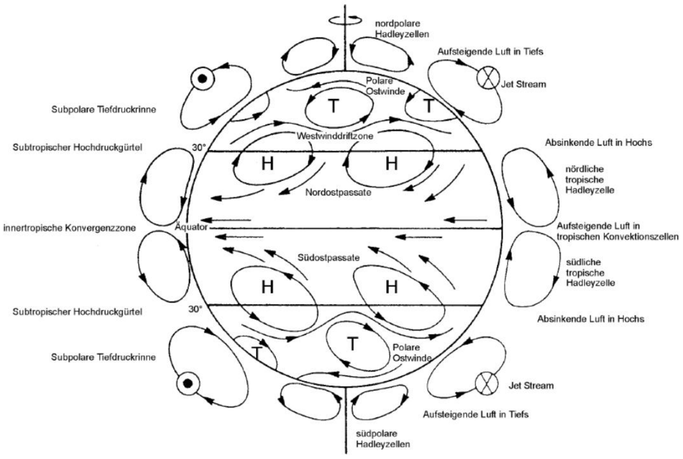


Abbildung 3-3: Tatsächlich beobachtete mittlere globale Zirkulation. Diese ist viel komplizierter als das einfache Modell von Hadley. Die tropische Zirkulationszelle reicht nicht bis zu den Polen sondern nur etwa bis jeweils zum 30. Breitengrad. Man erkennt den Aufbau mehrerer Zirkulationszellen sowie viele horizontale (nicht in Nord-Süd-Richtung verlaufende) Luftströmungen.

Atmosphärischer Transport und Chemie

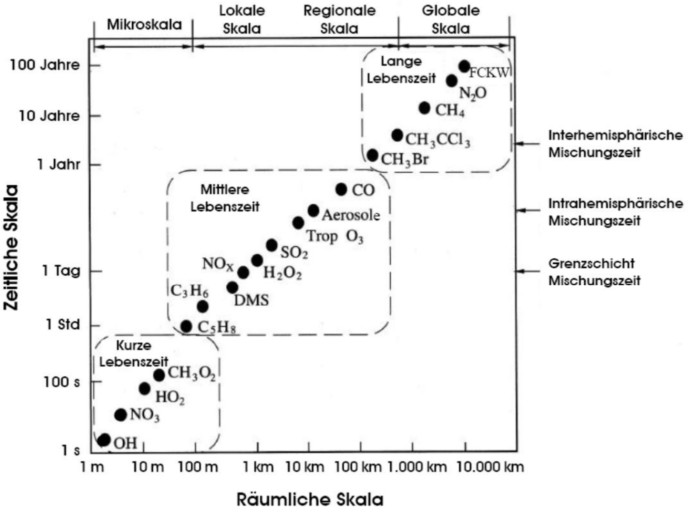
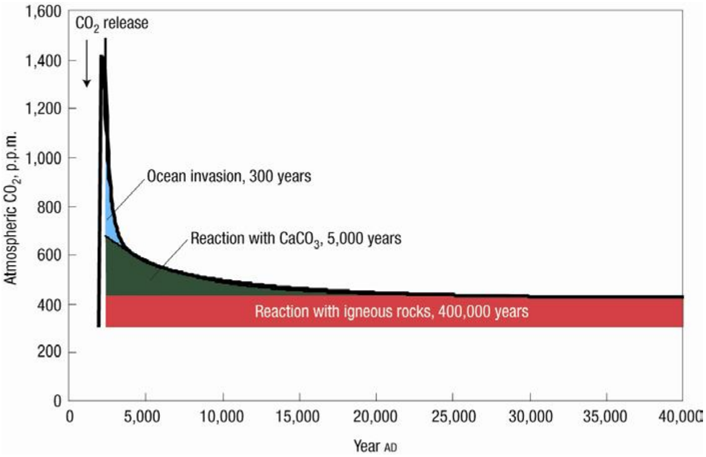


Abbildung 5-2: Skizze zur Verbreitung verschiedener Spurenstoffen in Abhängigkeit ihrer chemischen Lebenszeit in der Atmosphäre. Während sich kurzlebige Stoffe ($\tau \lesssim 1$ h) nur auf einer Skala von maximal wenigen hundert Metern verbreiten, können sich langlebige Stoffe ($\tau \gtrsim 1$ Jahr) global ausbreiten.

Spezialfall Atmosphärische Lebensdauer CO_2

nicht „nur“ chemische Senken (d.h. Abbau durch Oxidation oder Photolyse)



Long lifetime. Model simulation of atmospheric CO2 concentration for 40,000 years following after a large CO2 release from combustion of fossil fuels. Different fractions of the released gas recover on different timescales.
Nature reports climate change | VOL 2 | DECEMBER 2008

Probleme der Atmosphärenforschung

- London smog
  - Primary pollutants
- Photochemical (“LA”) smog
- Global tropospheric pollution
- Particles
  - Health
  - Visibility
- Acid deposition
- Stratospheric ozone depletion
- Global climate change

London Smog

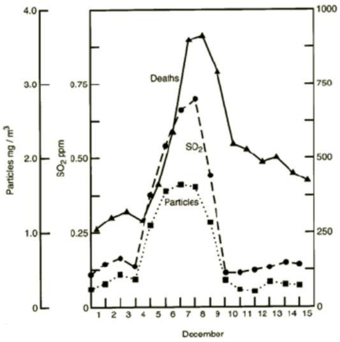


FIGURE 1.2 Concentrations of SO_2 and "smoke" as well as the death rate during the 1952 smog episode (adapted from Wilkins, 1954).

From FP & P

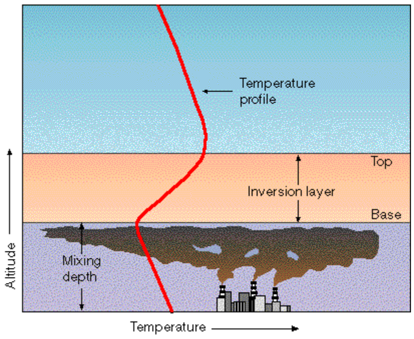
TABLE 1.1 Some Incidents of Excess Deaths Associated with Smog[a]

Year	Place	Number of excess deaths
1930	Meuse Valley, Belgium	63
1948	Donora, Pennsylvania	20
1952	London	4000
1962	London	700

[a] From Firket (1936), Wilkins (1954), Roueché (1965), and Cochran *et al.* (1992).

- Cold days, strong inversions, foggy
- Smoke + Fog = "Smog"

London Smog



Primär freigesetzte Luftverunreinigungen

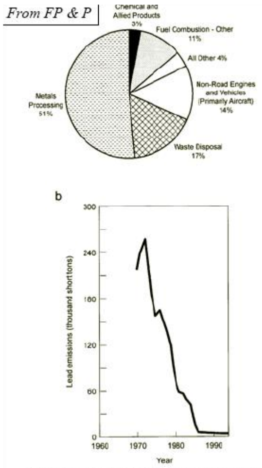


FIGURE 2.16 (a) Contribution of various sources to total anthropogenic Pb emissions in the United States in 1996. (b) Trend in lead emissions in the United States (from EPA, 1995, 1997).

- “Primary”: emitted directly, e.g. Pb
  - You reduce emission to reduce concentrations
- “Secondary”: formed in the atmosphere, e.g. O_3
- Pb was “easy”
  - Almost all from gasoline vehicles
  - Added to gasoline as anti-knock agent
  - Did without it after regulation required its removal
- Many countries still use leaded gasoline (~1/4 of gasoline in Spain, most in Africa)

Troposphärische Ozonbildung („LA Smog“)

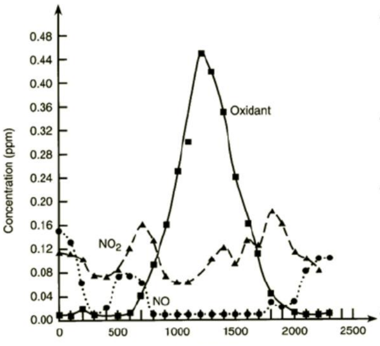


FIGURE 1.3 Diurnal variation of NO, NO_2, and total oxidant in Pasadena, California, on July 25, 1973 (adapted from Finlayson-Pitts and Pitts, 1977).

From FP & P

- Sharp contrast to London: sunny, hot days
- Eye irritation, plant damage
- 1950’s: Haagen-Smit:
  Organics + NO_x + sunlight → O_3 + “other products”
- Now widespread problem throughout the world

- max. Ozonkonz. 1955 LA ca. 700 ppbv

Troposphärische Ozonbildung („LA Smog“)

First recorded photo of smog in Los Angeles, July 26,1943

Troposphärische Ozonbildung

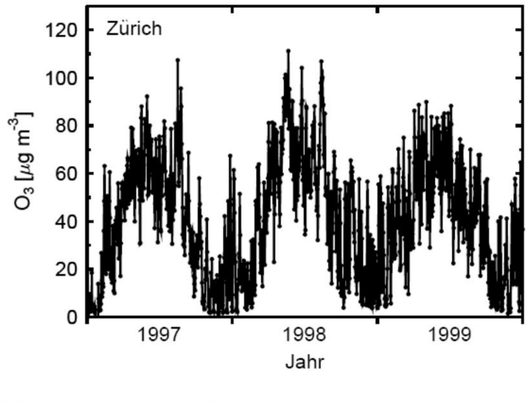


Abbildung 11-1: In Zürich gemessene Tagesmittelwerte für O_3.

Troposphärische Ozonbildung

Aus O_3 entsteht durch Photolyse und Reaktion mit Wasser OH. Die zugehörige Produktionsrate sei P_{HO_x}. Das entstandene OH reagiert in einer schadstoffbelasteten Atmosphäre mit Kohlenwasserstoffen (R-CH_3) wie folgt:

$$
\begin{array}{rcll}
\text{R-CH}_3 + \text{OH} & \longrightarrow & \text{R-CH}_2 + \text{H}_2\text{O} & \text{(R1a)} \\
\text{R-CH}_2 + \text{O}_2 + \text{M} & \longrightarrow & \text{R-CH}_2\text{O}_2 + \text{M} & \text{(R1b)} \\
\text{R-CH}_2\text{O}_2 + \text{NO} & \longrightarrow & \text{R-CH}_2\text{O} + \text{NO}_2 & \text{(R2)} \\
\text{R-CH}_2\text{O} + \text{O}_2 & \longrightarrow & \text{R-CHO} + \text{HO}_2 & \text{(R3)} \\
\text{HO}_2 + \text{NO} & \longrightarrow & \text{OH} + \text{NO}_2 & \text{(R4)} \\
\text{NO}_2 + h\nu & \longrightarrow & \text{NO} + \text{O} \quad (2\times) & \text{(R5a)} \\
\text{O} + \text{O}_2 + \text{M} & \longrightarrow & \text{O}_3 + \text{M} \quad (2\times) & \text{(R5b)} \\
\hline
\text{Netto: } \text{R-CH}_3 + 4\text{O}_2 + 2h\nu & \longrightarrow & \text{R-CHO} + 2\text{O}_3 + \text{H}_2\text{O} &
\end{array}
$$

Das hierbei gebildete R-CHO kann entweder photolysieren oder durch Reaktion mit OH eine weitere Reaktionskette durchlaufen. Senken für den Kreislauf sind

$$\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \qquad \text{(R6)}$$

sowie für hohe NO_x-Konzentrationen:

$$\text{NO}_2 + \text{OH} + \text{M} \longrightarrow \text{HNO}_3 + \text{M} \qquad \text{(R7)}$$

Troposphärische Ozonbildung

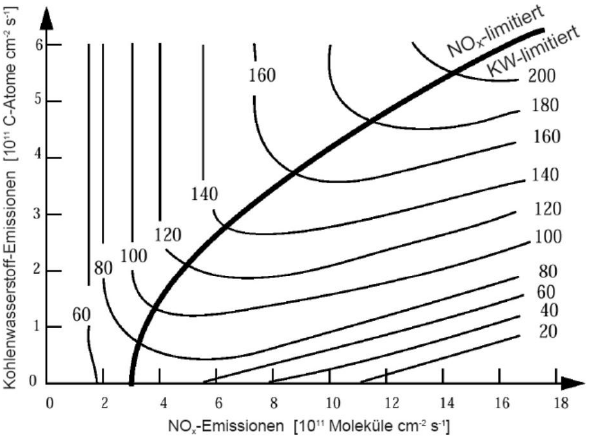
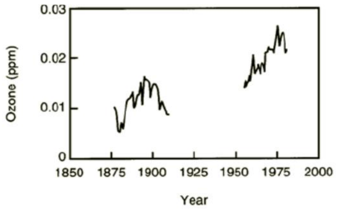


Abbildung 11-4: Mit einem photochemischen Modell berechnete Mischungsverhältnisse von Ozon in ppb (Linien) in Abhängigkeit von den Kohlenwasserstoff- und NO_x-Emissionen. Die fett gezeichnete Linie grenzt den NO_x-limitierten Bereich (oben links) und den Kohlenwasserstoff-limitierten Bereich (unten rechts) voneinander ab. Im NO_x-limitierten Bereich führt eine Verringerung der NO_x-Emissionen zu einer Erniedrigung der Ozonkonzentration, im Kohlenwasserstoff-limitierten Bereich allerdings im Gegenteil zu einer Erhöhung der Ozonkonzentration. Hier führt nur ein Reduktion der Kohlenwasserstoff-Emissionen zu einer Verringerung von Ozon.

Troposphärische Ozonbildung



From FP&P

FIGURE 1.6 Typical tropospheric ozone concentrations in the 1800's and present values (adapted from Volz and Kley, 1988).

- Tropospheric O_3
  - "Bad ozone," effects on humans, plants, materials
- Roughly same chemistry as LA smog
- Globally increasing trend
  - Thought to be due to shift in chemical regime as NO_x has increased

Ozon – Messmethoden (Impinger)

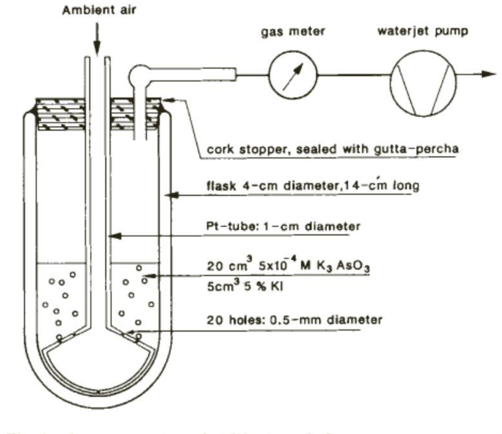
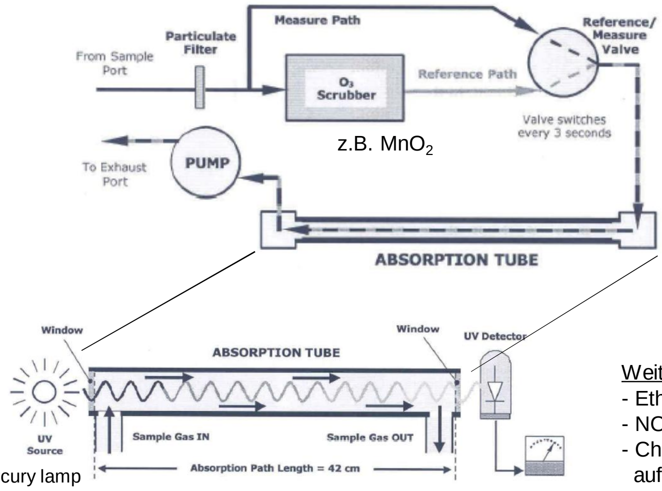


Fig. 1 Arrangement used at Montsouris for ozone measurements. The bubbler was mounted on a balcony ~5 m above the ground.

Die ersten systematischen Ozonmessungen wurden über einen Zeitraum von 30 Jahren (1877-1907) vom Chemiker Albert Levy im Parc Montsouris am Rande von Paris durchgeführt. Obgleich diese Messungen substanziell von der atmosphärischen Feuchte beeinflusst wurden, liefern sie doch einen Wert für das Mischungsverhältnis von Ozon an der Erdoberfläche im Europa des späten 19. Jahrhunderts: es lag wahrscheinlich bei 10-15 „parts per billion" (ppbv), und damit deutlich niedriger als die heute auf dem europäischen Kontinent typischerweise beobachteten 40-50 ppbv.

Ozon – Messmethoden

(photometrisch / UV-Absorption)



z.B. MnO_2

mercury lamp
(254 nm)

Quantifizierung

⇒ Lambert-Beer

⇒ Kalibration
z.B. nasschemisch
(Iodometrie)

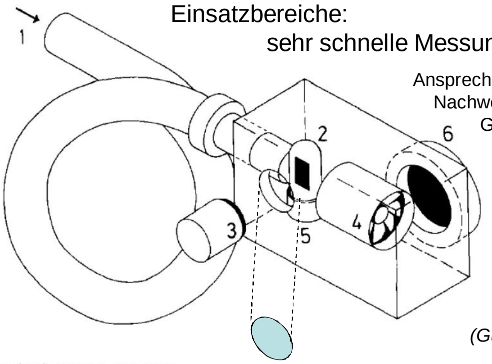
Weitere Methoden:
- Ethen-Chemilumineszenz
- NO-Chemilumineszenz
- Chemilumineszenzreakt. auf festen Phasen

Ozon – Messmethoden

(heterogene Chemilumineszenz)

Einsatzbereiche:
sehr schnelle Messung (z.B. Flussmessungen))

Ansprechzeit (response time) < 0,1 s
Nachweisgrenze < 50 ppt (S/N 3)
Gewicht ca. 1 kg (Ballonmessung)



(Güsten et al. 1991)

Fig. 1 Chemiluminescent ozone sensor
1. black Teflon sampling tube; 2: side-window photomultiplier;
3: thermostated head with chemiluminescent disc; 4: electric fan; 5: high voltage supply and amplifier (not shown); 6: exhaust wiht light trap.

Organischer Farbstoff (z.B. Coumarin) auf einer Trägerplatte (z.B. DC-Platte)

⇒ Wichtig - neben dem schnellen Ansprechverhalten - ist der Ausschluss von Querstörungen (positive und negative (quenching)) – insbesondere durch H_2O

Exkurs - Vertikaltransport und atmosphärische Deposition

im SoSe 2013 nicht behandelt

generell 2 Arten der Deposition:

Trockene Deposition (akzeptorabhängig)

Nasse Deposition (akzeptorunabhängig)

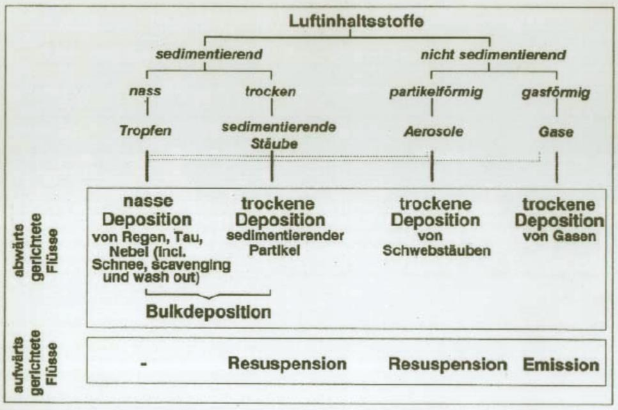


Abb. III-1: Übersicht über Formen vertikaler Flüsse in der bodennahen Atmosphäre (nach GRÜNHAGE et al. 1993)

Exkurs –Vertikaltransport und atmosphärische Deposition

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1.Konvektion: thermische Auf- und Abtriebsbewegungen (großräumig)

2.Turbulenz: Ausbildung von Wirbeln bzw. Turbulenzen (engl. Eddies) durch

- Dynamische Anregung
- Turbulenzanregung durch Auftriebskräfte

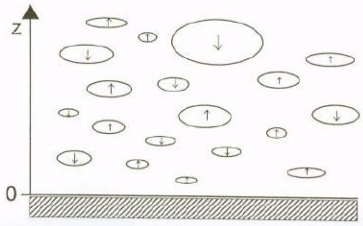

Bild II.2.8 Zur Veranschaulichung des turbulenten Transportes. Die Pfeile deuten die turbulente Zusatzgeschwindigkeit w' in der Vertikalen an. Wenn z.B. am Boden eine Quelle von χ existiert, ist in den von oben kommenden Teilchen im Mittel χ kleiner als in den von unten aufsteigenden. Bei verschwindender mittlerer vertikaler Massenflußdichte $\overline{\rho w}$ oder (bei konstantem ρ) verschwindendem $\overline{w}$ fließt im Mittel über die vielen Turbulenzelemente (Teilchen) genau so viel Masse nach oben wie nach unten; da aber die von unten kommenden Teilchen im Mittel mehr χ beinhalten als die von oben kommenden, ergibt sich hier ein turbulenter Transport der Eigenschaft χ von unten nach oben.

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Physikalisch-chemische Mechanismen der trockenen und nassen Deposition

- molekulare Diffusion
- turbulente Diffusion
- Impaktion und Interzeption
- Sedimentation
- sub-cloud scavening
- in-cloud scavening

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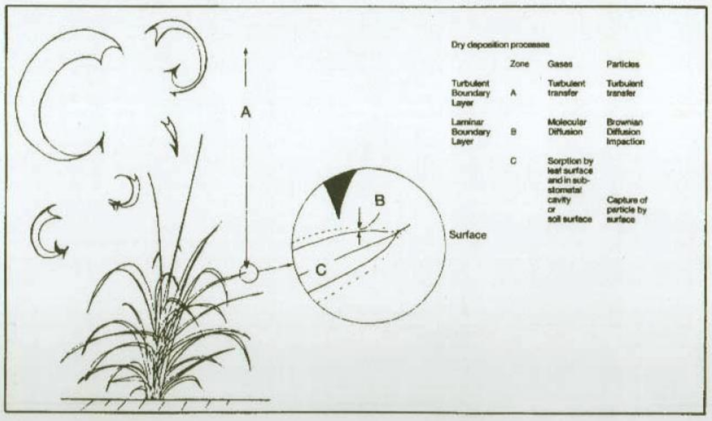
Prozess der trockenen Deposition



Dry deposition processes

	Zone	Gases	Particles
Turbulent Boundary Layer	A	Turbulent transfer	Turbulent transfer
Laminar Boundary Layer	B	Molecular Diffusion	Brownian Diffusion Impaction
	C	Sorption by leaf surface and in sub-stomatal cavity or soil surface	Capture of particle by surface

Figure 2–25: The dry deposition process (Fowler, 1980).

Exkurs - Vertikaltransport und atmosphärische Deposition

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Mechanismus der trockenen Deposition

1. Aerodynamischer (turbulenter) Transport durch die atmosphärische Oberflächenschicht bis an eine molekulare Grenzschicht an der Oberfläche
2. Transport durch die quasilaminare Grenzschicht für Moleküle und Partikel durch molekulare Diffusion, Impaktion, Interzeption
3. Ablagerung an der Oberfläche

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Rate der trockenen Deposition hängt ab:

Eigenschaften des luftgetragenen Spurenstoffes

z.B. Gas oder Partikel, Ausgangskonzentration, Diffusionskonstante, Löslichkeit, Sorptionsverhalten, Kompensationspunkt

Eigenschaften der atmosphärischen Grenzschicht

z.B. Turbulenz, Windgeschwindigkeit, Strahlung, Schichtungsstabilität, Luftfeuchte

Eigenschaften der Erdoberfläche

z.B. bewachsene oder bebaute Oberfläche, Artenzusammensetzung, Bestandeshöhe, Rauhigkeit, Bodenstruktur

Exkurs - Vertikaltransport und atmosphärische Deposition

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Ablagerung an der Oberfläche erfolgt durch:

- Ad-und Absorption bei Gasen
- Adhäsion bei Partikeln
- Lösungsvorgänge für Gase und Partikel
- Resorption durch Organismen
  - –Mensch, Tier: Atmung
  - –Pflanzen: Luftaustausch über Stomata (Blattöffnung)

Abb. Transportmechanismen von Partikeln durch die quasilaminareGrenzschicht

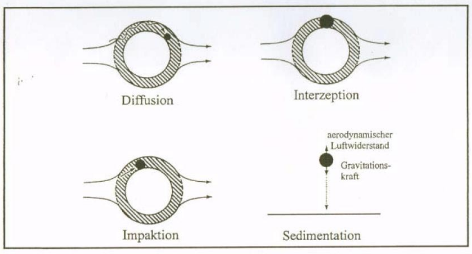

Abb. 2.2: Schematische Darstellung der vier Transportmechanismen von Partikeln durch die quasilaminare Grenzschicht (nach DAVIDSON and WU, 1990). Die Schraffur kennzeichnet die quasilaminare Grenzschicht.

Exkurs - Vertikaltransport und atmosphärische Deposition

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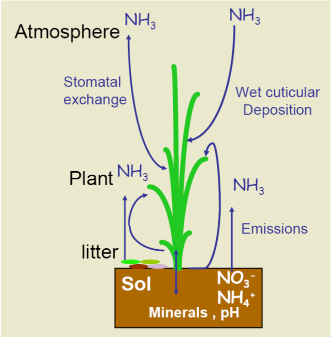
Kompensationspunkt

•Pflanze oder der Boden ist selbst Emittent der betrachteten Komponente
•NH_3, NO, CH_4-Gase mit bodengebundenen biogenen Quellen
•Kompensationspunkt liegt für NH_3 zwischen 0,1 ppb und bis zu 20 ppb (Gravenhorst et al., 2000)



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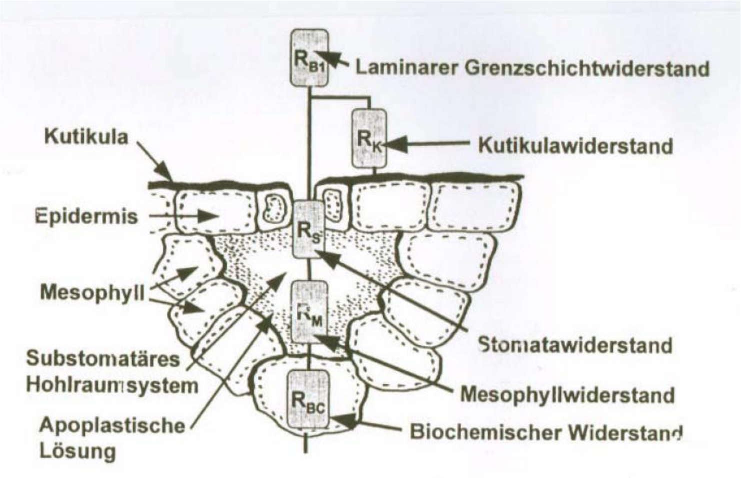
Schematische Darstellung der Transferwiderstände auf Nadel-/ Blattebene
Kompensationspunkt



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Messmethoden

Indirekte Methode

- Gradientenmethode:
  - Messung des Konzentrationsgradienten, Abschätzung der Diffusionskonstante aus Profilmessungen von Windgeschwindigkeit und Temperatur

Direkte Methoden

- Netto-Kronentraufe-Methode
  - Trockene Deposition aus der Spurenstoffdifferenz von Regenwasser über dem Kronenraum und Regenwasser unter dem Kronenraum
- Abwaschverfahren
  - Im Freiland exponierte Zweige, Blätter/ Nadeln werden mit einer künstlichen Regenlösung abgewaschen und diese auf die gesuchten Spurenstoffe untersucht
- Eddy-Korrelation/Accumulation

Exkurs - Vertikaltransport und atmosphärische Deposition

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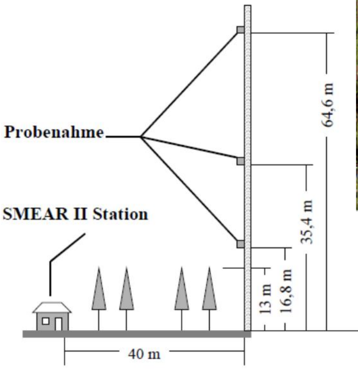

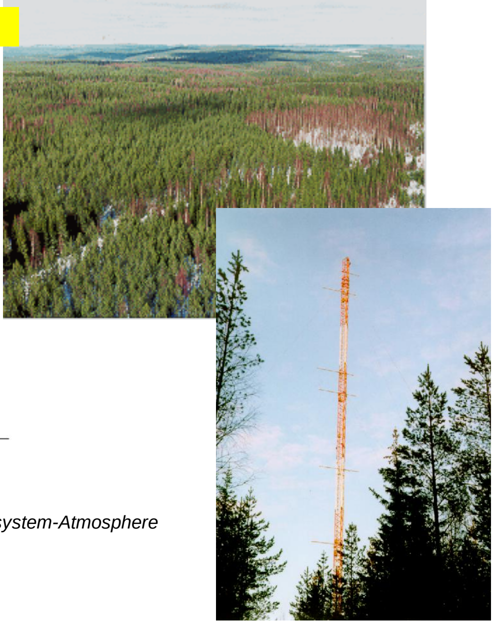

SMEAR II (*Station for Measuring Forest Ecosystem-Atmosphere Relations*) Station - Hyytälä, Finnland

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Exkurs - Vertikaltransport und atmosphärische Deposition

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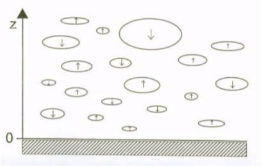
Messmethoden 2: Direkte Flussmessungen

Eddy-Korrelation:

Hochfrequente Messung (~10 Hz) der vertikalen Windgeschwindigkeit und der gewünschten Stoffkonzentration. Fluss ergibt sich direkt aus dem Produkt von Windgeschwindigkeit und Konzentration

Eddy-Accumulation:

Bedingungen wie bei Eddy-Korrelation. allerdings keine simultane Messung von Stoffkonzentration und Windgeschwindigkeit, sondern die zu untersuchende Komponente (z.B. Partikel) wird, getrennt nach Aufwind und Abwind, gesammelt und dann gemessen.



Ultraschall-
Anemometer

Exkurs - Vertikaltransport und atmosphärische Deposition

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Nasse Deposition

Austrag von Substanz aus der Atmosphäre in Verbindung mit Hydrometeoren (Regen, Schnee, Hagel) durch

Sedimentation
in-cloud scavening
sub-cloud scavening

Messmethoden

Wet-only Sammler (nur nasse Deposition)
Bulk Sammler, Sammelmethode nach Bergerhoff (sedimentierende Luftinhaltsstoffe)

Kohlenwasserstoffe in der Atmosphäre

- Most predominant: methane (CH_4)
- Non-methane hydrocarbons (NMHC) general formula (C_xH_{2x+2}), ethane, propane,…
- Aromatic NMHCs (toluene, xylenes)
- Oxygenated compounds (e.g.: acetone: CH_3COCH_3)
- Halogenated compounds CFCs
- Biogenic Compounds (Isoprene, MT, SQT)

biogenic and anthropogenic sources

⇒ on regional scales (populated areas) often anthropogenic NMHCs are more important

⇒ on the global scale biogenic NMHCs

Kohlenwasserstoffe in der Atmosphäre

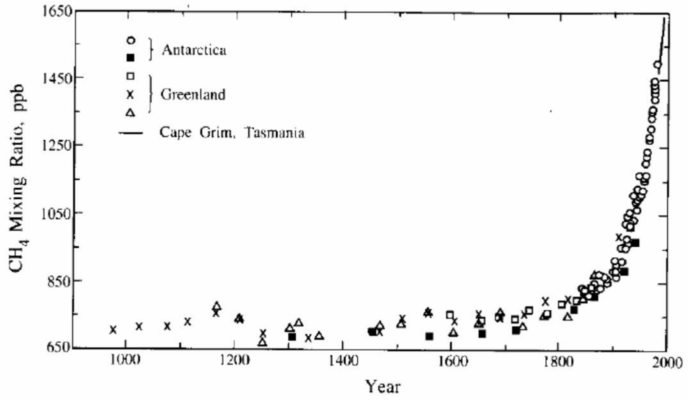
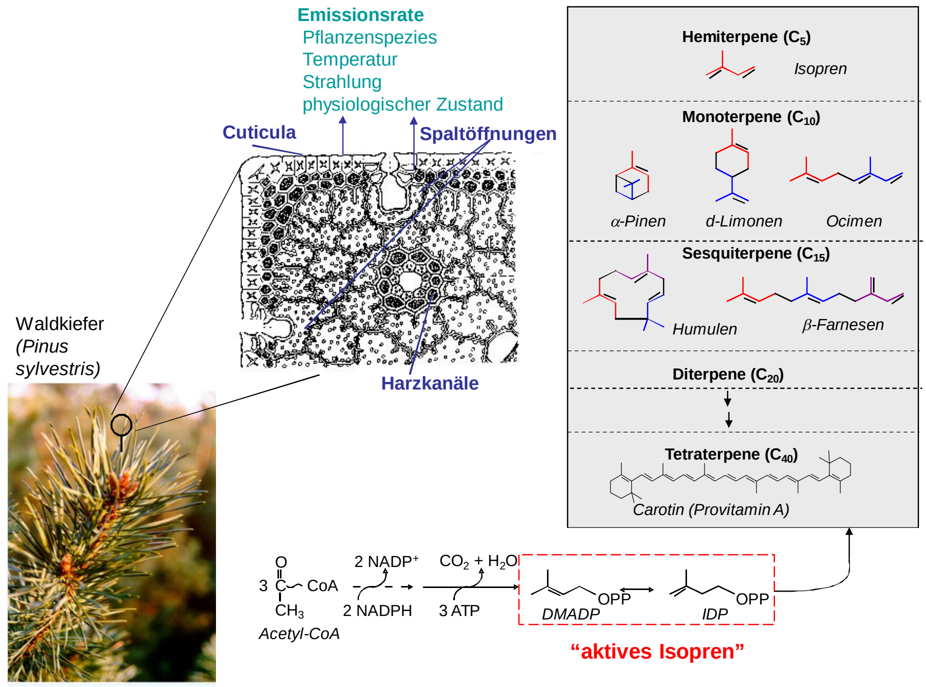


FIGURE 2.8 Methane mixing ratios over the last 1000 years as determined from ice cores from Antarctica and Greenland (IPCC, 1995). Different data points indicate different locations. Atmospheric data from Cape Grim, Tasmania, are included to demonstrate the smooth transition from ice core to atmospheric measurements.

Kohlenwasserstoffe in der Atmosphäre

Importance of atmospheric NMHC

- Tropospheric ozone formation
- Particle formation – air quality issues
- CFCs and the Ozone hole
- NMHC can yield insight into air mass history; i.e. what type of pollution has occurred?
- They can also tell us about the age of an air mass; i.e.: when was the last pollution event?
- Where was the sample taken, remote, rural or urban?



Emissionsrate
Pflanzenspezies
Temperatur
Strahlung
physiologischer Zustand

Cuticula

Spaltöffnungen

Harzkanäle

Waldkiefer
(Pinus sylvestris)

Hemiterpene (C_5)

Isopren

Monoterpene (C_{10})

α-Pinen *d-Limonen* *Ocimen*

Sesquiterpene (C_{15})

Humulen *β-Farnesen*

Diterpene (C_{20})

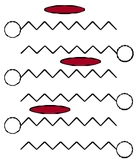
Tetraterpene (C_{40})

Carotin (Provitamin A)

“aktives Isopren”

Kohlenwasserstoffe in der Atmosphäre
Biogene Kohlenwasserstoffe

Hypothesen zur Rolle und Funktion flüchtiger biogener Kohlenwasserstoffe

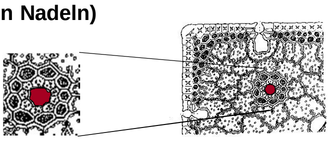


- **Erhöhung der Hitzetoleranz von Pflanzen**
  (Beinflußung der Stabilität der Zellmembranen)

- **Anlockung von Bestäubern**
  (z.T. durch chemische Täuschung)

  Freisetzung von insektenspezifischen Signal-und Lockstoffen (*Pheromone*) durch Blüten ⇒ Anlockung des Bestäubers

- **Verteidigung - Fraßschutz**
  (hohe Monoterpengehalte in jungen Nadeln)



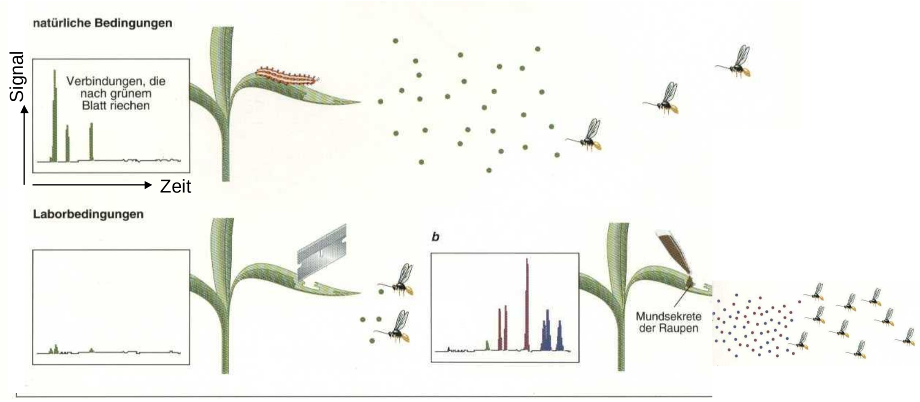
Kohlenwasserstoffe in der Atmosphäre
Biogene Kohlenwasserstoffe

Indirekte Verteidigungsmechanismen von Pflanzen

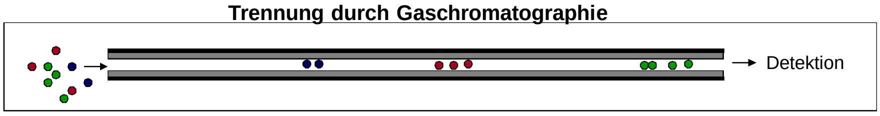
Ein Schlupfwespenweibchen greift eine an der Pflanze fressende Schmetterlingsraupe an

Frage:
Wie findet die Wespe ihr Opfer?

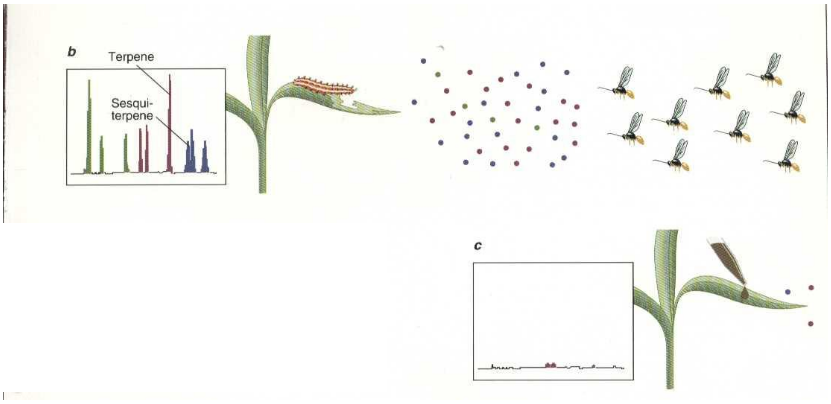
Indirekte Verteidigungsmechanismen von Pflanzen



Trennung durch Gaschromatographie



Indirekte Verteidigungsmechanismen von Pflanzen



Indirekte Verteidigungsmechanismen von Pflanzen

Befall mit pflanzenfressenden Schädlingen

⬇

induzierte Emission von Mono- oder Sesquiterpenen

⬇

Beeinflußung des Aggregationsverhaltens anderer Insektenarten (z.B. Wespen)

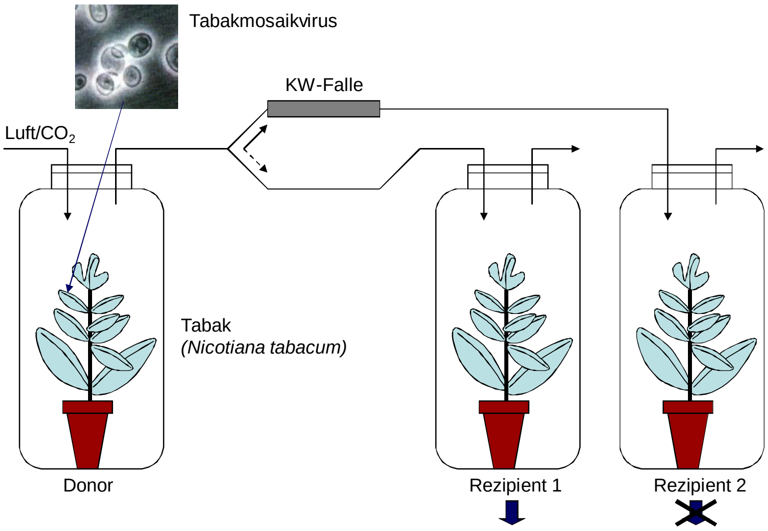
⬇

Nutzung des pflanzenfressenden Schädlings als Nahrungsquelle oder zur Eiablage

⬇

Vermeidung eines lange anhaltenden Befalls

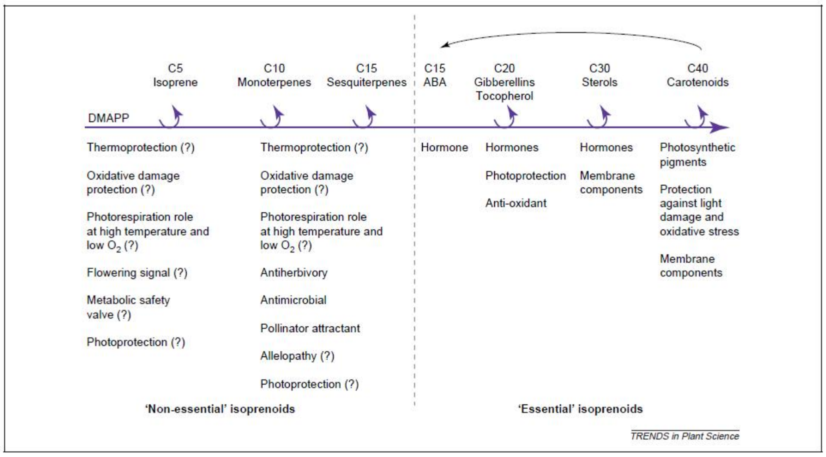
Flüchtige Kohlenwasserstoffe als Botenstoffe zur pflanzlichen Kommunikation ?



antimikrobielle Abwehrreaktion

Summary – physiological role of biogenic VOCs

The roles of isoprenoid compounds in plants

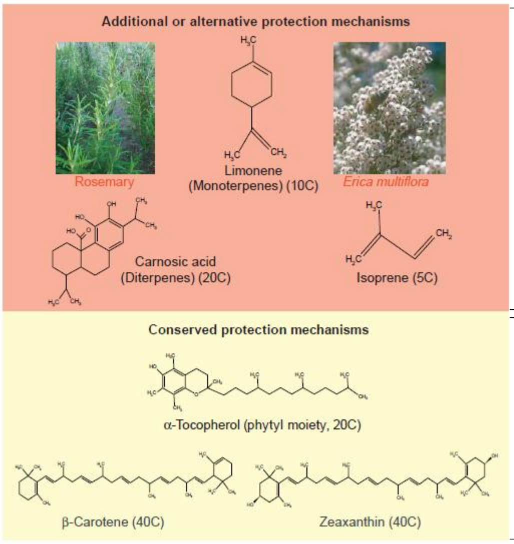


A question mark (?) indicates that the role has not been demonstrated in all isoprenoid volatile organic compound emitting plant species

Owen et al., Trends in Plant Science, 2005

Summary – physiological role of biogenic VOCs

Plant VOC emissions: making use of the unavoidable



‘opportunist hypothesis’

(i) volatile isoprenoid production takes advantage of DMAPP and IPP, which are synthesized primarily to produce essential isoprenoids

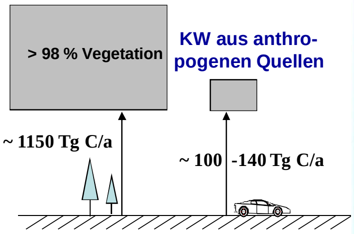
(ii) conditions affecting synthesis of the higher isoprenoids will affect the production and emission of volatile isoprenoids.

‘essential isoprenoids’ play an important photoprotective role

(by dissipating excess excitation energy as heat or by scavenging reactive oxygen species (ROS) and suppressing lipid peroxidation)

Penuelas et al., Trends in Plant Science, 2005

Bedeutung flüchtiger biogener Kohlenwasserstoffe für die Chemie der Atmosphäre



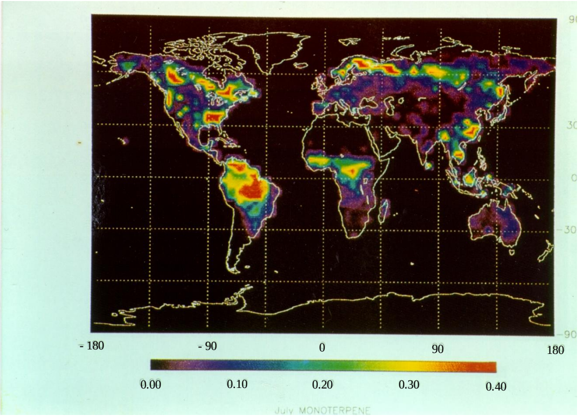
KW aus natürlichen Quellen

> 98 % Vegetation

KW aus anthropogenen Quellen

~ 1150 Tg C/a

~ 100 -140 Tg C/a



Emissionsraten von biogenen Kohlenwasserstoffen
[g C m^{-2} month $^{-1}$]

Kohlenwasserstoffe in der Atmosphäre – Biogene Kohlenwasserstoffe

Um die Nettoemission an reaktiven biogenen flüchtigen organischen Verbindungen abschätzen zu können, wurden Freilandmessungen durchgeführt.
Hier ein Blick auf den während des ECHO-Projektes Eingesetzten Messturm im Stetternicher Forst in Jülich. Die Messungen erfolgten höhenaufgelöst vom Boden bis oberhalb des Kronenraums.

Kohlenwasserstoffe in der Atmosphäre – Biogene Kohlenwasserstoffe

ABB. 3 | SPURENSTOFFEMISSIONEN

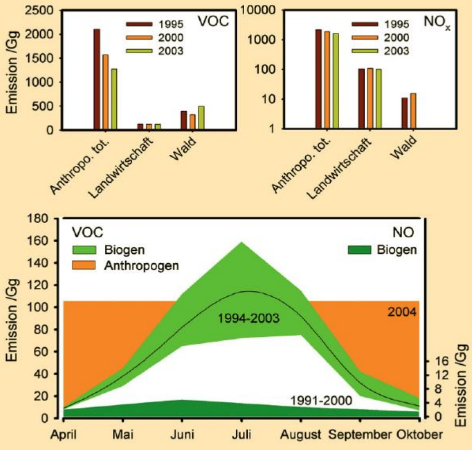


ABB. 5 | ANALYTIK

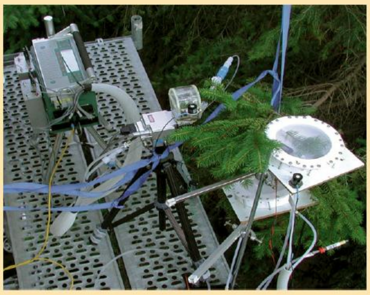
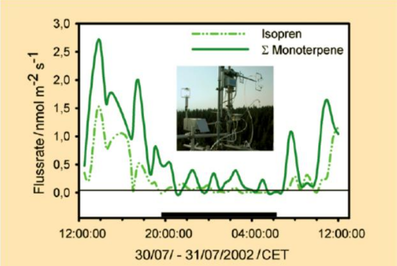


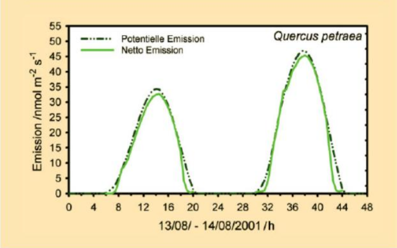
Abb. 3 *Biogene und anthropogene Spurenstoffemissionen in Deutschland. In den beiden oberen Graphiken ist die Veränderung der Quellstärke an VOC und NO_x für die Jahre 1995 bis 2003, gegliedert nach Quelltyp, als Jahressumme dargestellt. In der unteren Graphik ist die Emission als Monatsmittel angegeben.*

Abb. 5 *Küvettensysteme zur Bestimmung von Emissionsfaktoren von biogenen flüchtigen organischen Verbindungen am Beispiel der Fichte (Picea abies L. [Karst]). Die Messkammern sind mit Temperatur-, Licht-, und Feuchtesensoren ausgestattet.*

Kohlenwasserstoffe in der Atmosphäre – Biogene Kohlenwasserstoffe



Isopren und Monoterpenflussraten über einem Fichtenwald im Tagesverlauf an sonnigen Sommertagen



Isoprenemission eines mitteleuropäischen Eichenwaldes im Sommer an zwei wolkenlosen Tagen.

Kohlenwasserstoffe in der Atmosphäre Anthropogene Kohlenwasserstoffe

Hauptquellen:

Individual- und Berufsverkehr
- direkte Emission der Treibstoffkomponenten während der Produktion und Verteilung
- Freisetzung unverbrannter oder bei der Verbrennung gebildeter Kohlenwasserstoffe

Verbrennungsprozessen fossiler Energieträger zur Energie- und Wärmegewinnung

Brennholznutzung und Brandrodungsaktivitäten

Kohlenwasserstoffe in der Atmosphäre
Anthropogene Kohlenwasserstoffe

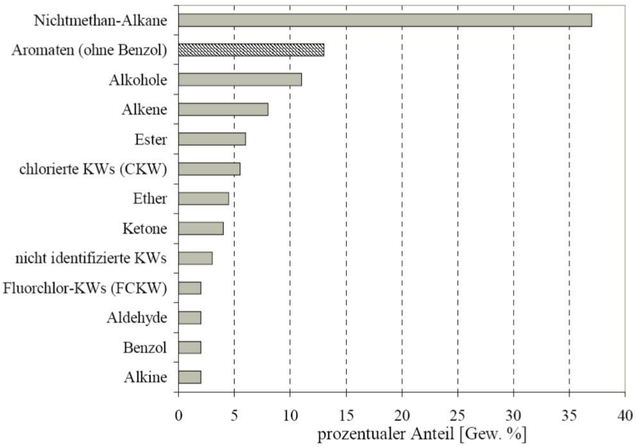
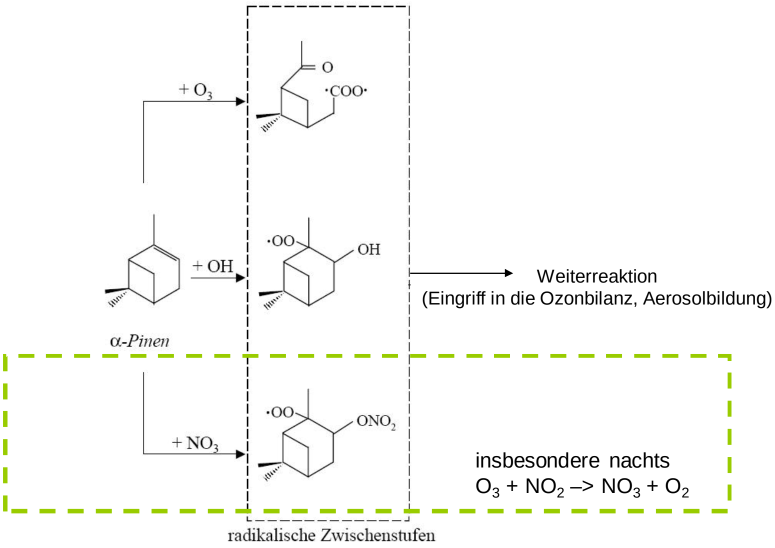


Abb. 2 Mittlere Zusammensetzung anthropogener VOC-Emissionen (Baden-Württemberg), [Friedrich und Obermeier (1999)]

Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport



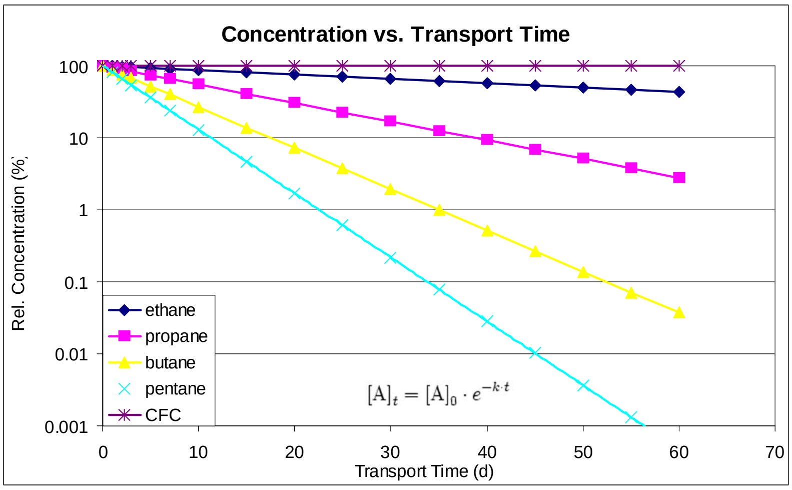
Weiterreaktion
(Eingriff in die Ozonbilanz, Aerosolbildung)

insbesondere nachts
$O_3 + NO_2 \rightarrow NO_3 + O_2$

Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport

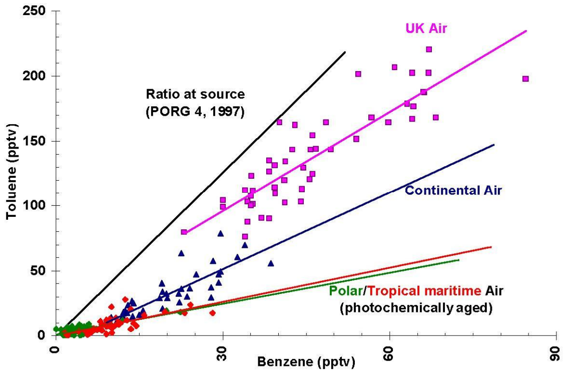
Compound	Molecular Structure	OH Rate Constant (cm3 (molec s)$^{-1}$	Ozone rate constant (cm3 (molec s)$^{-1}$	Estimated Atmospheric Lifetime
Ethane	C_2H_6	2.68E-13		66 d
Ethene	C_2H_4	8.52E-12	1.59E-18	1.7 d
Ethyne	C_2H_2	9.00E-13		20 d
Propane	C_3H_8	1.15E-12		15 d
Propene	C_3H_6	2.68E-11	1.01E-17	11 h
iso-Butane	C_4H_{10}	2.54E-12		7.0 d
n-Butane	C_4H_{10}	2.34E-12		7.6 d
n-Pentane	C_5H_{12}	3.94E-12		4.5 d
Isoprene	C_5H_8	1.01E-10	1.22E-17	3.7 h
Benzene	C_6H_6	1.40E-12		13 d
Toluene	C_7H_8	5.96E-12		3.0 d

Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport



$[OH] = 6*10^5$ molec cm^{-3}

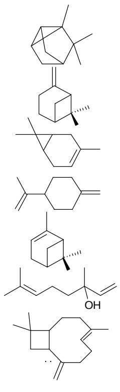
Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport



The changes in ratio between a pair of hydrocarbon species is commonly used as an indicator of the extent of photochemical processing between source region and monitoring location. For example anthropogenic pollution contains considerably higher levels of toluene than benzene (~4:1) a result of emission profiles at source. The reaction with the hydroxyl radical is the major loss process of both species, and toluene reacts considerably faster (~ x4) than benzene. Hence, as the time since emission into the air mass increases, the ratio of the two species decreases - a result of photochemical action. Dispersion and dilution processes also occurring during transport affect both species equally, having no impact on the change in ratios observed. The figure shows benzene and toluene ratios observed in different air masses.

Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport

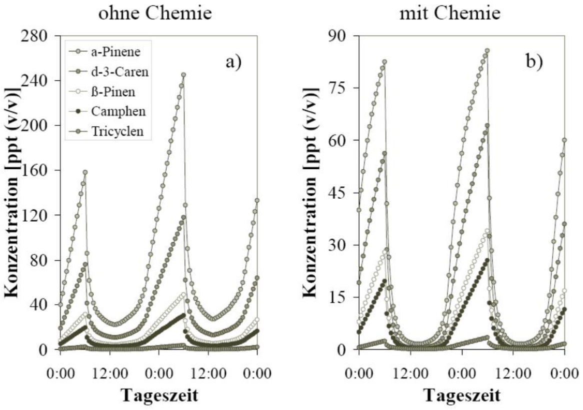
Mean atmospheric lifetime of biogenic VOCs



	lifetime [h]	
	OH	O_3
tricyclene	27.8	>1000
β-pinene	3.5	12.5
δ-3-carene	3.2	5.1
limonene	1.6	0.9
α-pinene	5.2	2.2
linalool	1.7	0.4
caryophyllene	1.4	0.02

$[O_3]$= 60ppb, $[OH]=1 \cdot 10^6$ molecules/cm^3

Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport



Modellrechnungen zu tageszeitlichen Variationen der *Konzentrationen* biogener Kohlenwasserstoffe in einem Waldbestand

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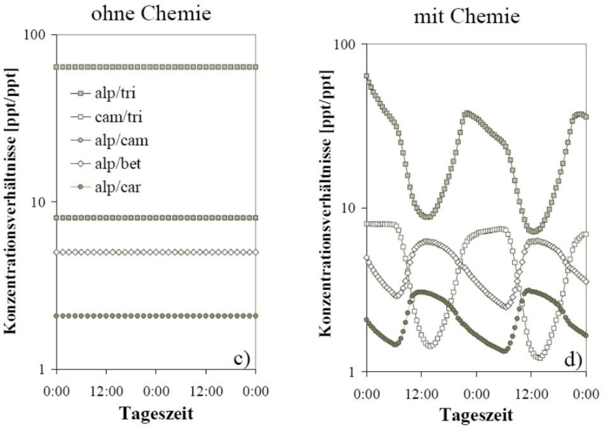
Kohlenwasserstoffe in der Atmosphäre
Chemischer Abbau und Transport



Modellrechnungen zu tageszeitlichen Variationen der *Konzentrationsverhältnisse* biogener Kohlenwasserstoffe in einem Waldbestand

Kohlenwasserstoffe - Analytik

(Beispiele für analytische Fragestellungen)

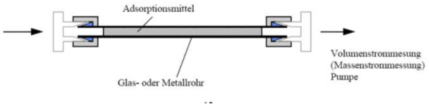
- VOC in ambient (outside) air, seen before
- Petrochemical industry, quality of crude oil and destillates
- Solvents at the work place (benzene, toluene) and other carcinogenic substances
- Evaporation of solvents (formaldehyde) from other materials such as carpets or glue
- Fragrance industry
- Breath analysis

Kohlenwasserstoffe - Analytik

- Main technique: Gas Chromatographic Measurements
- Detectors: Flame Ionization Detector (FID), Mass Spectrometer (MS), Electron Capture Detector (ECD), Atomic Emission Detector (AED)
- Sample Collection: whole air sampling in canisters (e.g.: NOAA network, CARIBIC), passive/active adsorbent trapping
- Inlet Systems: cryogenic, or adsorbent prefocussing systems

Kohlenwasserstoffe - Analytik

- Unpractical to take a full GC set-up in the jungle, on a mountain, on a plane or to multiple sampling locations unless long-term study
- Solution: bring the sample to the GC
- Collect whole air in a container: electropolished stainless steel (mostly used for VOC) or glass-flasks (used by NOAA network and CARIBIC)
- Other options are the sample preconcentration on an adsorbent cartridge
- Both methods need extensive testing to avoid interference



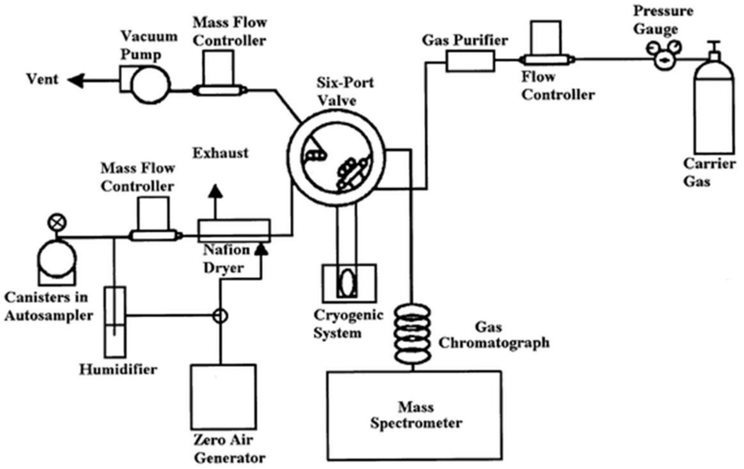
Kohlenwasserstoffe - Analytik

(whole air – canister sampling)

- Sample must be preconcentrated due to the extremely low concentrations (< 100 pptv) prior to GC analysis
- An air sample (1-10 L) is drawn through a trap and less volatile compounds of air (H_2O, VOC, etc.) are retained
- Two options: liquid N_2 trap, Tube cooled to -196 °C (see next figure)
- Solid adsorbent trap: elemental carbon material with extremely large surface area: 1000 m^2 g^{-1}

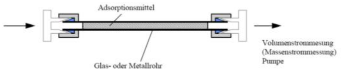
Kohlenwasserstoffe – Analytik

(whole air – canister sampling)



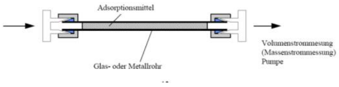
Kohlenwasserstoffe – Analytik

(adsorptive preconcentration)

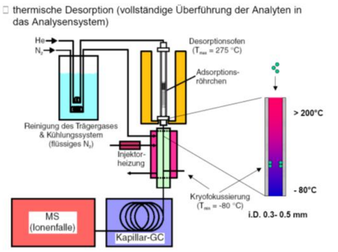


- Desorption techniques
  - Thermal desorption
  - Solvent extraction
- Most common thermal desorption
- Adsorbent is rapidly heated to ~ 300 °C under carrier gas flow
- Trap contents are flushed onto column
- Advantage over solvent extraction: sample remains pure, faster, no injection of solvent onto GC column

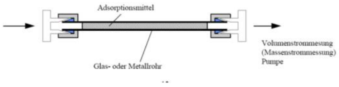
Kohlenwasserstoffe – Analytik
(adsorptive preconcentration)



- Low diameter stainless steel tube or fused silica tube submerged in liquid or gaseous N_2
- Volatile compounds condense remaining air passes through
- Trap is rapidly heated trapped compounds evaporate and are transferred on a GC column
- Problems: water, CO_2, CO and O_3 all condensate as well and need to be removed prior to trapping


☐ thermische Desorption (vollständige Überführung der Analyten in das Analysensystem)

Kohlenwasserstoffe – Analytik
(adsorptive preconcentration)

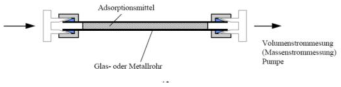


Interferences: Water

- Water occupies micropores which then are not available for trapping of VOC
- Water has to be removed prior to trapping
- Methods: Freeze-out, $CaSO_4$ trap or semi-permeable membranes such as Nafion

Kohlenwasserstoffe – Analytik

(adsorptive preconcentration)



Interferences: Ozone

- Ozone is present in the air by up to 200 ppbv (much more in extremely polluted environments: Mexico City, LA)
- Ozone reacts efficiently with unsaturated compounds (Lifetimes: days to minutes)
- Ozone needs to be removed prior to trapping process
- Options: $Na_2S_2O_3$ coated filters, heated metall surfaces, titration with NO or C_3H_6, catalytic surfaces (e.g. MnO_2)

Kohlenwasserstoffe – Analytik

(adsorptive preconcentration)

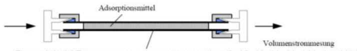
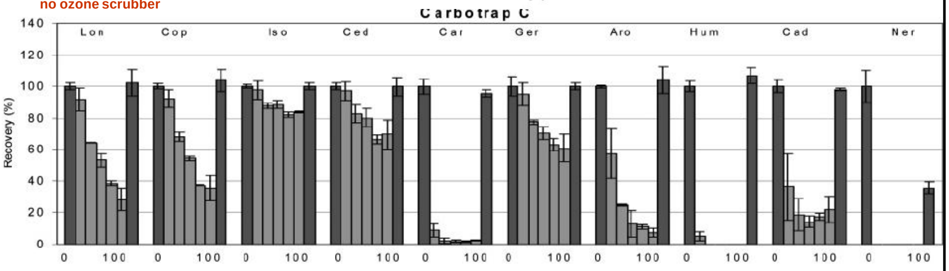
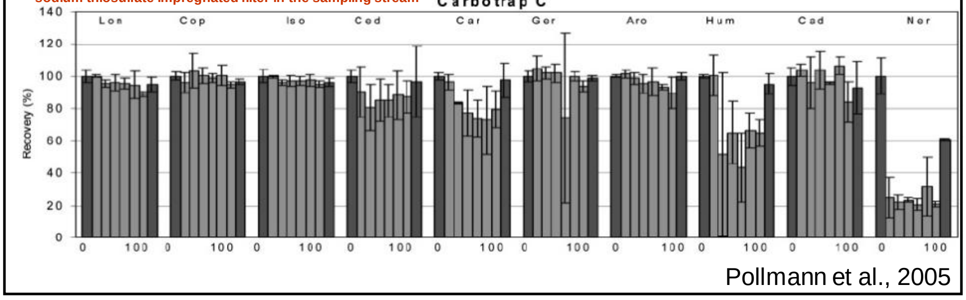


Figure 3.2: SQT recovery vs. ozone concentration (0, 20, 40, 60, 80, 100, 0 ppbV) for ten investigated BVOCs (from left to right in order of GC retention time). Abbreviations are: Lon: longipinene, Cop: α-copaene, Iso: isolongifolene, Ced: α-cedrene, Car: *trans*-caryophyllene, Ger: geranyl-acetone, Aro: aromadendrene, Hum: α-humulene, Cad: δ-cadinene, Ner: nerolidol, average of the *cis* and *trans* isomer). Error bars represent the relative standard deviation over two runs. Dark gray columns indicate runs without the addition of ozone; light gray indicates runs with added ozone.

no ozone scrubber



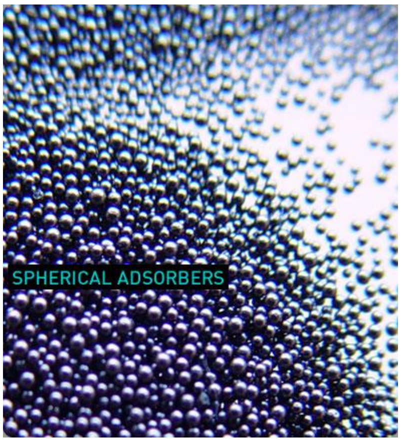
sodium thiosulfate impregnated filter in the sampling stream

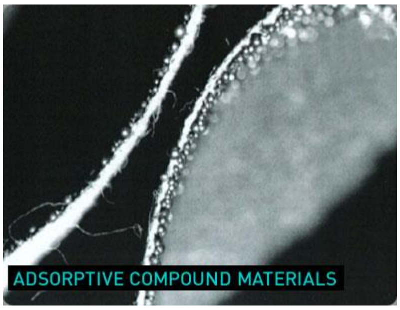


Pollmann et al., 2005

Kohlenwasserstoffe – Analytik
(adsorptive preconcentration)

New adsorbent materials





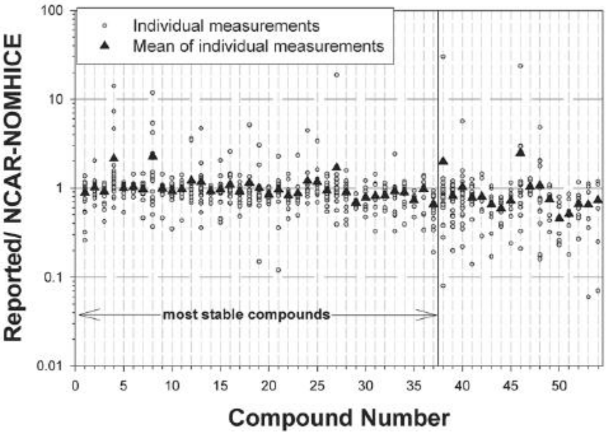
Kohlenwasserstoffe – Analytik

Intercomparisons

- Lots of different systems available
- All should give the same results but don‘t
- Intercomparisons Apel et al. 2003 and Plass-Dülmer et al., 2006
- Differences between certified reference and individual systems were up to a factor of 30 (3000%)
- Quality Control and Quality Assurance is the most important task in instrument development

Kohlenwasserstoffe – Analytik

Intercomparisons



Apel et al., 2003

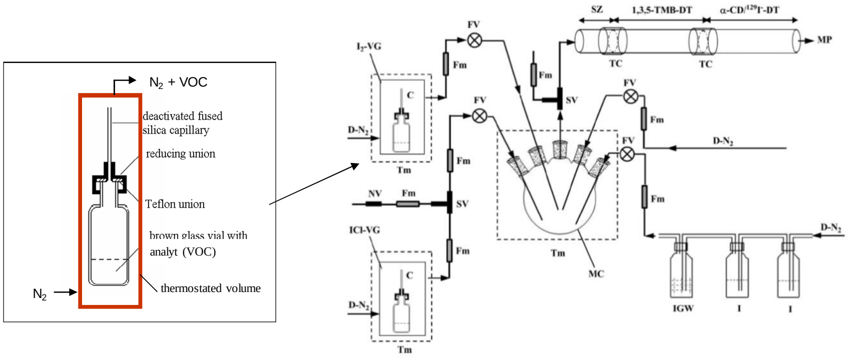
Kohlenwasserstoffe – Analytik

Calibration

- Major challenge (most important step)
- Measuring the instrumental response of your instrument to a given concentration
- Frequent test of instrumental background (analysis of zero-air samples)
- Correct peak identification
- Complete transfer of analytes into detector

Kohlenwasserstoffe – Analytik - Kalibration

Gravimetric calibration of diffusion tubes used for the preparation of gas standards (Huang 2009)



Testgasausstoß pro Zeit (z.B. in ng/min):

~ Kapillardurchmesser
~ Länge der Kapillare
~ Temperatur (Dampfdruck)
~ Analyt (Diffusionskoeffizient, Dampfdruck)

gegebenfalls Verdünnungsschritt nach Testgasgenerator

Kohlenwasserstoffe – Analytik - Kalibration

Gravimetric calibration of permeation tubes used for the preparation of gas standards for air pollution analysis (Tumbioli 2005)

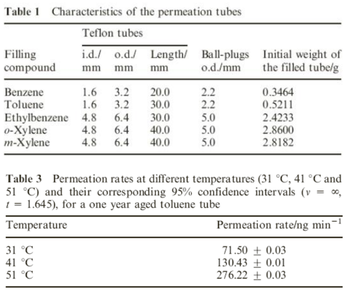
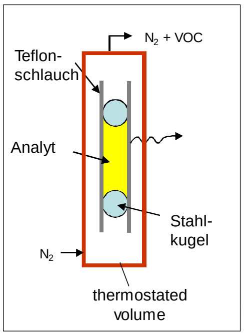


Table 1 Characteristics of the permeation tubes

Filling compound	Teflon tubes i.d./mm	o.d./mm	Length/mm	Ball-plugs o.d./mm	Initial weight of the filled tube/g
Benzene	1.6	3.2	20.0	2.2	0.3464
Toluene	1.6	3.2	30.0	2.2	0.5211
Ethylbenzene	4.8	6.4	30.0	5.0	2.4233
o-Xylene	4.8	6.4	40.0	5.0	2.8600
m-Xylene	4.8	6.4	40.0	5.0	2.8182

Table 3 Permeation rates at different temperatures (31 °C, 41 °C and 51 °C) and their corresponding 95% confidence intervals ($\nu = \infty$, $t = 1.645$), for a one year aged toluene tube

Temperature	Permeation rate/ng min^{-1}
31 °C	71.50 ± 0.03
41 °C	130.43 ± 0.01
51 °C	276.22 ± 0.03



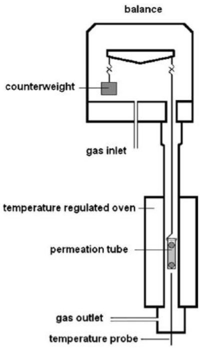


Fig. 1 Scheme of the thermobalance used for the weight-loss monitoring of permeation tubes.

Testgasausstoß pro Zeit (z.B. in ng/min):

~ Fläche (exponierte Schlauchoberfläche)
~ Dicke der Permeationsmembran (Dicke des Schlauchs)
~ Temperatur
~ Analyt (Diffusionskoeffizient, Löslichkeit)

Kohlenwasserstoffe – Analytik - Kalibration

- Gas cylinders with known concentrations of the analytes (one-step microgravimetric method, adding pressurized N_2)

  even with such a simple technique reliable results are difficult to get:
  - analyte stability (unsaturated-, oxidized- or low volatile-compounds)
  - sample handling e.g. discrimination of sample composition (e.g. Helmig, Anal. Chem. 2004)

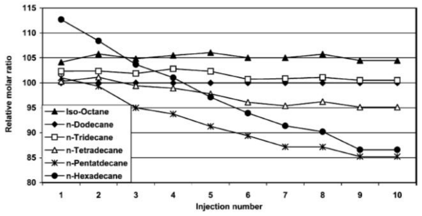


Figure 4. Discrimination of heavier *n*-alkanes (normalized to *n*-dodecane) using a gas regulator. Ten consecutive injections were made at 30-min intervals while the regulator and transfer lines were continuously purged with the standard at ~20 mL min^{-1}. This experiment was performed on day 145 after the standard preparation.

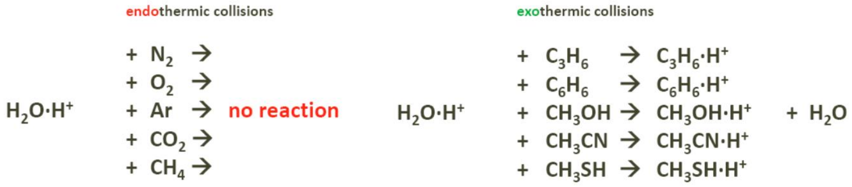
- Compressed ambient air sample (certified) as reference gas
  - representative composition
  - same restrictions as the method above (e.g. stability etc.)

Kohlenwasserstoffe - Analytik – PTR-MS

Proton-Transfer-Reaction Mass Spectrometry

(→ Skript Org. Spurenanalytik)

- PTR-MS VOC are protonated via H_3O^+ ions
- $H_3O^+ + R \rightarrow H_2O + RH^+$
- H_3O^+ is generated by protonating H_2O at a hollow cathode
- Sample is introduced and transferred through a drift tube to allow enough time for above reaction
- Detection is only possible for compounds with higher proton affinity than water



endothermic collisions

$H_2O{\cdot}H^+$ + N_2 → / + O_2 → / + Ar → / + CO_2 → / + CH_4 → no reaction

exothermic collisions

$H_2O{\cdot}H^+$ + C_3H_6 → $C_3H_6{\cdot}H^+$ / + C_6H_6 → $C_6H_6{\cdot}H^+$ / + CH_3OH → $CH_3OH{\cdot}H^+$ / + CH_3CN → $CH_3CN{\cdot}H^+$ / + CH_3SH → $CH_3SH{\cdot}H^+$ + H_2O

Kohlenwasserstoffe - Analytik – PTR-MS

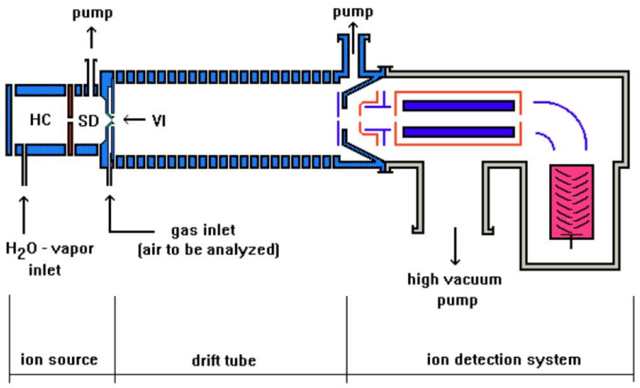


Figure 1. Schematic representation of the PTR-MS system. HC, hollow cathode; SD, source drift region; VI, Ventury-type inlet.

(Hansel et al. 1999)

Kohlenwasserstoffe – Analytik – PTR-MS

Detection of organic reactants R

e.g. benzene *PA* = 7,78 eV, acetonitrile *PA* = 8,16 eV, acetone *PA* = 8,42 eV
isoprene *PA*= 8,63 eV

having low volume mixing ratios in air rely on exothermic proton transfer reactions:

$$H_3O^+ + R \xrightarrow{k} RH^+ + H_2O \qquad (1)$$

At the end of the reaction section the density of product ions $[RH^+]$ is given by:

$$[RH^+] = [H_3O^+]_0(1 - e^{-k[R]t}) \sim [H_3O^+]_0[R]kt \qquad \textit{oder} \qquad [R] \sim [RH^+]/[H_3O^+]_0 \cdot 1/kt$$

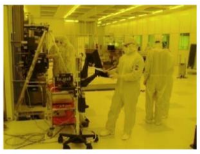
where the density of H_3O^+ ions at the end of the DT (reaction section) is about the same, with and without the presence of trace compounds, thus $[H_3O^+]_0 \approx [H_3O^+]$. *k* is the reaction rate constant for the proton transfer reaction (1) and *t* is the average time or ‘reaction time’ the ions spend in the DT. As [R] denotes small concentrations of trace constituents, then $[RH^+] << [H_3O^+] \approx [H_3O^+]_0$ = constant. The ion detection system measures count rates $i(H_3O^+)$ and $i(RH^+)$, which are proportional to the respective densities of these ions. To reach a high sensitivity thus requires generating a high ion count rate $i(RH^+)$ of the compound R to be quantified. This obviously can be achieved by keeping the density $[H_3O^+]$ high and by not diluting the gas to be analysed. Under typical operation conditions (reaction time, t = 0,1 ms, reaction pressure, p = 2 mbar, count rates, $i(H_3O^+ = 3 \cdot 10^6\ s^{-1}$ and a reaction rate constant, $k = 3 \cdot 10^{-9}\ cm^3\ s^{-1}$), the smallest detectable mixing ratio of organic compounds is about 10 pptv (Hansel et al. 1999).

Kohlenwasserstoffe – Analytik – PTR-MS

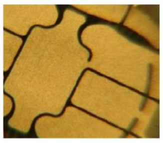
Problems in the quantification can arise when the humidity changes, since humidity can influence the formation of water clusters $(H_3O^+)H_2O_n$ (larger clusters at higher humidities), which have a different proton affinity => some compounds can be ionized with H_3O^+ but not with $(H_3O^+)H_2O_n$.

Applications:

VOC monitoring in clean rooms
- Airborne molecular contamination
- Semiconductor industry



Picture: AMTC

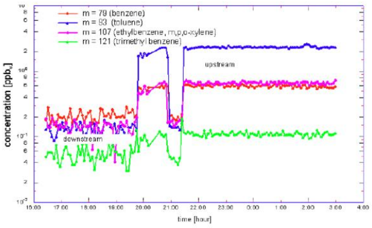


Picture: Pixelio.de

- Hazing of wafers, optics
- Filter-system lifetime

→ Process analysis

→ Straightforward and sensitive online monitoring with PTR-MS

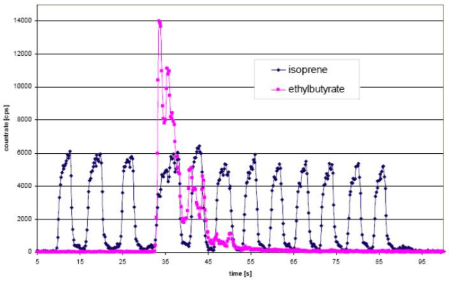


Kohlenwasserstoffe – Analytik – PTR-MS

Applications:

Food and flavor science
- Nose space air breath by breath analysis,
- Swallowing of strawberry flavored drink

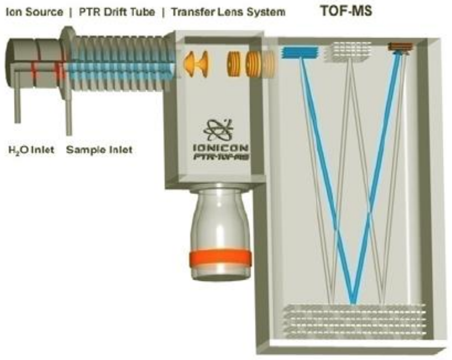
High time resolution



Kohlenwasserstoffe - Analytik - PTR – TOF - MS

Advantages

- full mass spectra acquisition with high time resolution
- isobaric species can be distinguished due to the high resolution (5000-7000)
- almost no instrumental mass range limitation
- linearity range over several orders of magnitude

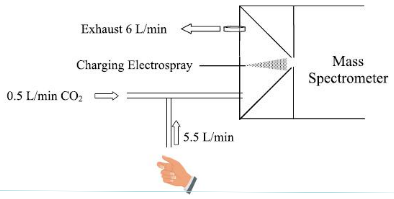


Disadvantages

- relatively expensive
- experts are needed for operation

Kohlenwasserstoffe - Analytik

Secondary Electrospray Ionization-MS (SESI-MS) zur on-line Analyse organischer Verbindungen



Blank-subtracted mass spectrum
(1) pyruvaldehyde;
(2) glyoxylic acid;
(3) pyruvic acid;
(4) lactic acid;
(5) 4-hydroxybutanoic acid;
(6) 3-methyl-2-oxobutanoic acid;
(7) 3-hydroxypentanoic acid;
(8) 4-methyl-2oxopentanoic acid.

andere C12-C18 Fettsäuren

neg. Ionen

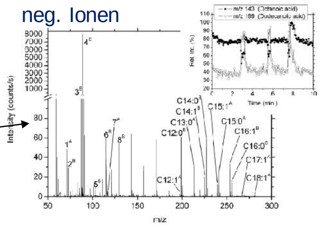
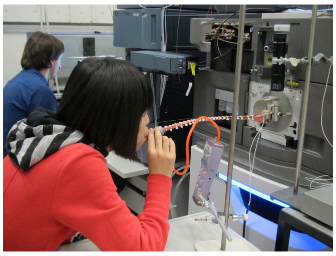


Abb. Aufbau einer einfachen SESI-Quelle (hier zur Untersuchung von der Abgabe flüchtigen Verbindungen der Haut (oben) oder in Atemluft (unten)



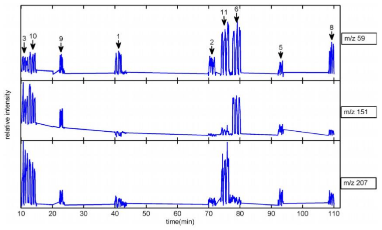


Figure 1. Real-time analysis allows for the rapid breathprinting of subjects. During the 1.5 hours experiment shown above, nine subjects breathed into the mass spectrometer. The subjects' label codes are indicated at the top of each of the three replicate measurements in the top trace. The three traces correspond to the ion intensity as a function of time for m/z 59, 151 and 207. Each subject breathed in triplicate, which is illustrated by the three steps of the signal above the background per subject. This snapshot already illustrates the high inter-subject breathprint variability.

Spektrum an chemischen Substanzen in der Atemluft eines Menschen ändert sich zwar im Tagesverlauf - dennoch beobachtet man eine individuelle Grundsignatur – einen „Atemabdruck“

⇒ personalisierte Medizin

Kohlenwasserstoffe - Analytik

The Comparative Reactivity Method (Sinha et al. 2008)

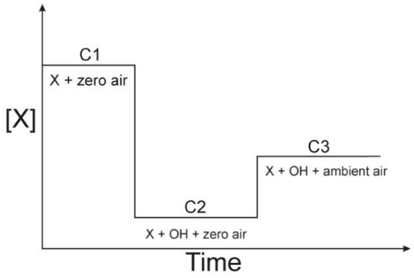


Fig. 1. Schematic illustrating concept of the Comparative Reactivity Method.

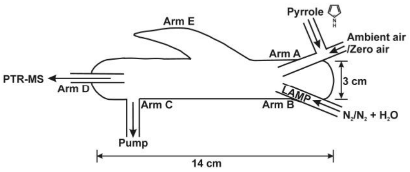


Fig. 2. Schematic of the glass reactor used in the Mainz CRM instrument.

- A reactive molecule (X), is introduced into a glass reactor and its concentration C1 is monitored with a PTR-MS, in the air exiting the reactor.

- After some time when C1 is well determined, synthetically generated OH radicals (OH<[X]) are introduced into the reactor at a constant rate to react with X. This causes C1 to decrease to C2, as X reacts with the OH radicals.

- Next, an air sample containing reactive species is introduced into the glass reactor. The various species present in ambient air then compete with X for the available OH radicals, so that the concentration of X in the air exiting the reactor increases to C3.

- Comparing the amount of X exiting the reactor without (C2) and with the ambient air (C3) allows the introduced air sample's OH reactivity to be determined in a quantitative manner, provided the system is suitably calibrated.

Kohlenwasserstoffe - Analytik

The Comparative Reactivity Method (Sinha et al. 2008)

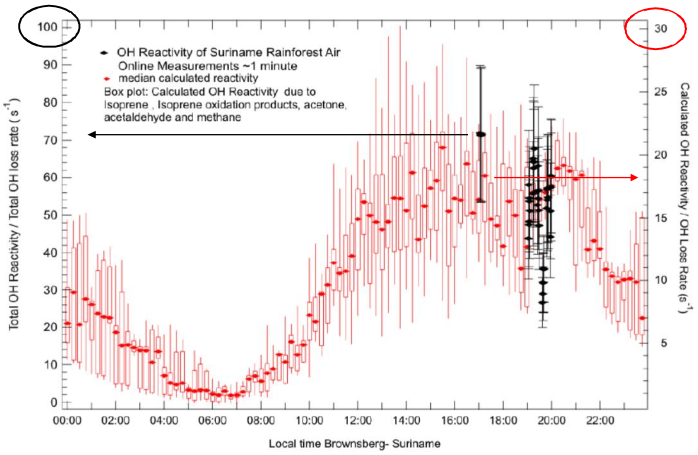


Fig. 11. Total OH reactivity measurements (black markers) of rainforest air in Brownsberg, Suriname along with diel median profile of calculated OH reactivity (red markers) due to isoprene, mvk, methacrolein , acetone and acetaldehyde), obtained during the dry season in October 2005.

Halogene in der Atmosphäre

[von Glasow and Crutzen, 2007]

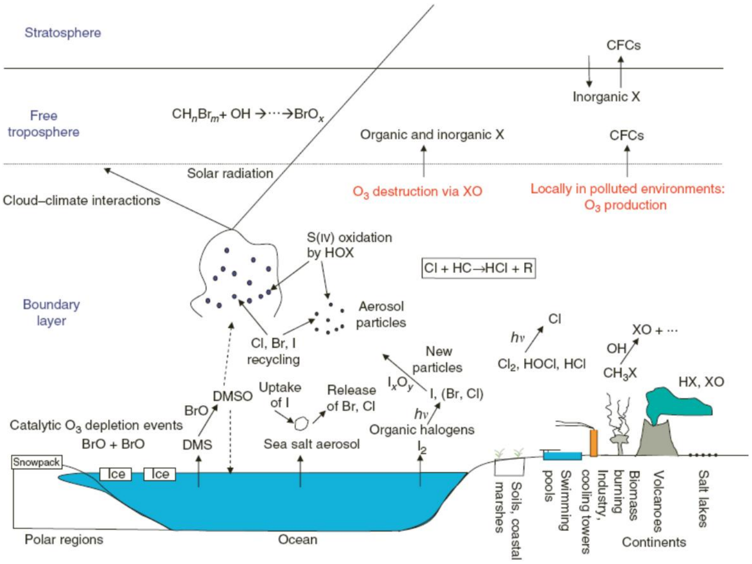


Figure 1 Schematic depiction of the most important halogen-related processes in the troposphere.

Halogene in der Atmosphäre

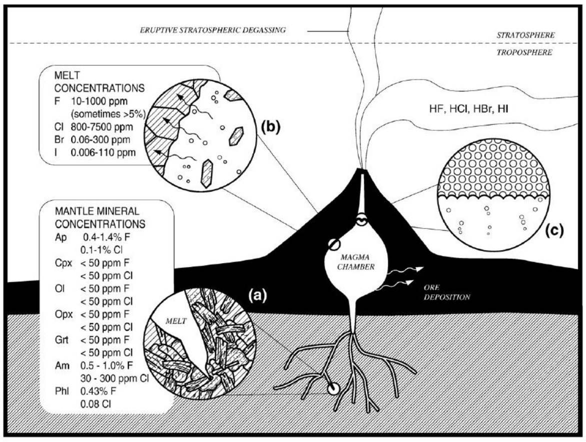


Fig. 1. Schematic diagram of halogen behaviour from melting in the mantle (inset a) to crystallization and melt inclusion entrapment (inset b) and through vesiculation and the initiation of eruption (inset c) and the injection of halogens into the atmosphere.

From: Halogens in volcanic systems, A. Aiuppa, D.R. Baker, J.D. Webster, 2009, Chemical Geology

Sources of halogens :
Deep (a) and shallow (b) sources:

a) Associated with melt generation, evolution and exsolution of vapour and/or hydrosaline fluids

b) Revolatilization of sea water or other crustal fluids; thermal decomposition of hydrothermal deposits within the volcano

Halogene in der Atmosphäre

Imposant: Der in Zentralafrika gelegene, 3500 Meter hohe Nyiragongo-Vulkan trumpft mit einem aktiven Lavasee auf.

aus: N. Bobrowski, Forschung (DFG Magazin), Feb. 2012

Halogene in der Atmosphäre

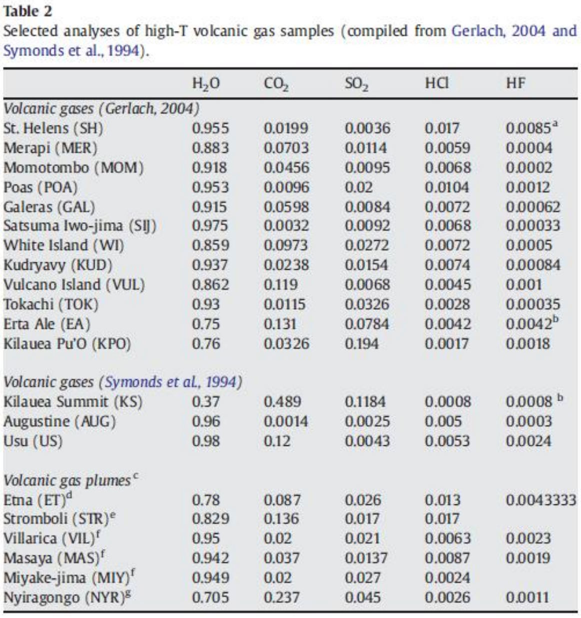


Table 2

Selected analyses of high-T volcanic gas samples (compiled from Gerlach, 2004 and Symonds et al., 1994).

	H_2O	CO_2	SO_2	HCl	HF
Volcanic gases (Gerlach, 2004)					
St. Helens (SH)	0.955	0.0199	0.0036	0.017	0.0085[a]
Merapi (MER)	0.883	0.0703	0.0114	0.0059	0.0004
Momotombo (MOM)	0.918	0.0456	0.0095	0.0068	0.0002
Poas (POA)	0.953	0.0096	0.02	0.0104	0.0012
Galeras (GAL)	0.915	0.0598	0.0084	0.0072	0.00062
Satsuma Iwo-jima (SIJ)	0.975	0.0032	0.0092	0.0068	0.00033
White Island (WI)	0.859	0.0973	0.0272	0.0072	0.0005
Kudryavy (KUD)	0.937	0.0238	0.0154	0.0074	0.00084
Vulcano Island (VUL)	0.862	0.119	0.0068	0.0045	0.001
Tokachi (TOK)	0.93	0.0115	0.0326	0.0028	0.00035
Erta Ale (EA)	0.75	0.131	0.0784	0.0042	0.0042[b]
Kilauea Pu'O (KPO)	0.76	0.0326	0.194	0.0017	0.0018
Volcanic gases (Symonds et al., 1994)					
Kilauea Summit (KS)	0.37	0.489	0.1184	0.0008	0.0008 [b]
Augustine (AUG)	0.96	0.0014	0.0025	0.005	0.0003
Usu (US)	0.98	0.12	0.0043	0.0053	0.0024
Volcanic gas plumes[c]					
Etna (ET)[d]	0.78	0.087	0.026	0.013	0.0043333
Stromboli (STR)[e]	0.829	0.136	0.017	0.017	
Villarica (VIL)[f]	0.95	0.02	0.021	0.0063	0.0023
Masaya (MAS)[f]	0.942	0.037	0.0137	0.0087	0.0019
Miyake-jima (MIY)[f]	0.949	0.02	0.027	0.0024	
Nyiragongo (NYR)[g]	0.705	0.237	0.045	0.0026	0.0011

Cl concentrations range from 0.08 to 1.7 mol% (average 0.6 mol%)

- especially HCl is emitted
- few data on Br and I
- concentrations in arc volcanoes are expected to be higher (Seawater/crustial fluid components)
- existing data indicates much higher Cl/I ratio in volcanic condensates (recycling of iodine-containing organic matter-rich sediments

Halogene in der Atmosphäre

A. Aiuppa et al. / Chemical Geology 263 (2009) 1–18 11

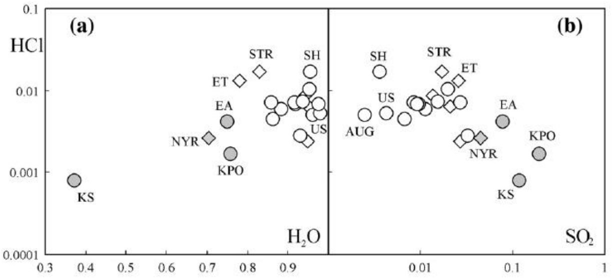


Fig. 3. Scatter plots of (a) H_2O vs. HCl concentrations (in mol%) and (b) SO_2 vs. HCl concentrations (in mol%) for the volcanic gas (circles) and volcanic gas plume (diamonds) data listed in Table 2. The contrasting gas compositions of arc (open symbols) and non-arc (filled symbols) volcanoes are evident in both diagrams.

Halogene in der Atmosphäre

- Halogen emission for global volcanic sources are poorly constrained (spread over 1-2 orders of magnitude) – relatively well constrained for SO_2 (10-14 Tg year-1) – however, large variation of the S/Cl and S/F ratio in volcanic gases makes a precise estimate based on sulfur difficult (next page)
- Further complication: volcanic gas measurements have been made at passively-degasing (quiescent) volcanoes – measurements of eruptive volcanoes are limited to the relatively mild basaltic eruptions (explosive volcanism poorly constrained)

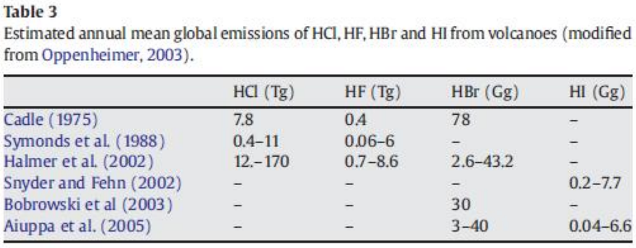


Table 3
Estimated annual mean global emissions of HCl, HF, HBr and HI from volcanoes (modified from Oppenheimer, 2003).

	HCl (Tg)	HF (Tg)	HBr (Gg)	HI (Gg)
Cadle (1975)	7.8	0.4	78	–
Symonds et al. (1988)	0.4–11	0.06–6	–	–
Halmer et al. (2002)	12.–170	0.7–8.6	2.6–43.2	–
Snyder and Fehn (2002)	–	–	–	0.2–7.7
Bobrowski et al (2003)	–	–	30	–
Aiuppa et al. (2005)	–	–	3–40	0.04–6.6

From: Halogens in volcanic systems, A. Aiuppa, D.R. Baker, J.D. Webster, 2009, Chemical Geology

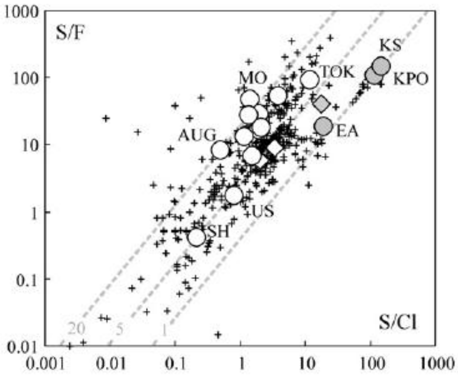


Fig. 4. S/Cl molar ratios in the volcanic gas data of Table 2 contrasted against the relative S/F molar ratios. The dashed diagonal lines indicate Cl/F ratios of 1, 5 and 20, respectively, demonstrating increasing Cl/F ratios from non-arc (filled symbols) to arc (open symbols) volcanism. For comparison, the volcanic gas data compiled by Aiuppa (2009-this issue) are also shown (crosses).

From: Halogens in volcanic systems, A. Aiuppa, D.R. Baker, J.D. Webster, 2009, Chemical Geology

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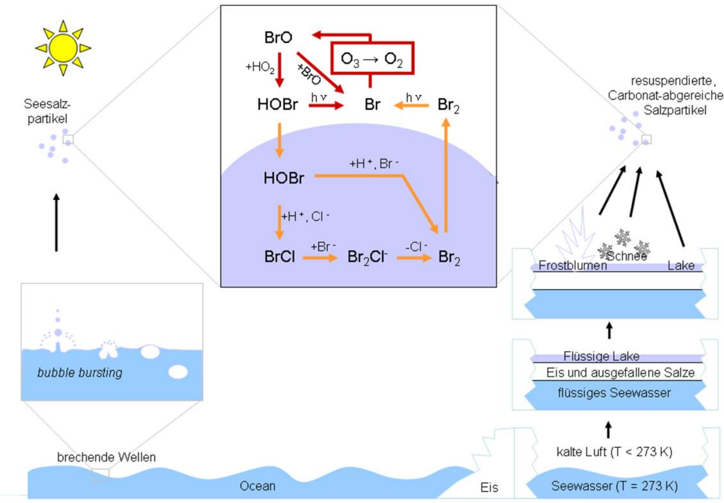
Halogene in der Atmosphäre (Halogenaktivierung aus Seesalz-Aerosol)

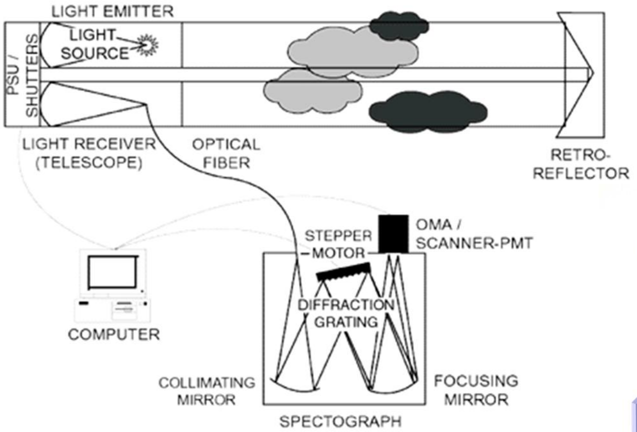


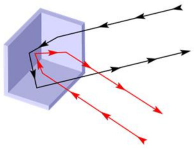
Mechanismus der Halogenaktivierung aus Seesalz-Aerosol
(links – Bildung von Seesalzpartikeln durch „bubble bursting“, rechts – Bildung von besonders effizienten, da weniger gepufferten, Carbonat-armen Salzpartikeln im polaren Frühling.

Innerer Kasten – Reaktionszyklen bei der Halogenaktivierung **(Bromexplosion)**(orange Pfeile) und dem dadurch hervorgerufenen **troposphärischen Ozonabbau** (rote Pfeile).

Halogene in der Atmosphäre - Messmethoden

DOAS (Differential Optical Absorption Spectroscopy)
(etabliertes Messverfahren für Halogene, Halogenoxide)





Halogene in der Atmosphäre - Messmethoden

DOAS (Differential Optical Absorption Spectroscopy)

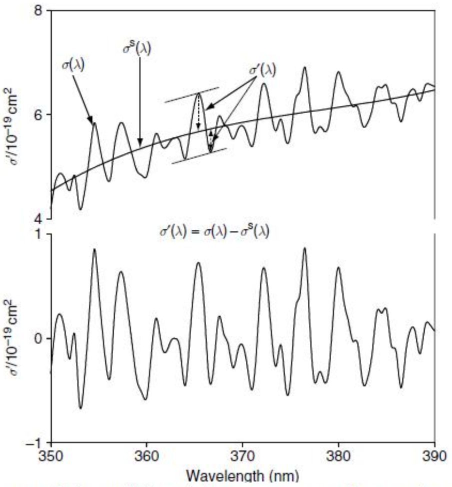


Figure 3.1 Absolute and differential absorption cross sections for NO_2 in the 350–390 nm region. In the top panel a 3rd degree polynomial (smooth line) is fitted to the absolute cross-section, $\sigma(\lambda)$, to account for the slowly varying trend of the spectrum $\sigma^s(\lambda)$. In the lower panel the differential absorption cross-section $\sigma'(\lambda)$, obtained after removing $\sigma^s(\lambda)$ is shown.

differential absorption cross section
(varies rapidly with wavelength)

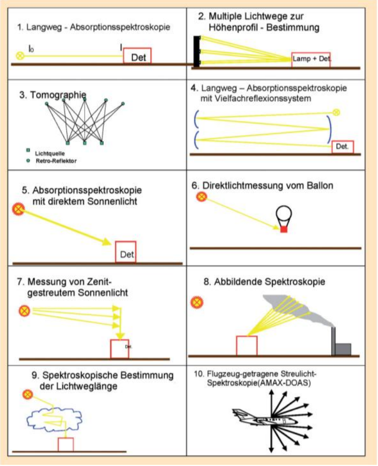
$$\sigma_i(\lambda) = \sigma_i'(\lambda) + \sigma_i^s(\lambda)$$

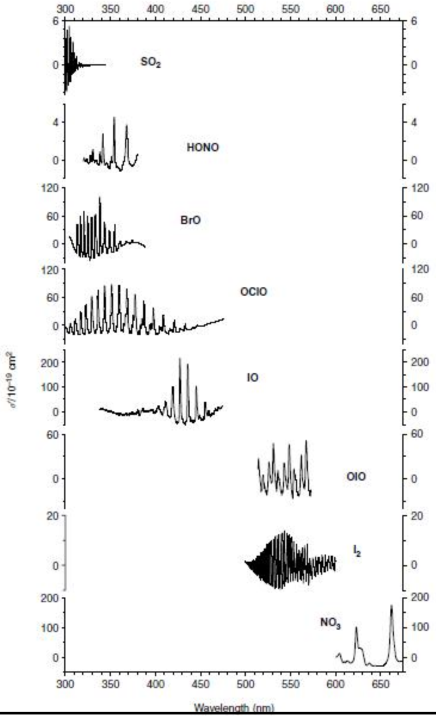
absolute cross section

slowly varying absorption cross section
(e.g. aerosols)

Halogene in der Atmosphäre
- Messmethoden

DOAS (Differential Optical Absorption Spectroscopy)





Halogene in der Atmosphäre
- Messmethoden

DOAS (Differential Optical Absorption Spectroscopy)

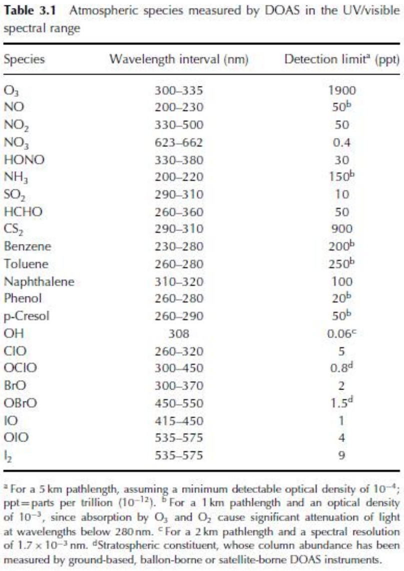


Table 3.1 Atmospheric species measured by DOAS in the UV/visible spectral range

Species	Wavelength interval (nm)	Detection limit[a] (ppt)
O_3	300–335	1900
NO	200–230	50[b]
NO_2	330–500	50
NO_3	623–662	0.4
HONO	330–380	30
NH_3	200–220	150[b]
SO_2	290–310	10
HCHO	260–360	50
CS_2	290–310	900
Benzene	230–280	200[b]
Toluene	260–280	250[b]
Naphthalene	310–320	100
Phenol	260–280	20[b]
p-Cresol	260–290	50[b]
OH	308	0.06[c]
ClO	260–320	5
OClO	300–450	0.8[d]
BrO	300–370	2
OBrO	450–550	1.5[d]
IO	415–450	1
OIO	535–575	4
I_2	535–575	9

[a] For a 5 km pathlength, assuming a minimum detectable optical density of 10^{-4}; ppt = parts per trillion (10^{-12}). [b] For a 1 km pathlength and an optical density of 10^{-3}, since absorption by O_3 and O_2 cause significant attenuation of light at wavelengths below 280 nm. [c] For a 2 km pathlength and a spectral resolution of 1.7×10^{-3} nm. [d] Stratospheric constituent, whose column abundance has been measured by ground-based, ballon-borne or satellite-borne DOAS instruments.

Halogene in der Atmosphäre - Messmethoden

DOAS (Differential Optical Absorption Spectroscopy)

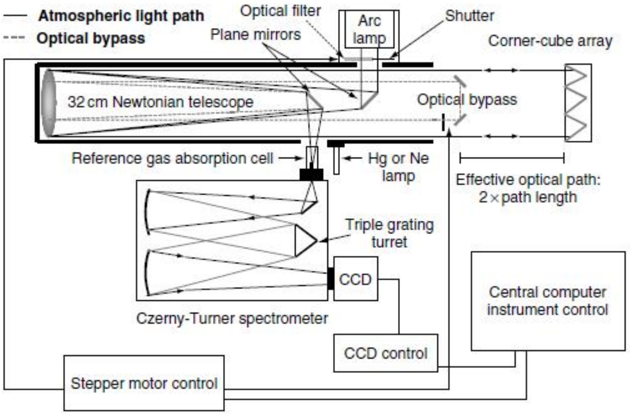
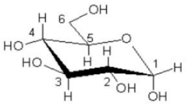


Figure 3.3 Schematic diagram of a coaxial LP-DOAS instrument where a single telescope houses both the transmitting and receiving optics, and the light beam is folded back by an array of corner cube reflectors.

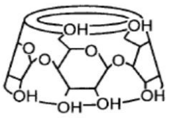
further reading: Dwayne Heard, Analytical Techniques for Atmospheric Measurements
Blackwell Publishing, 2006.

Halogene in der Atmosphäre - Messmethoden

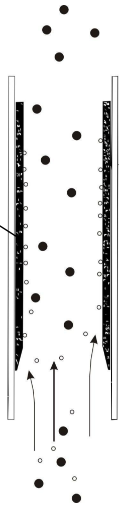
Sampling of molecular iodine using an cyclodextrin coated diffusion denuder

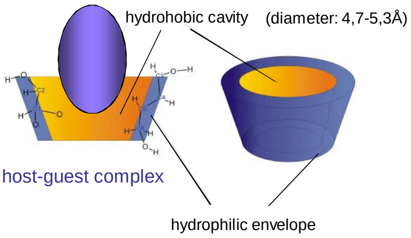


α-D-glucose molecule



α-cyclodextrin

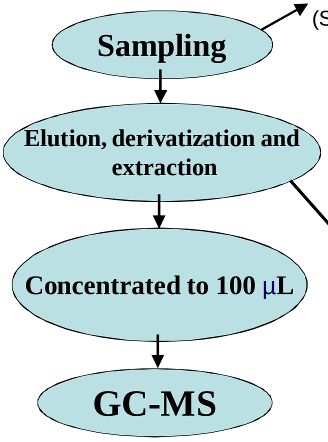




Halogene in der Atmosphäre - Messmethoden

Sample preparation and analysis

addition of Iodide-129 standard solution (SRM 4949C) $^{127}I/^{129}I$ ratio of **0.17**

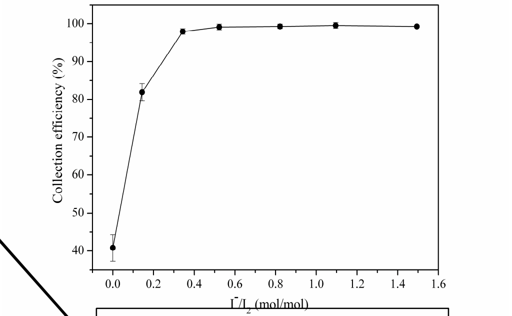


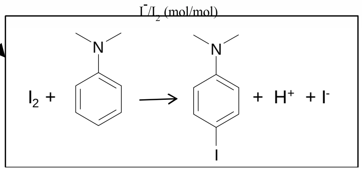
Sampling

Elution, derivatization and extraction

Concentrated to 100 µL

GC-MS

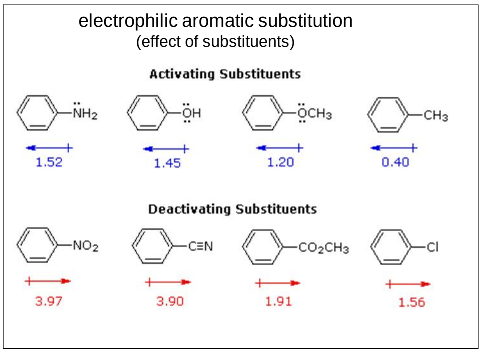




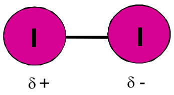
[Huang and Hoffmann, 2009]

Halogene in der Atmosphäre - Messmethoden

Sampling of molecular iodine using an cyclodextrin coated diffusion denuder

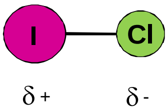


electrophilic aromatic substitution
(effect of substituents)



molecular iodine

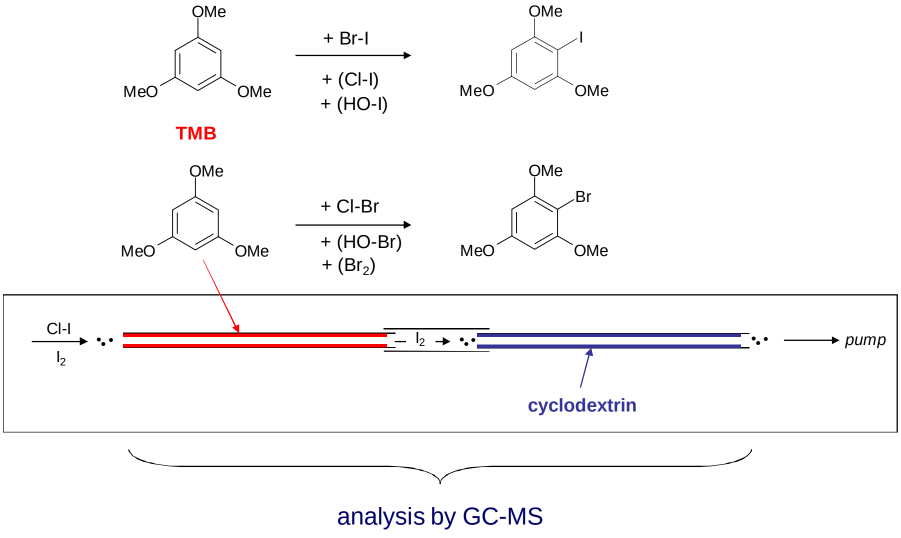
Iodine shows a much higher reactivity
towards electrophilic attack
to organic molecules



positively polarized
iodine (interhalogens,
HOI, $IONO_2$)

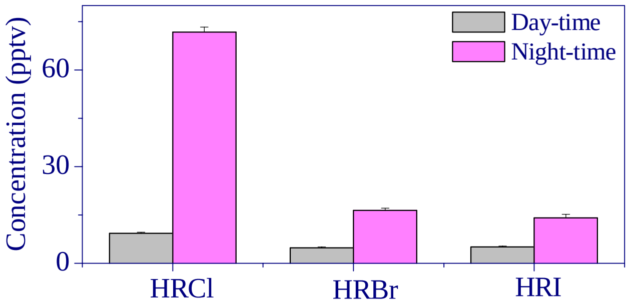
Halogene in der Atmosphäre - Messmethoden

Selective preconcentration of iodine compounds with a positively polarized iodine atom



Halogene in der Atmosphäre - Messmethoden

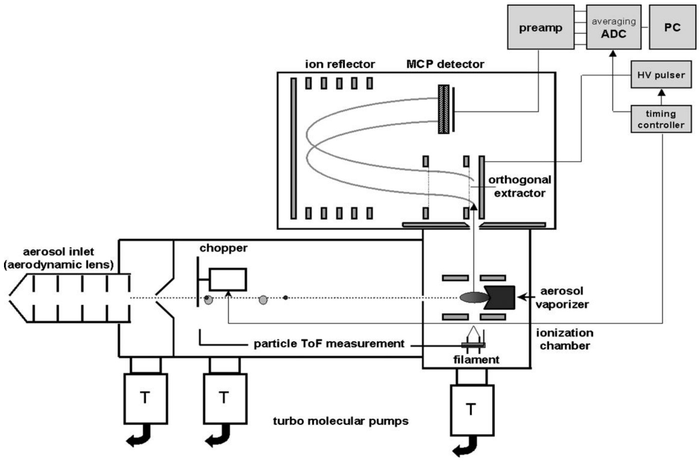
Field measurements at the west coast of Ireland - results



Currently: analysis of samples from measurements of the British Antartic Survey (Helen Atkinson)

Halogene in der Atmosphäre - Messmethoden

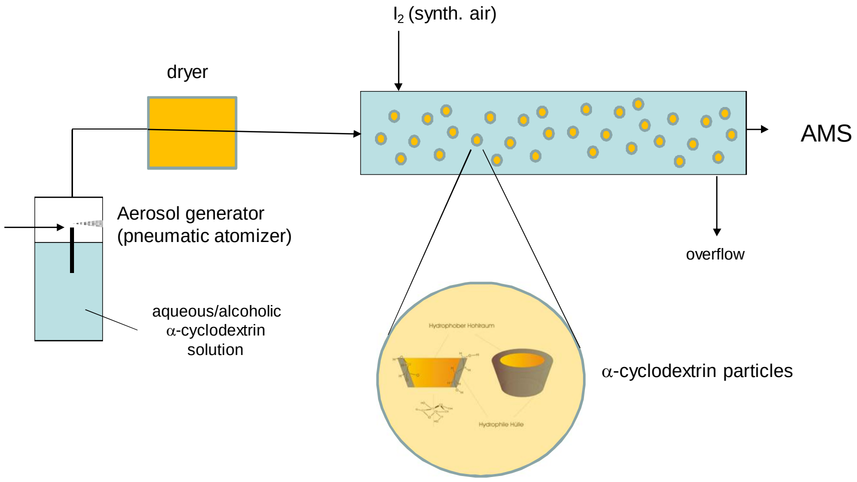
AerodyneTime-of-flight AMS



[Drewnick et al., 2007]

Halogene in der Atmosphäre - Messmethoden

Iodine sampling by selective uptake into cyclodextrin particles

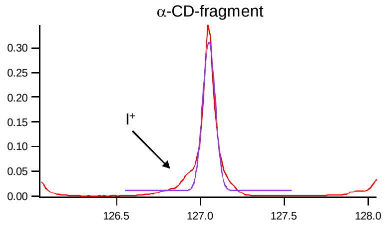


Halogene in der Atmosphäre - Messmethoden

AMS data evaluation

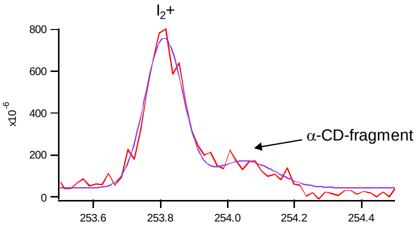
m/z 127

m/z 126.9 → I^+
m/z 127.05 → α-CD-fragment



m/z 254

m/z 253.8 → I_2^+
m/z=254.05 → α-CD-fragment

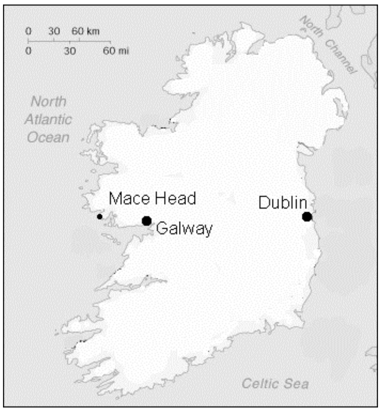


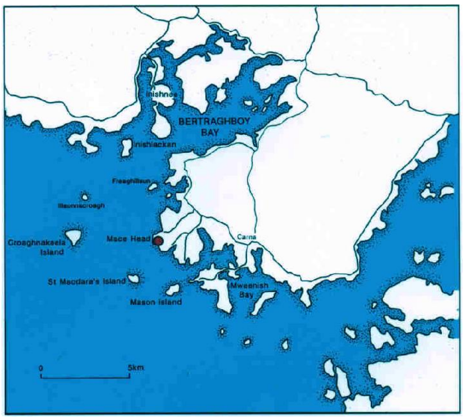
Halogene in der Atmosphäre – eine Fallstudie

Quantification of Aerosol Nucleation in the
European Boundary Layer

QUEST / BIOFLUX / NAMBLEX

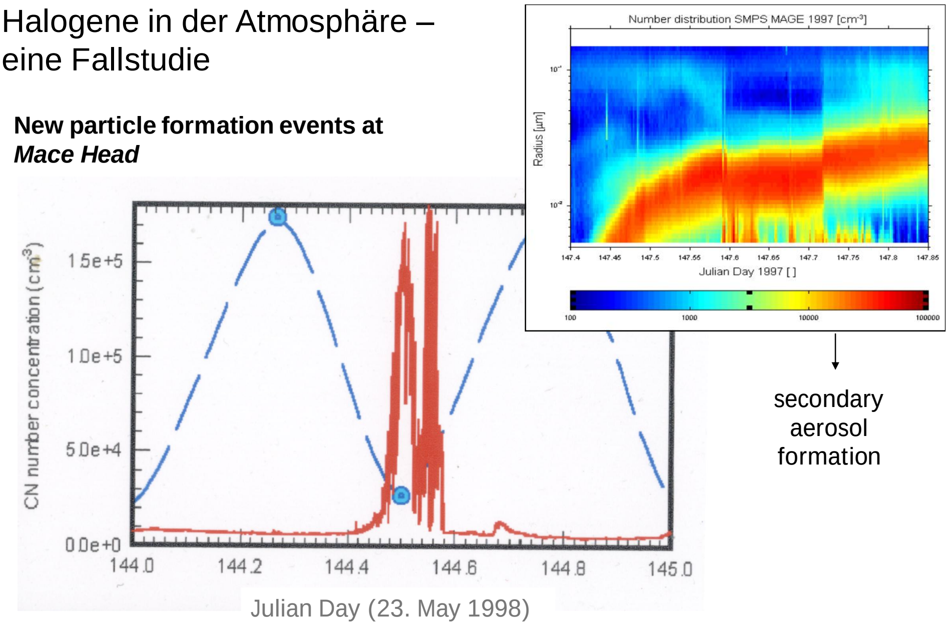
Research station *Mace Head*





Halogene in der Atmosphäre – eine Fallstudie

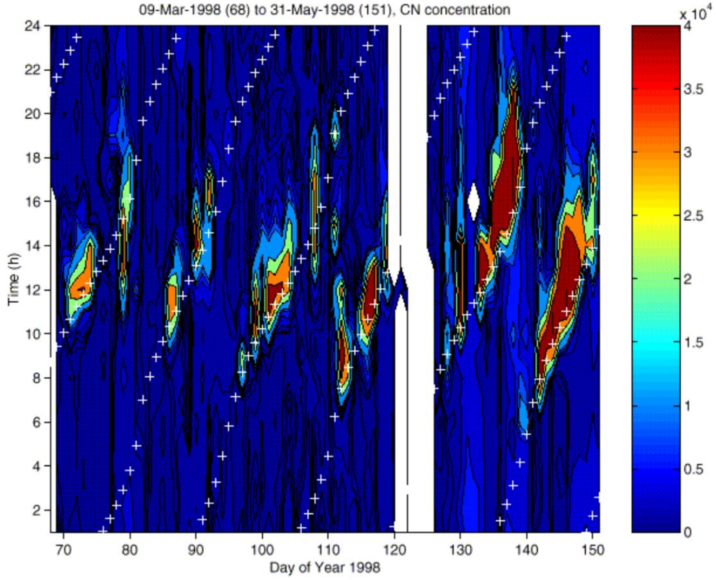
New particle formation events at *Mace Head*



secondary
aerosol
formation

Halogene in der Atmosphäre – eine Fallstudie

New particle formation events at Mace Head over a period of 3 month



Halogene in der Atmosphäre – eine Fallstudie

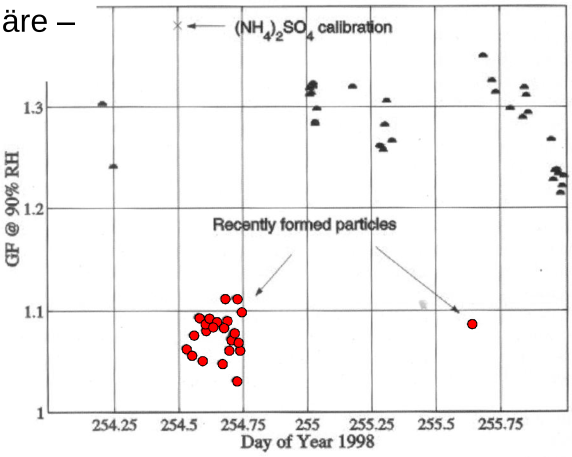
Formation of nanometer particles
⇒ secondary aerosol formation

Events during low tide <u>and</u> daylight
⇒ release of precursors from shore biota ?
(light induced emission or photochemistry)

What are the precursors ?

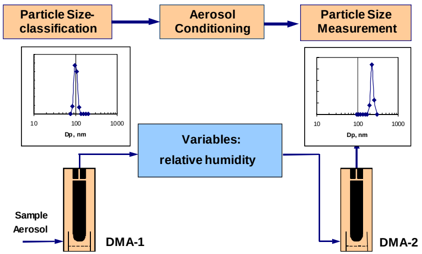
Dimethylsulphide ⇒ chemistry too slow
Organic precursors ⇒ ???
(e.g. sesquiterpenes ???)

Halogene in der Atmosphäre – eine Fallstudie



[Väkelä et al., *JGR*, 2002]

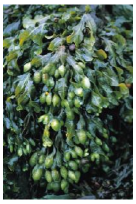
Investigation of the hygroscopicity of the freshly formed particles



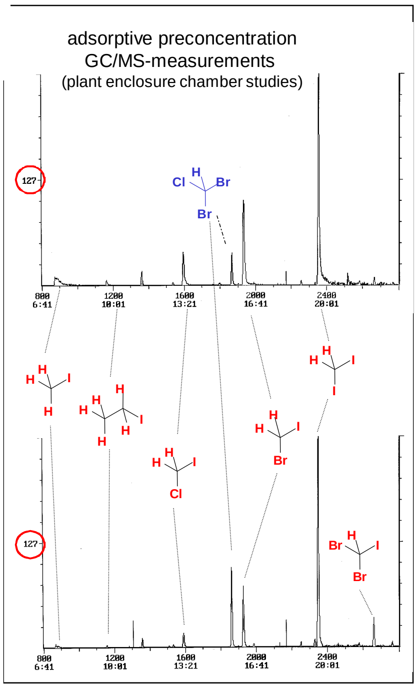
observation:
⇒ low hygroscopicity of the nanometer particles
⇒ no sulphate particles !
⇒ organic aerosol particles?

Halogene in der Atmosphäre – eine Fallstudie

Fucus vesiculosus



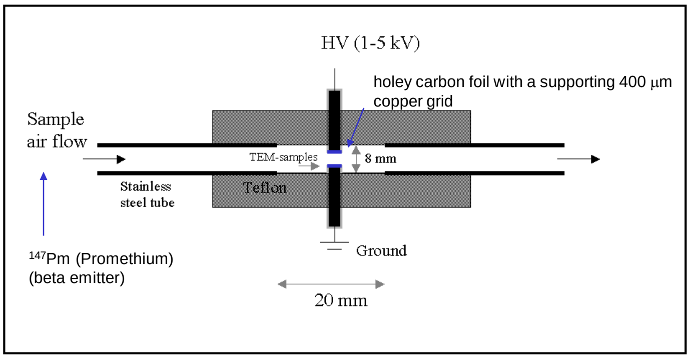
Fucus spiralis



adsorptive preconcentration
GC/MS-measurements
(plant enclosure chamber studies)

Halogene in der Atmosphäre – eine Fallstudie

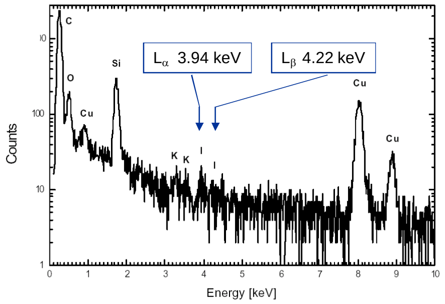
Sampling of nanometer particles
(electrostatic precipitation (based on Cheng et al. 1981))

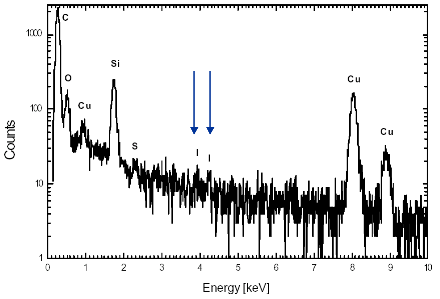


Halogene in der Atmosphäre – eine Fallstudie

EDX spectra of ultrafine particles (sampled during the nucleation events at Mace Head)

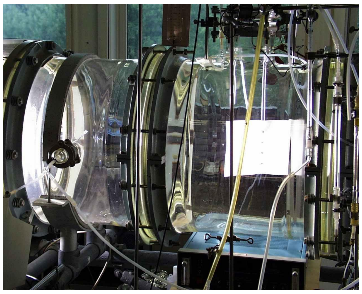
ca. 10 nm particles with signals from iodine and potassium





ca. 7-8 nm particles with signals from iodine ans sulphur

[Mäkelä et al., *JGR*, 2001]



Halogene in der Atmosphäre – eine Fallstudie

Laboratory experiments of the particle formation potential of iodomethanes and of the chemical composition of the particles formed

⇒ high melting point
  (low vapour pressure)
⇒ low solubility

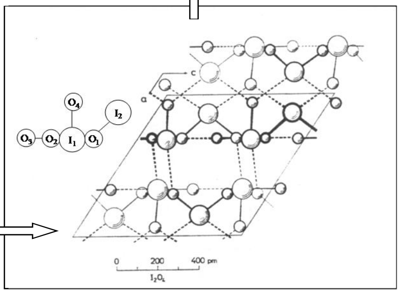
$CH_2I_2 + h\nu \rightarrow I + CH_2I$

$I + O_3 \rightarrow IO + O_2$

$IO + IO \rightarrow OIO + I$

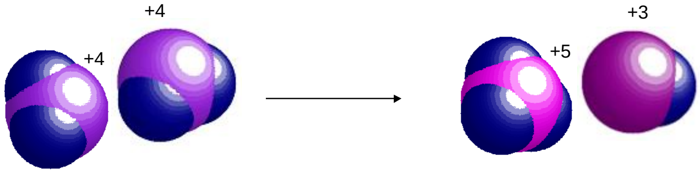
$OIO + OIO \rightarrow I_2O_4$ (oder $[IO]^+[IO_3]^-$)

$I_2O_4 + n\,OIO \rightarrow [\text{-I-O-IO}_2\text{-O-}]_{1+n/2}$



[Hoffmann et al., *GRL*, 2001]

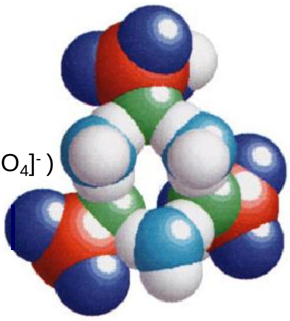
Molecular properties of iodine oxides



$\text{OIO} \quad \text{OIO} \longrightarrow [\text{IO}_3]^- \cdot [\text{IO}]^+$

- ⇒ when two OIO molecules collide and form an ion pair, the dipole moment is drastically increased
- ⇒ more monomers are attracted

- ⇒ Ion pair formation ⇒ faster growth and stabilisation of the cluster

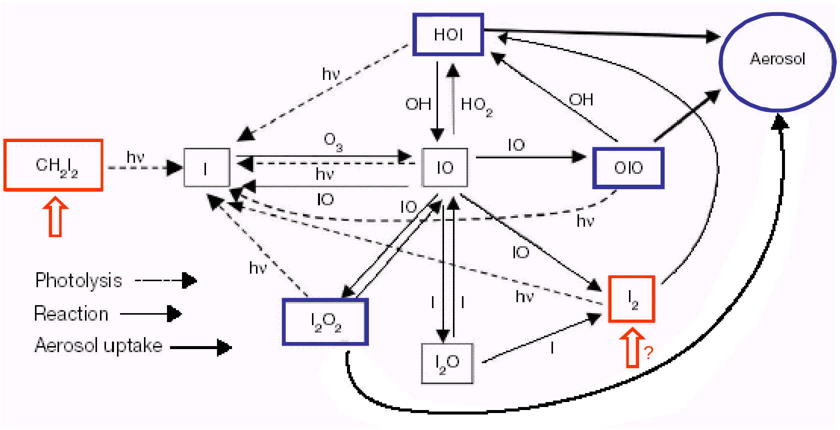


$H_2O + H_2SO_4 \longrightarrow n \cdot ([H_3O]^+ \cdot [HSO_4]^-)$

Tammet & Kulmala, 2005
Kusaka, Wang & Seinfeld, 1998

Halogene in der Atmosphäre – eine Fallstudie

Iodine chemistry in coastal areas



[O‘Dowd et al., *Nature*, 2002]

Halogene in der Atmosphäre – eine Fallstudie

Already in the 1890's John Aitken observed high particle concentrations at the west coast of Scotland during sunny conditions ("*sun-formed nuclei*")

(Aitken 1897 *Trans. R. Soc. Edinburgh)*

He also noticed:

"… that these high concentrations were not accompanied by a reduction in visibility, suggesting either that the plumes were so thin as not to have any transparency effects, or the particles were so small that they did not effectively scatter sunshine."

(Aitken 1911 *Proc. R. Soc. Edinburgh)*

Aitken already speculated

"… that chlorine, iodine or sulphur are involved in particle formation"

Halogene in der Atmosphäre – eine Fallstudie

"I feel that an apology is due for presenting this paper. The subject is an uninteresting one to most people, and I have to admit that its presentation is badly focused and gives a hazy impression. If it had not been for the discovery of the origin of the sun-formed nuclei at Kingairloch, the work would not have been done. Perhaps the difficulty of experimenting on a subject in such extremely small quantities of matter that produce such marked effects, and the varied nature of the contents of the paper may be some excuse for these effects."

Halogene in der Atmosphäre – eine Fallstudie

Some hypothetical mechanisms about the volatilisation of molecular iodine:

A) Macroalgae exposed to air (low tide) ⇒ oxidative stress
⇒ haloperoxidase-mediated oxidation of iodine:

$$I^- + H_2O_2 \rightarrow HOI + OH^-$$
$$HOI + I^- + H^+ \rightarrow I_2\uparrow + H_2O$$

McFiggans et al. **2004**, *ACPD*

B) Direct photochemical oxidation (sea-air interface)

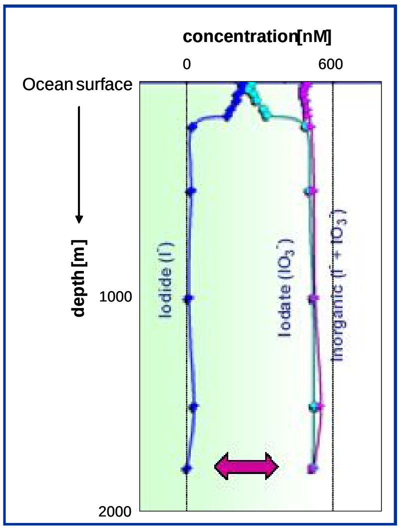
$$2\,I^- + 0.5\,O_2 + H_2O + h\nu \rightarrow I_2\uparrow + 2\,OH^-$$

Miyake and Tsunogai **1963**, *J. Geophys. Res.*

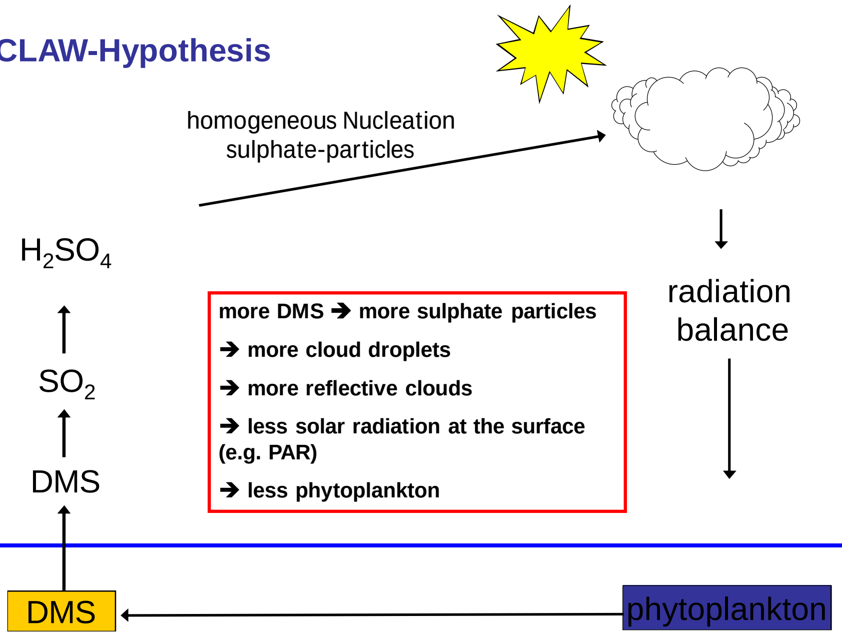
C) Direct oxidation by ozone (sea-air interface)

$$2\,I^- + O_3 + 2H^+ \rightarrow I_2\uparrow + O_2 + H_2O$$

Garland and Curtis **1981**, *J. Geophys. Res.*



CLAW-Hypothesis



more DMS ➔ more sulphate particles

➔ more cloud droplets

➔ more reflective clouds

➔ less solar radiation at the surface (e.g. PAR)

➔ less phytoplankton

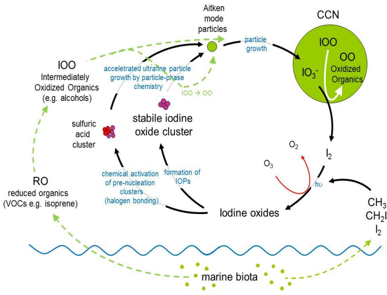
Charlson et al., Nature 1987

JOHANNES GUTENBERG
UNIVERSITÄT MAINZ

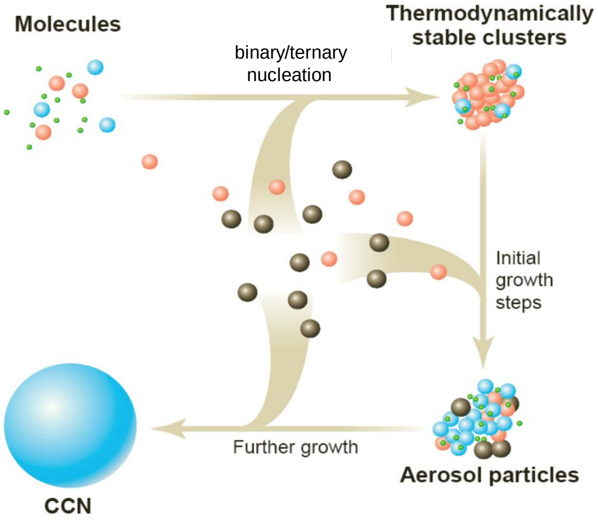
Atmospheric Cycling of Iodine and New Particle Formation in the Marine Atmosphere

A few experiments and a collection of hypotheses

Ru-Jin Huang
Michael Kundel
Ute Thorenz
Christopher Kampf
Thorsten Hoffmann



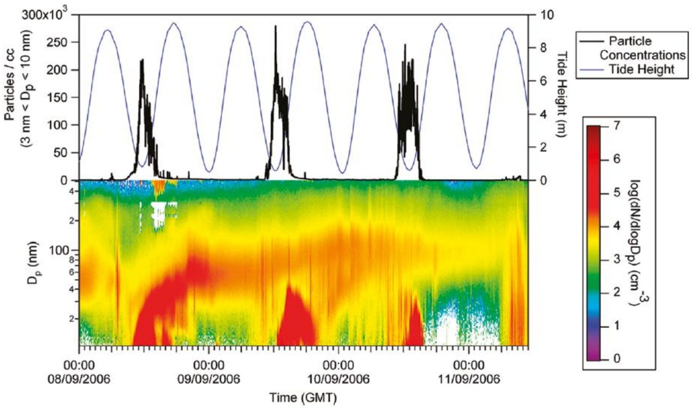
Concepts to explain atmospheric new particle formation

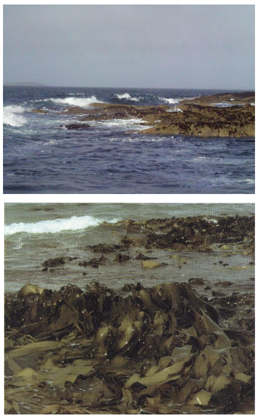


Markku Kulmala, How Particles Nucleate and Grow, Science, 2003, VOL 302, 1000-1001

Field observations – European coastal sites

Reactive Halogens in the Marine Boundary Layer (RHaMBLe)
Roscoff (North West coast of France) coastal study





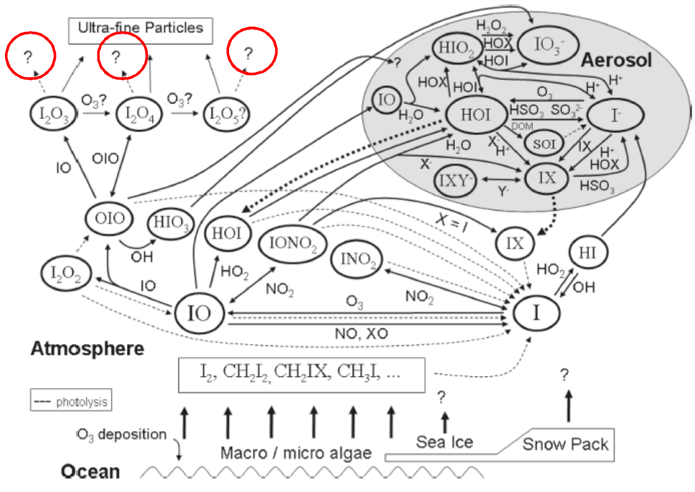
⇒ iodine-mediated coastal particle formation is an evident mechanism (Mace Head, Roscoff)

⇒ the events show a very strong daytime low tide signature, entirely consistent with the emission of iodine by macroalgal species

McFiggans et al., ACP, 2010

Motivation

JG|U
JOHANNES GUTENBERG UNIVERSITÄT MAINZ

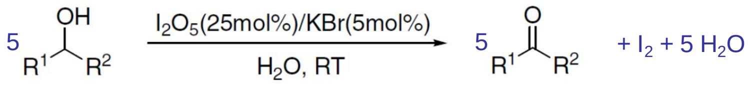


⇒ What is the fate of the iodine oxides in the particles ?

Iodine oxides in organic synthesis

I_2O_5: mild and efficient reagents for the oxidation of alcohols in water

Z.-Q. Liu et al. / Tetrahedron Letters 48 (2007) 3017–3019

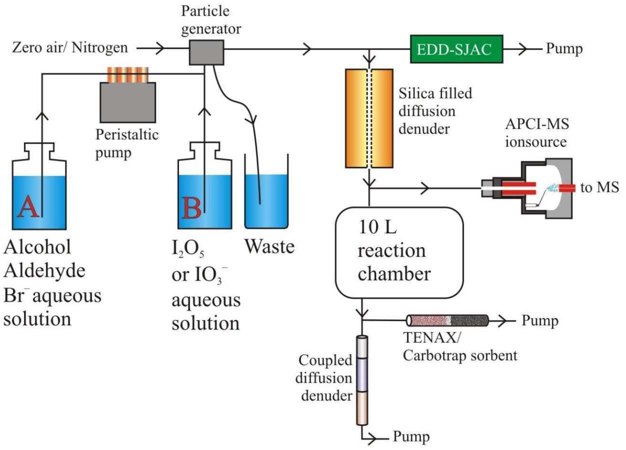


2 HIO_3 + 5 R-C(OH)H-R → 5 R-CO-R + I_2 + 6 H_2O — alcohols → carbonyls

2 HIO_3 + 5 R-CHO → 5 R-COOH + I_2 + H_2O — aldehydes → acids

---

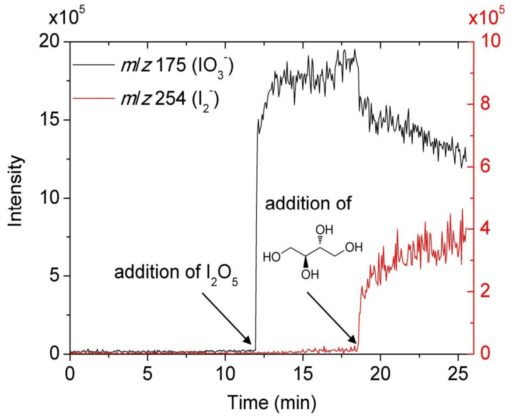
Experimental Setup



Schematic diagram of the experiment setup.

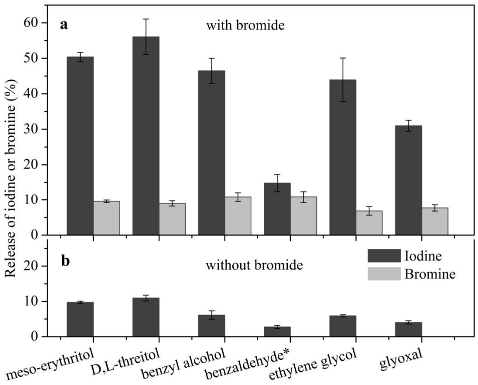
Rapid reduction of I_2O_5 by alcohols

Reduction of I_2O_5 by alcohols in laboratory-generated particles (APCI–MS - negative ion mode)



⇒ Molecular iodine (I_2) is formed immediately in the particles (rapid increase of m/z 254 (I_2^-) - decrease of m/z 175 (IO_3^-))

Comparison of different organics (alcohols/carbonyls)

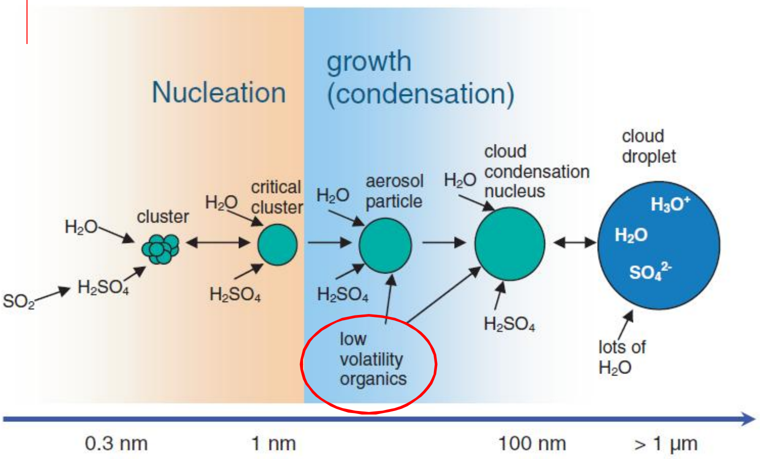


molar ratio studied was organic (100) : (Br− (30) :) I2O5 (1) and the particle pH was ~3.

⇒ both aromatic and aliphatic alcohols can be oxidized by I_2O_5 and aldehydes can be further oxidized (to form carboxylic acids (e.g. oxalic acid from glyoxal))

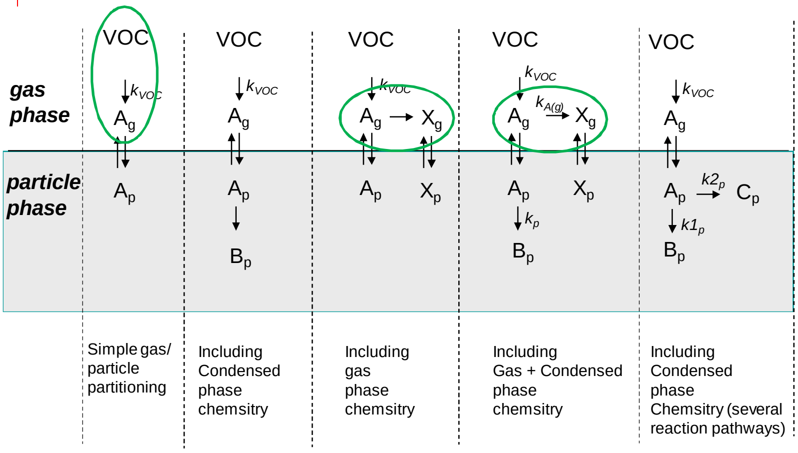
⇒ this oxidation will influence the volatility of the condensing organics

Schematic representation of the nucleation and subsequent growth process for atmospheric binary homogeneous nucleation



Curtius **2009** Eur. Phys. J. Conferences

Modelling the chemistry of SOA components



Simple gas/ particle partitioning

Including Condensed phase chemsitry

Including gas phase chemsitry

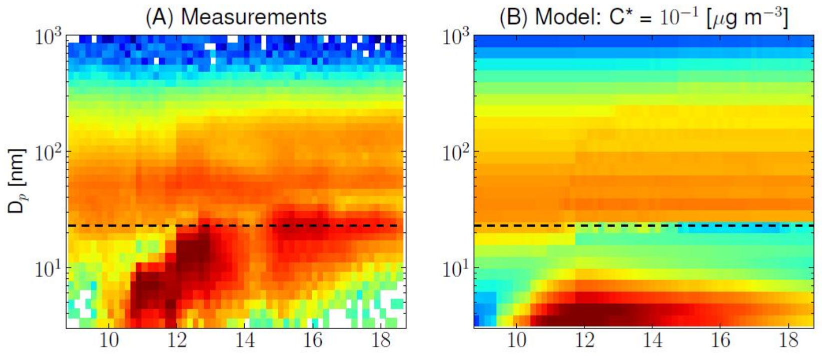
Including Gas + Condensed phase chemsitry

Including Condensed phase Chemsitry (several reaction pathways)

(modified based on Kroll et al. 2007)

Incorporation of gas phase chemistry into models

Comparison of model-predicted growth of nucleated aerosol to measurements (boreal forest)



Pierce et al., ACP, 2011, Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events

⇒ pure gas phase chemistry has difficulties to explain ultrafine particle growth

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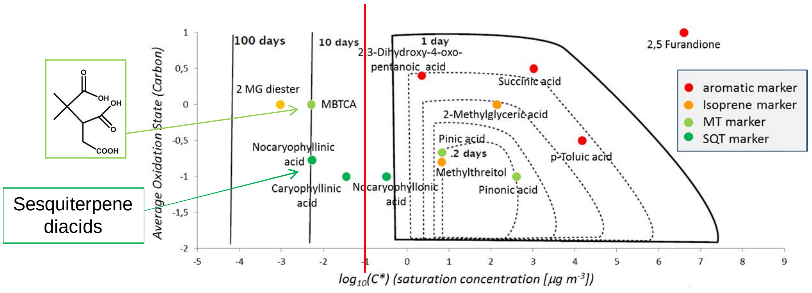
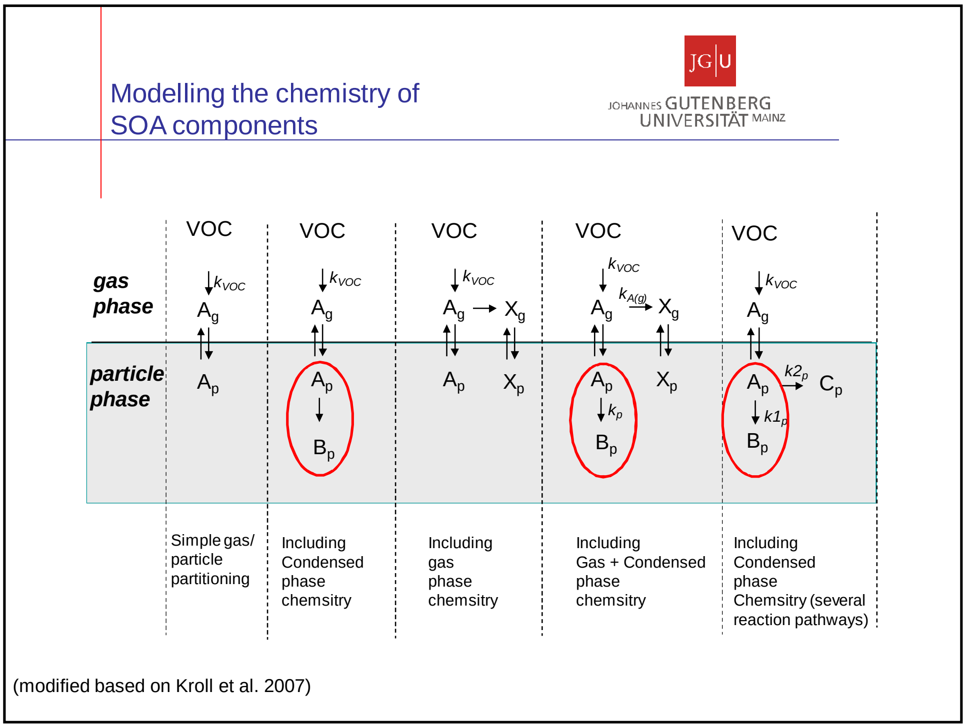
Incorporation of gas phase chemistry into models

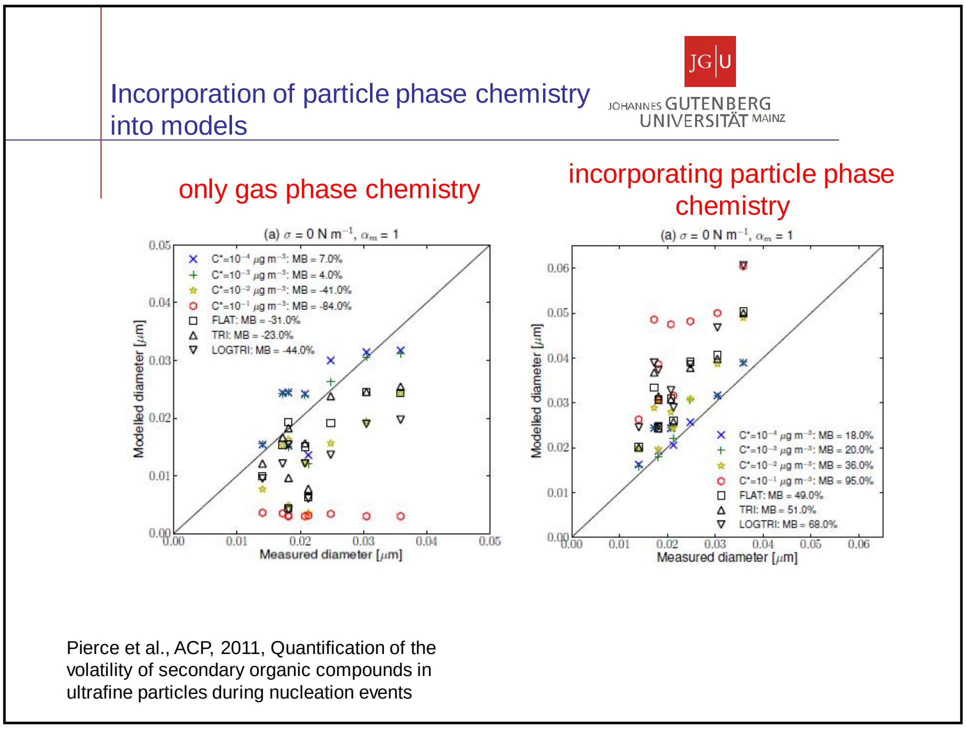


Sesquiterpene diacids



Modelling the chemistry of SOA components

(modified based on Kroll et al. 2007)



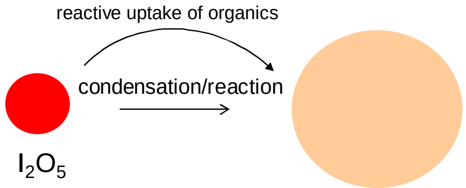
Incorporation of particle phase chemistry into models

only gas phase chemistry

incorporating particle phase chemistry

Pierce et al., ACP, 2011, Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events

Incorporation of particle phase chemistry into models



- ⇒ particle-phase chemistry in ultrafine particles can be more effective for growing the ultrafine particles than when the low-volatility SOA is formed in the gas phase
- ⇒ this accelerated growth of ultrafine particles only occurs if the composition of ultrafine particles makes particle-phase chemistry more favorable in these particles than larger particles

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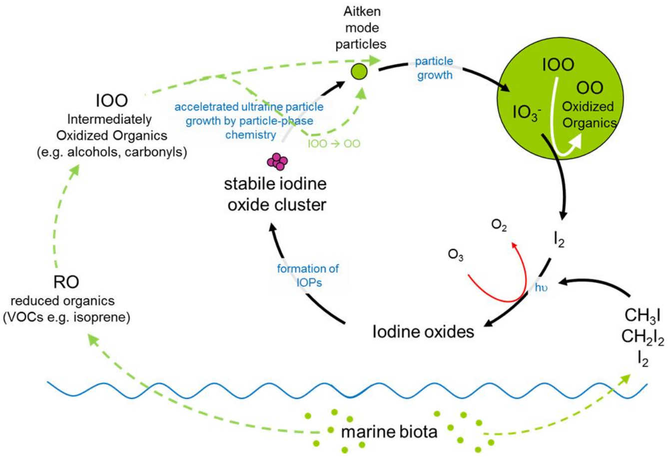
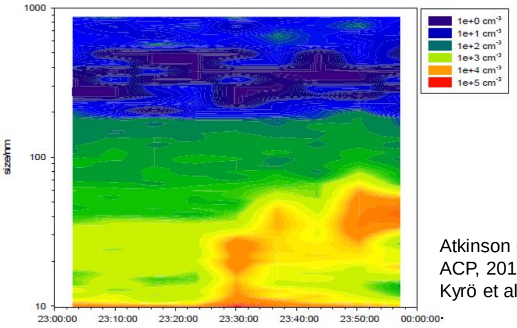
Atmospheric Iodine Recycling Hypothesis I



The atmospheric cycling of iodine and possible connection to the formation of new particles in the marine boundary layer.

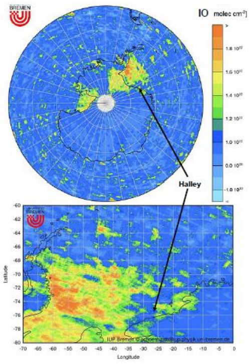
Field observations – Polar regions



Atkinson et al., ACP, 2012
Kyrö et al., ACP, 2013

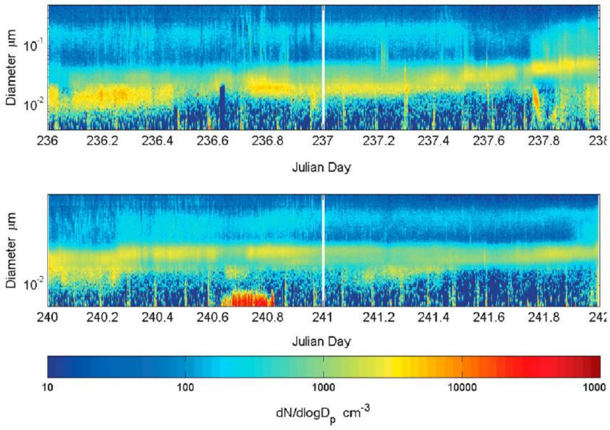
Particle number size distribution (cm^{-3}), showing new particle formation the ship broke through the sea ice of the Weddell Sea on 13 February 2009.

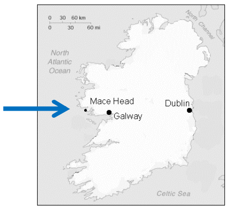
- ⇒ Weddell Sea is an iodine hotspot
- ⇒ Indications that also here particle formation is strongly linked with iodine chemistry
- ⇒ New particle formation are also common in the Artic summer (Tunved et al., ACP, 2013)



Average IO vertical column densities over Antarctica measured by satellite from 25 January to 7 March 2009. The highest amounts of IO are observed over the ice covered Weddell Sea.

Field Observations – Open Ocean Nucleation





On the occurrence of open ocean particle production and growth events
O'Dowd et al., Geophys. Res. Lett., 2010

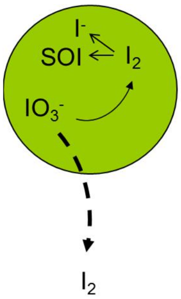
- ⇒ report events during which a recently-formed nucleation mode (~15 nm diameter) is detected and is observed to grow into an Aitken mode (~50 nm diameter) over periods up to 48 hours
- ⇒ A growth rate of 0.8 nm hour^{-1} is estimated in a typical case study, pointing to a source region ~700 km off-shore

Field Observations
Iodine speciation in the particle phase

Current models of iodine chemistry predict that IO_3^- is the dominant Iodine species in the particle phase

In contrast, field measurements show that I^- or organic iodine compounds are often more abundant (in fact IO_3^- can partly not even be measured (Baker, 2004))

However, the molecular iodine formed from the reduction by organics might also hydrolyse in the particle phase:



$I_2 + H_2O \longrightarrow HOI + I^- + H^+$

shifts the I^-/ IO_3^- -ratio towards higher iodide concentrations as observed in the field measurements

HOI + condensed phase organics ⟶ Organic iodine compounds (SOI)

⇒ Consequently, the consideration of the condensed phase chemistry reduce the existing discrepancies between measured and modeled particulate inorganic and organic iodine

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Formation of IOP as a function of IO

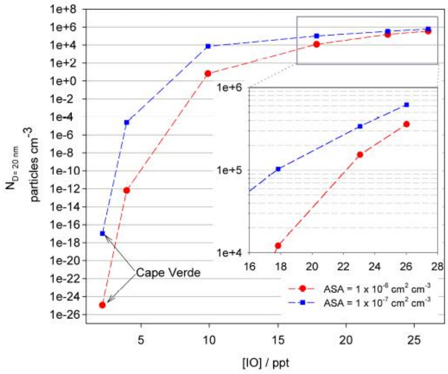

Fig. 7. The number of potential CCN formed at 10 m after 24 h, as a function of the mean daytime IO mixing ratio at 10 m. The [IO] is changed by altering the sea-to-air flux of I_2 species in addition to the halocarbon flux as mentioned in Sect. 4.2. Two cases are illustrated in the figure to show the sensitivity to the background aerosol surface area (ASA), which is set to a typical remote MBL value of 1×10^{-6} cm^2 cm^{-3} (red) or an ultra-clean value of 1×10^{-7} cm^2 cm^{-3} (blue).

⇒ New particle formation only by nucleation of iodine oxides (IOP formation) in the open ocean is probably not significant

Mahajan et al., ACP, 2010

Dipole moments of halogen oxides

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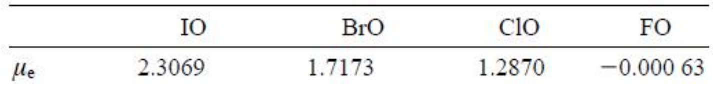
Comparison of Electric Dipole Moments (D) of XO



	IO	BrO	ClO	FO
μ_e	2.3069	1.7173	1.2870	−0.000 63

McGrath and Rowland, J. Phys. Chem., 1996

⇒ especially IO possesses a large dipole moment and a positively polarized halogen atom which can act as an acceptor of electron density

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Hydrogen-Bonding Interaction in Molecular Complexes

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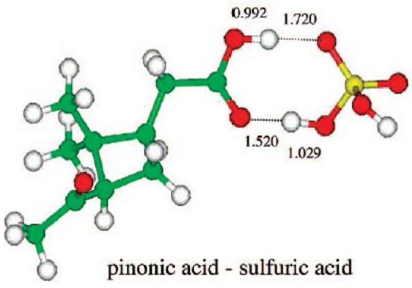


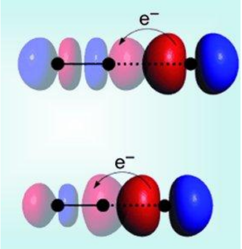
pinonic acid - sulfuric acid

⇒ the driving forces for the formation of atmospheric molecular complexes are hydrogen bonds between the participating species (e.g. sulfuric acid, water, ammonia, and organics), whose strength determines their thermodynamic stability

Jun Zhao, Alexei Khalizov, Renyi Zhang, and Robert McGraw, J. Phys. Chem. A, 2009,

Halogen bonding (XB)

Halogen bonding (XB) is the non-covalent interaction that occurs between a halogen atom (Lewis acid – electron acceptor) and a Lewis base (electron donator)



Halogen bonding: D ··· X-A

Hydrogen bonding: D ··· H-A

In both cases, D (donor) is the atom, group, or molecule that is electron rich and donates them to the electron poor species (H or X). A (acceptor) is the electron poor species withdrawing the electron density from H or X, accordingly.

Halogens participating in halogen bonding include: iodine (I), bromine (Br), chlorine (Cl), and sometimes fluorine (F). All four halogens are capable of acting as XB donors (as proven through theoretical and experimental data) and follow the general trend: F < Cl < Br < I, with iodine normally forming the strongest interactions

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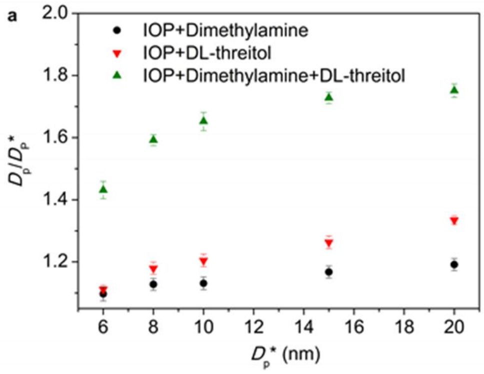
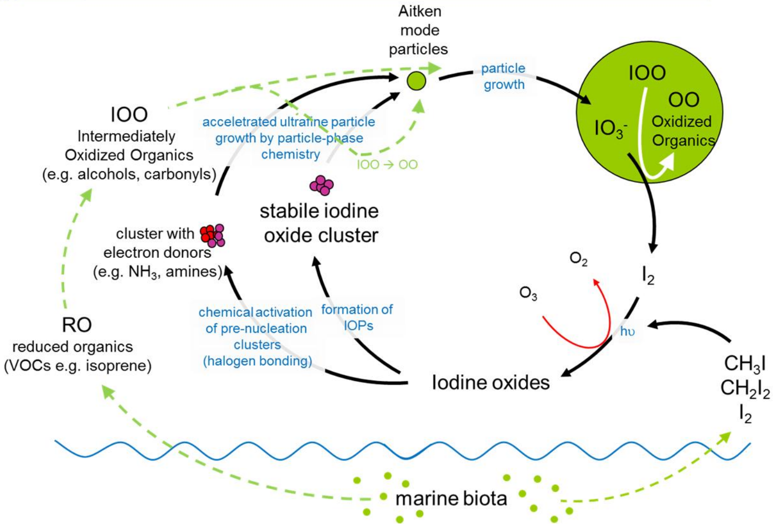
Growth experiments with IOP Nanoparticles (in cooperation with Renyi Zhang)



⇒ Especially the presence of amines plus a semivolatile VOC that can be oxidized by IOPs are <u>accelerating</u> the growth of nanometer particles (formation of organic acids -> alkylaminium salts -> uptake of water ?)

⇒ IOPs, organics and amines act synergistically

Atmospheric Iodine Recycling Hypothesis II



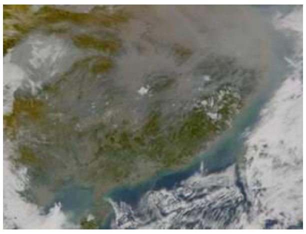
The atmospheric cycling of iodine and possible connection to the formation of new particles in the marine boundary layer.

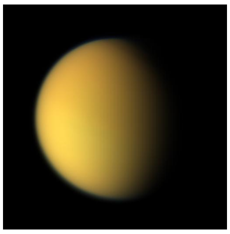
Conclusions

- Iodine (like other elements involved in particle formation e.g. Sulfur, Carbon) is released in the reduced form (or an intermediate oxidation state) into the atmosphere (essentially biogenic sources) and than oxidized in the troposphere to low-volatile species (usually acids – HIO_3, H_2SO_4, carboxylic acids)
- However, in contrast to other elements iodate is not an inert end product which is stable in the particle phase, iodate can be readily reduced by other naturally occurring substances (e.g. SOA components) and the iodine recycled back into the gas phase
- The concurrent oxidation of the condensing organics will likely result in an accelerated growth of the particles – increasing their survival probability
- Since the regenerated reactive element can also play a role in new particle formation, iodine might act like a chemical activator for particle formation in the marine atmosphere (polar regions?)
- The iodine recycling from the particle phase might also be relevant for the transport of iodine in the atmosphere, e.g. UT/LS (Upper Troposphere/Lower Stratosphere), with potential consequences for the gas phase chemistry (e.g. oxidation capacity, ozone)

Teil 2 – Die atmosphärische Partikelphase

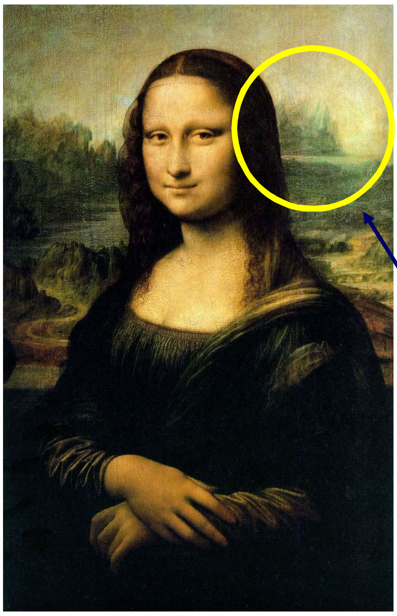
Atmospheric Organic Aerosols





Introduction and Fundamentals

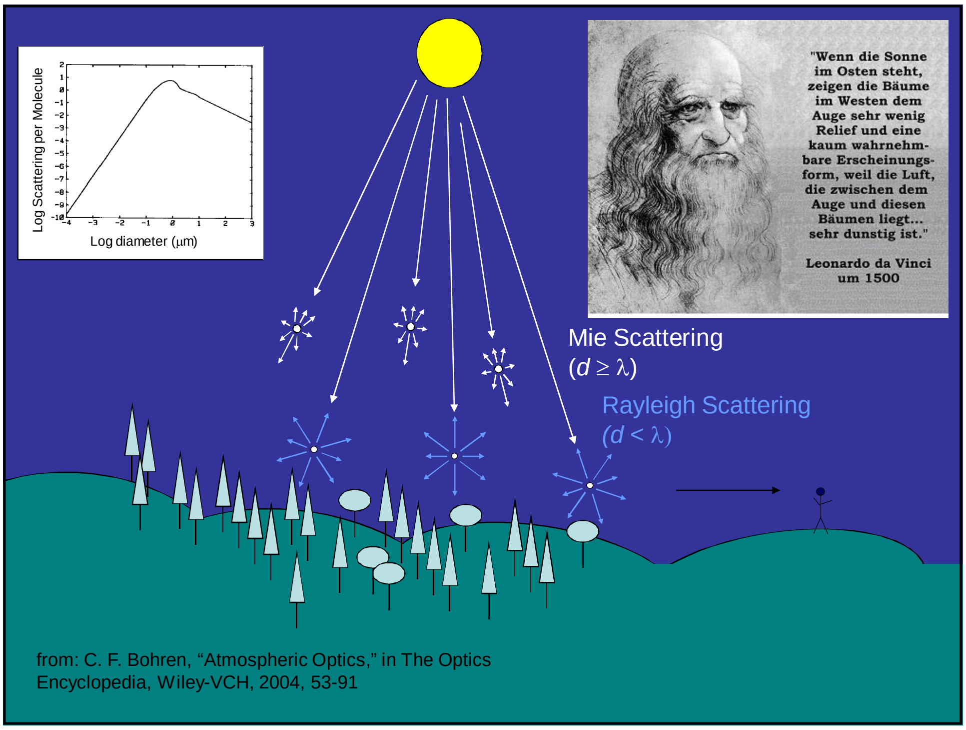
Historical and visual observations



Landschaftgemälde (Mitte 19tes Jhd)

„aerial perspective"
Luftperspektive

Leonardo da Vinci (1492-1519)
Portrait der Mona Lisa



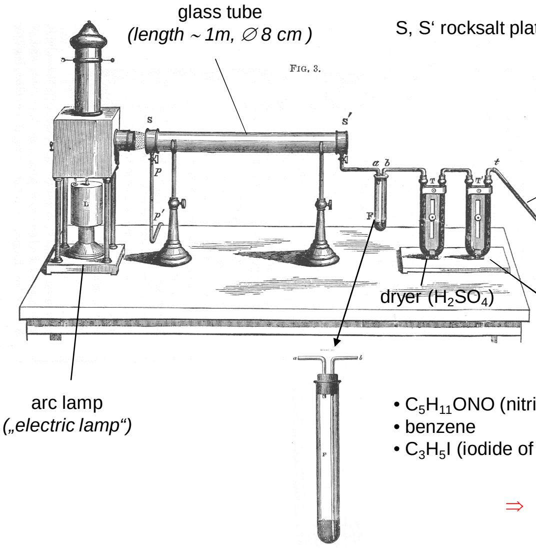
"Wenn die Sonne
im Osten steht,
zeigen die Bäume
im Westen dem
Auge sehr wenig
Relief und eine
kaum wahrnehm-
bare Erscheinungs-
form, weil die Luft,
die zwischen dem
Auge und diesen
Bäumen liegt...
sehr dunstig ist."

Leonardo da Vinci
um 1500

Mie Scattering
($d \geq \lambda$)

Rayleigh Scattering
($d < \lambda$)

from: C. F. Bohren, "Atmospheric Optics," in The Optics
Encyclopedia, Wiley-VCH, 2004, 53-91



glass tube
(length ~ 1m, ∅ 8 cm)

S, S‘ rocksalt plates

particle filter
(cotton wool)

ambient air

dryer (H_2SO_4)

CO_2 trap (KOH)
(caustic potash)

arc lamp
(„electric lamp“)

- $C_5H_{11}ONO$ (nitrite of amyl)
- benzene
- C_3H_5I (iodide of allyl)

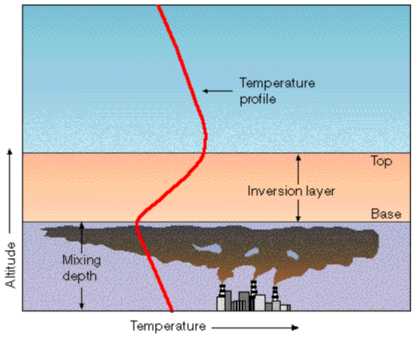
⇒ formation of ‚sky matter‘

from: John Tyndall, “Fragments of Science” 1892, 96-109, experiments from 1868-69, *New chemical reactions produced by light*

Los Angeles Smog

First recorded photo of smog
in Los Angeles, July 26,1943

London Smog

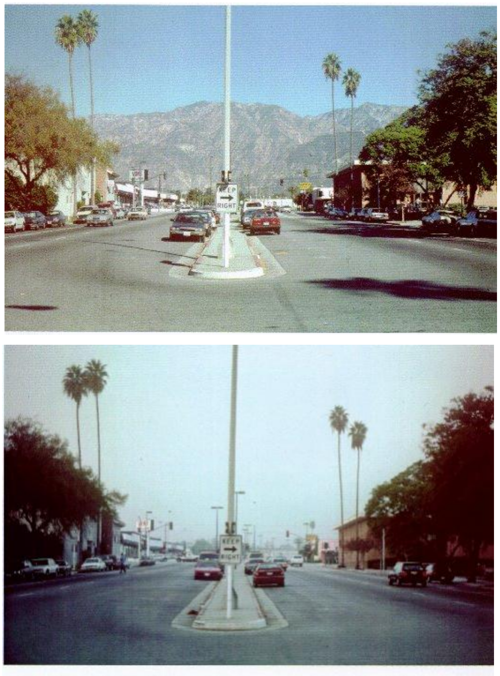


© 1998 Wadsworth Publishing Company/ITP

December 1952

Atmospheric Aerosols (biogenic blue haze)

Blue Mountains, Australia



Anthropogenic Aerosols

(organic and inorganic)
(Pasadena, CA)

Definition

Aerosol:

- Suspension of liquid or solid particles in a gas, usually in air.
  → 2-phase-system, consisting of gas and particles

Aerosol particles:

- The suspended particles (droplets, dust particles etc.)
- Aerosol particles are frequently (but incorrectly) called "aerosols"
- Liquid particles are also called droplets.

Analogous: Hydrosol

- Suspension of solid particles in a liquid
- Emulsion of liquid particles in a liquid

Frequently used terms for various aerosols:

Dust:	A solid-particle aerosol formed by mechanical processes (crushing of a parent material, wind erosion, etc.).
Mist, Fog:	Liquid-particle visible aerosol, formed by water vapour condensation.
Smoke:	Visible aerosol formed by (mostly incomplete) combustion, liquid or solid particles, agglomerates.
Smog:	Term derived from "smoke" und "fog": used for photochemically formed aerosol from anthropogenic precursor gases, as hydrocarbons and nitrogen oxides (NO_x).
Cloud:	Visible aerosol (mainly water, liquid or ice) with defined boundaries.
Bioaerosol:	Aerosol of primary biological origin: Viruses, bacteria, fungi, fungal spores, pollen…

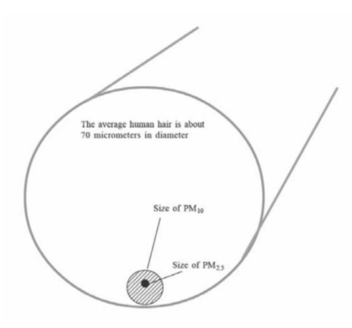
from Hinds, W.C., Aerosol Technology, 1999.

Definition

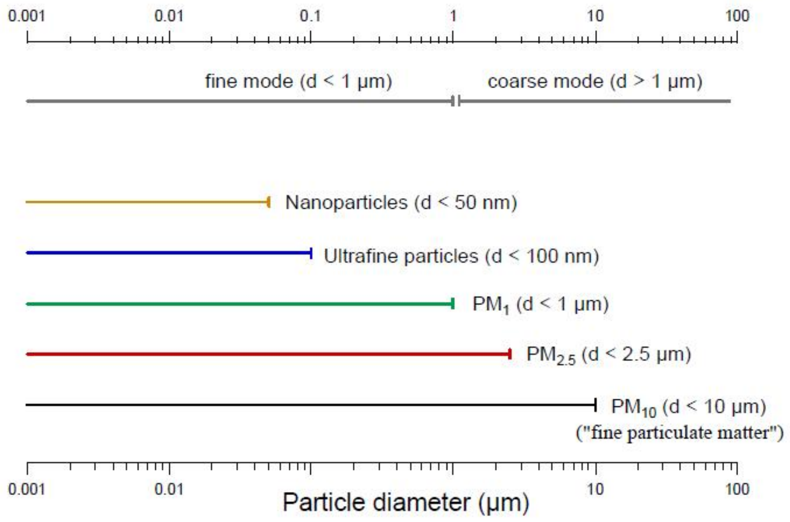
An aerosol is a relatively stable suspension of fine solid or liquid particles in a gas

Aerosol = Particles = Particulate Matter (PM)

PM_x: Particles with diameters smaller than x µm (e.g., $PM_{2.5}$, PM_{10})



Terminology for particle size ranges



fine mode (d < 1 µm)

coarse mode (d > 1 µm)

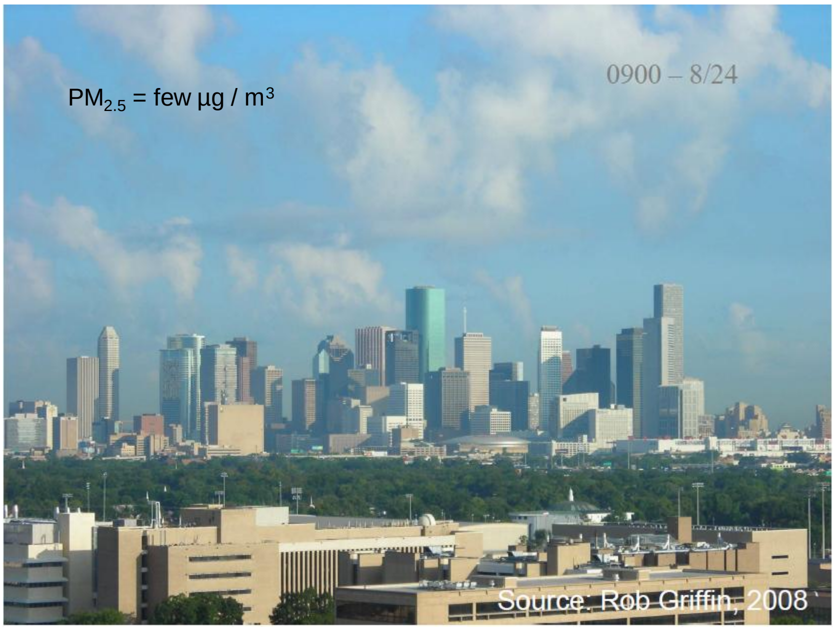
Nanoparticles (d < 50 nm)

Ultrafine particles (d < 100 nm)

PM_1 (d < 1 µm)

$PM_{2.5}$ (d < 2.5 µm)

PM_{10} (d < 10 µm)
("fine particulate matter")



$PM_{2.5}$ = few µg / m^3

0900 – 8/24

Source: Rob Griffin, 2008

$PM_{2.5}$ = several tens µg / m^3

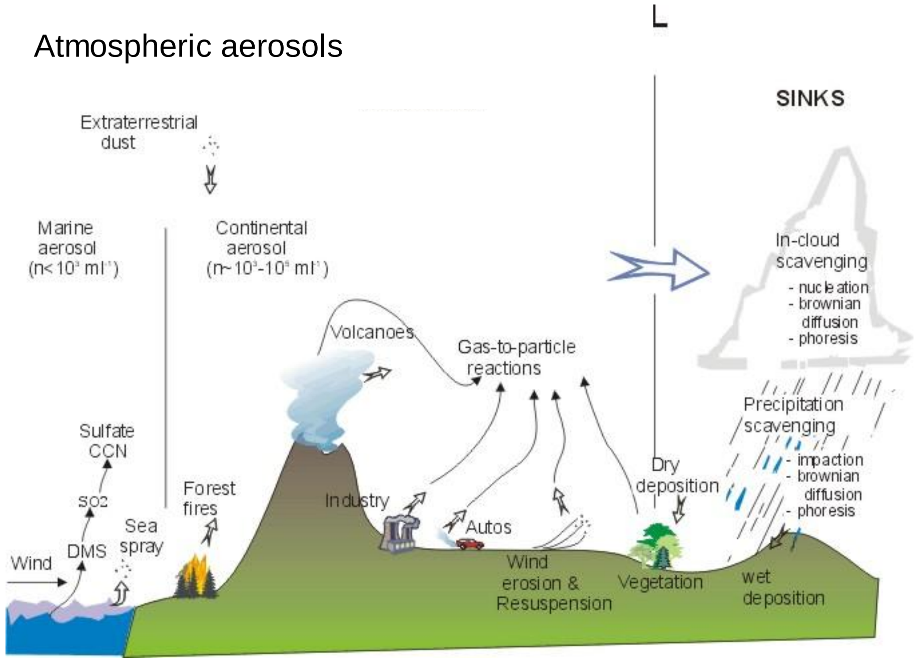
0900 – 9/08

Source: Rob Griffin, 2008

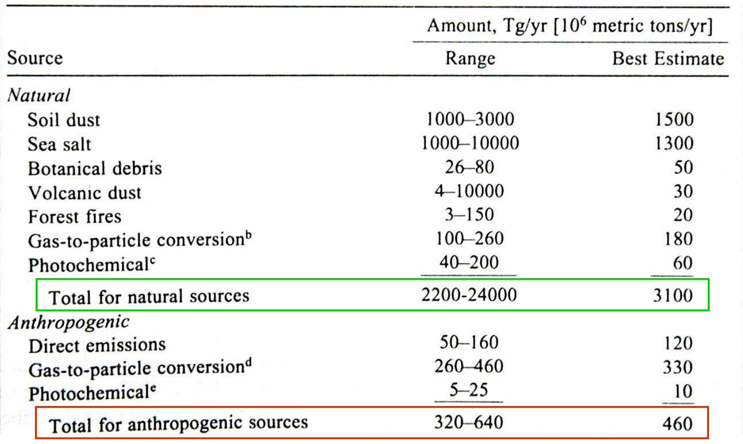
Introduction and Fundamentals

Sources

Atmospheric aerosols



Sources and estimates of global emissions of atmospheric aerosols



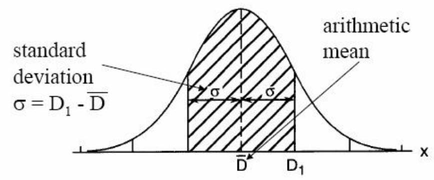
Source	Amount, Tg/yr [10^6 metric tons/yr] Range	Amount, Tg/yr [10^6 metric tons/yr] Best Estimate
Natural		
Soil dust	1000–3000	1500
Sea salt	1000–10000	1300
Botanical debris	26–80	50
Volcanic dust	4–10000	30
Forest fires	3–150	20
Gas-to-particle conversion[b]	100–260	180
Photochemical[c]	40–200	60
Total for natural sources	2200-24000	3100
Anthropogenic		
Direct emissions	50–160	120
Gas-to-particle conversion[d]	260–460	330
Photochemical[e]	5–25	10
Total for anthropogenic sources	320–640	460

Introduction and Fundamentals

Size distribution

Mathematical description of size distributions

Normal distribution (bell shaped)



- A normal distribution is fully characterized by the $\overline{D}$ and the σ
- 68% of the particles have sizes in the range of $\overline{D} \pm \sigma$

FIGURE 9.12 Meaning of standard deviation for a normal distribution. The hatched area represents 68% of total area under curve.

Finlayson-Pitts & Pitts

The size distributions of atmospheric aerosols are best described by lognormal distributions (i.e., the logarithm of particle sizes is normally distributed). →

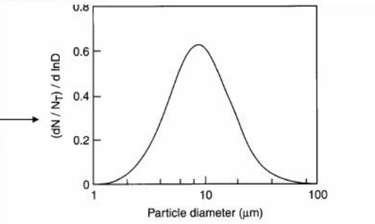


FIGURE 9.13 Frequency distribution curve (logarithmic size scale) (adapted from Hinds, 1982). *Finlayson-Pitts & Pitts*

Lognormal distribution

- Describe ambient aerosol sizes by a lognormal distribution function → use 2 parameters (σ_g, and $\overline{D}_{pg}$) to describe the size dependency of key aerosol parameters (e.g., number, surface area, volume, mass)

$$n_N^e(\ln D_p) = \frac{dN}{d\ln D_p} = \frac{N}{(2\pi)^{1/2}\ln\sigma_g}\exp\left(-\frac{(\ln D_p - \ln\overline{D}_{pg})^2}{2\ln^2\sigma_g}\right) \quad \text{(S\&P eqn. 7.42)}$$

N: Number of particles having logarithmic diameters between ln$D$ and ln$D$ + dln$D$

σ_g: Geometric standard deviation. It is the ratio of the diameter below which 84.1% of the particles lie to the median diameter.

$\overline{D}_{pg}$: the median diameter

for a comprehensive discussion see Seinfeld and Pandis, Atmospheric Chemistry and Physics

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Lognormal distribution

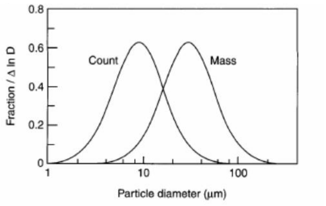


FIGURE 9.14 Count and mass distributions for a hypothetical log-normal sample. The spread, σ_g, of the two curves is seen to be the same, but the mean diameters associated with each are different (adapted from Hinds, 1982). *Finlayson-Pitts & Pitts*

σ_g is the same for a given sample for all types of distributions – #, mass, S, & V.

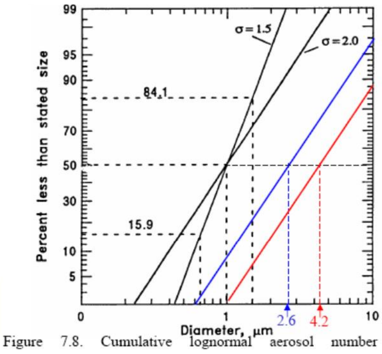


Figure 7.8. Cumulative lognormal aerosol number distributions. The distributions have mean diameter of 1 µm and σ_g =2 & 1.5, respectively. *Seinfeld & Pandis*

Surface mean diameter:

$$\ln\overline{D}_{pgS} = \ln\overline{D}_{pg} + 2\ln^2\sigma_g$$

Volume mean diameter:

$$\ln\overline{D}_{pgV} = \ln\overline{D}_{pg} + 3\ln^2\sigma_g$$

Exercise:

Know $\sigma_g = 2$, $\overline{D}_{pg}$= 1µm, determine $\overline{D}_{pgS}$ and $\overline{D}_{pgV}$

$\overline{D}_{pgS} = 2.6$ µm $\quad$ $\overline{D}_{pgV} = 4.2$ µm

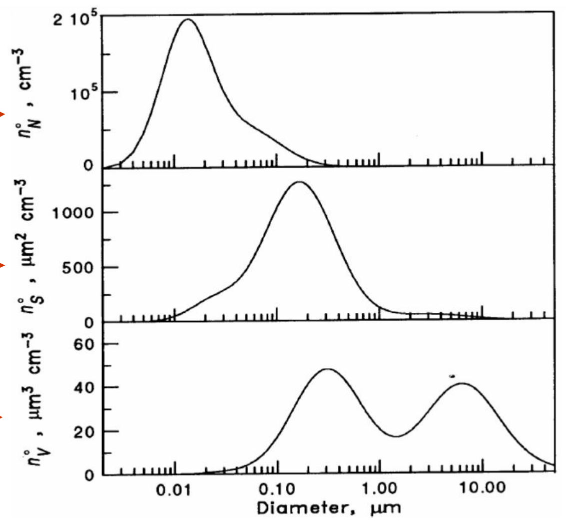
S&P: Seinfeld and Pandis, Atmospheric Chemistry and Physics, Jose Jiminez Atmospheric chemistry lecture CHEM-5151/ATOC-5151

Typical tropospheric size distributions

number

surface

volume



from: Seinfeld and Pandis, Atmospheric Chemistry and Physics

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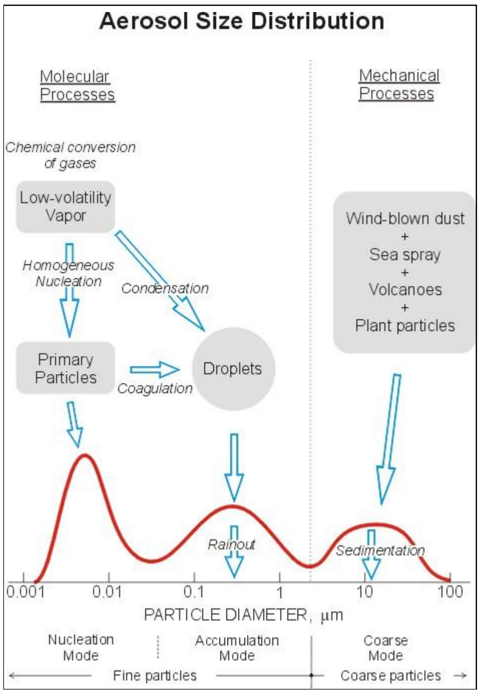
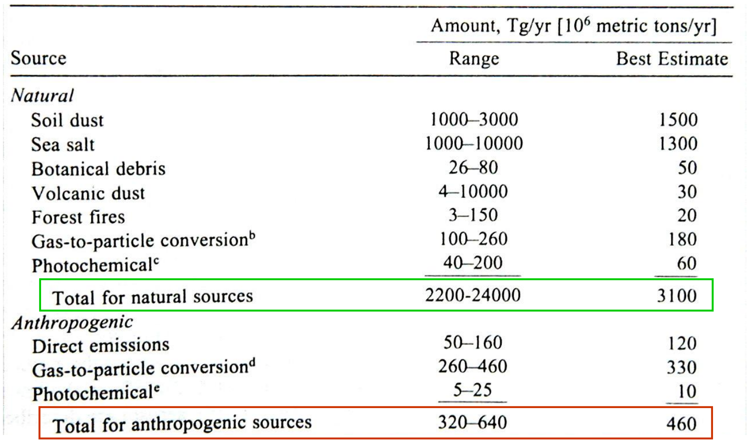
secondary particles

primary particles



aus: http://www.ems.psu.edu/~lno/Meteo437/
(Pennsylvania State University)

Loss processes and lifetime of aerosol particles



Source	Amount, Tg/yr [10^6 metric tons/yr] Range	Best Estimate
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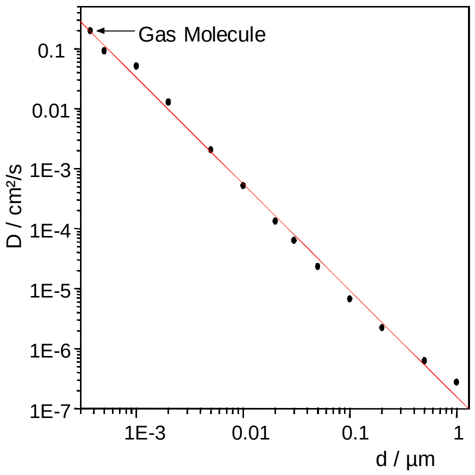
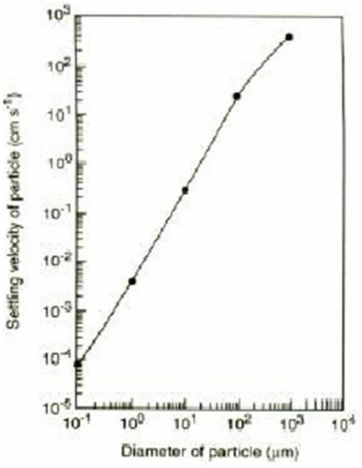
Direct emissions	50–160	120
Gas-to-particle conversion[d]	260–460	330
Photochemical[e]	5–25	10
Total for anthropogenic sources	320–640	460

Loss processes and lifetime of aerosol particles

diffusion coefficient



sedimentation velocity



Particle diameters

Aerosol sizes are usually reported as diameters.

Yet many atmospheric particles have irregular shapes have to use equivalent / effective diameter that depends on a physical property:

Why PM size matters?

- Particle toxicity (deposition efficiency are size dependent)

- Light scattering (0.1 – 1 µm most efficient for scattering solar radiation)

- Surface rxns (w/ same PM mass, smaller particles higher total surface area)

- PM life time (coagulational loss of small PM, faster sedimentation of bigger PM)

Commonly used effective diameters:

Aerodynamic diameter, D_a: the diameter of a sphere of unit density (1 g cm^{-3}) that has the same terminal falling speed in air as the particle under consideration. Measured by inertial methods such as impactors and cyclones, depends on particle shape, density & size

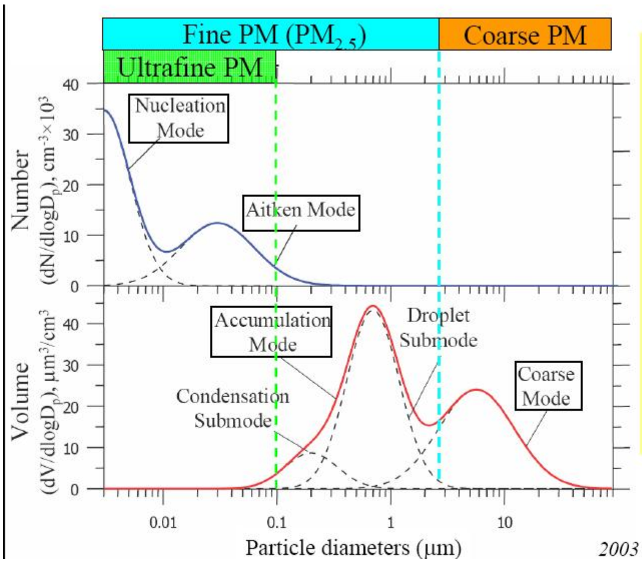
Electrical mobility diameter, D_m: the diameter of a charged sphere with the same migration velocity of the charged particle under consideration in a constant electric field at atmospheric pressure. Obtained by electrostatic mobility analyzers (e.g., DMA) depends on particle shape and size.

Vacuum aerodynamic diameter, D_{va}: the diameter of a sphere, <u>in the free molecular regime</u>, with unit density (1 g/cm^3) and the same terminal velocity as the particle under consideration. Measured by e.g., Aerodyne AMS, under high vacuum, depends on particle shape, density & size.

Optical diameter, D_o: obtained by light scattering detectors, depends on particle refractive index, shape, and size.

taken from Jose Jiminez Atmospheric chemistry lecture CHEM-5151/ATOC-5151

Nomenclature



2003 NARSTO Assessment

Nucleation mode: < 0.01 µm

Ultrafine mode: < 0.1 µm

Accumulation mode: 0.1 – 2.5 µm

Fine mode: < 2.5 µm

Coarse mode: > 2.5 µm

Introduction and Fundamentals

Life cycle of atmospheric aerosols

Life cycle of atmospheric aerosols I

micro-physical processes

chemical processes

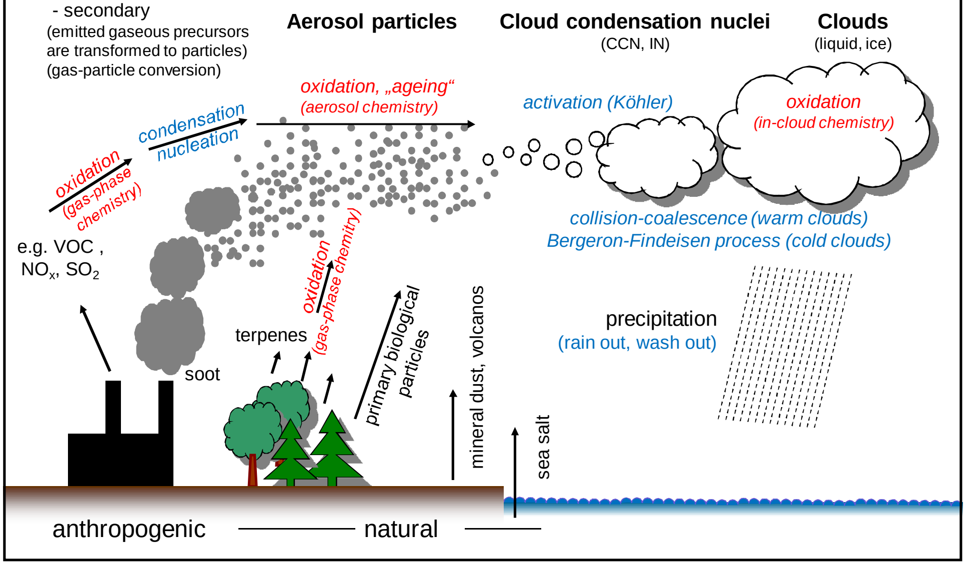
Sources:

- primary

(direct emission of particles)

- secondary

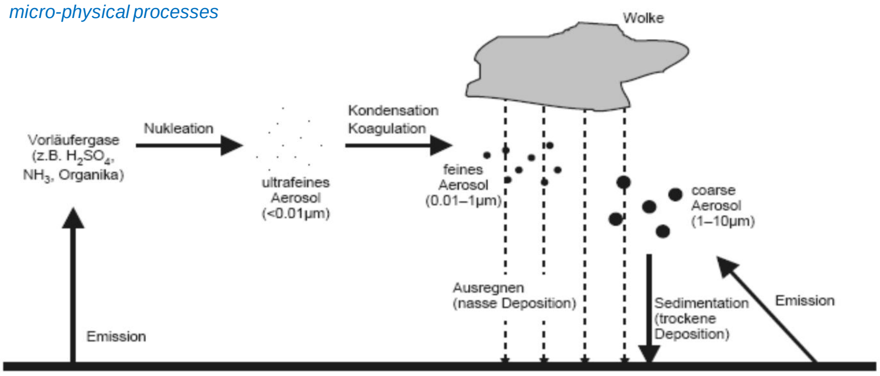
(emitted gaseous precursors are transformed to particles) (gas-particle conversion)



Life cycle of atmospheric aerosols II

Particle size is essential for transport und removal of atmospheric

micro-physical processes



Wolke

Vorläufergase
(z.B. H_2SO_4,
NH_3, Organika)

Nukleation

ultrafeines
Aerosol
(<0.01µm)

Kondensation
Koagulation

feines
Aerosol
(0.01–1µm)

coarse
Aerosol
(1–10µm)

Ausregnen
(nasse Deposition)

Sedimentation
(trockene
Deposition)

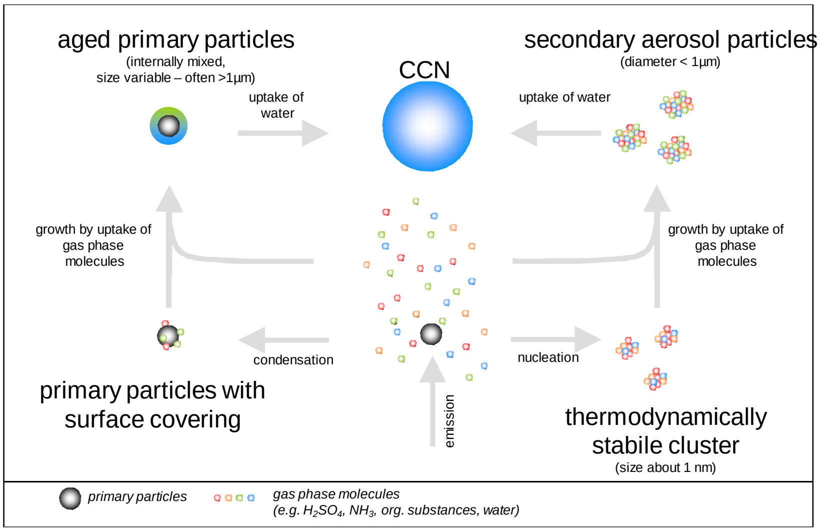
Emission

Emission

Coagulation: diffusion constant is most important

Life cycle of atmospheric aerosols III

Evolution of atmospheric aerosol particles



aged primary particles
(internally mixed,
size variable – often >1µm)

CCN

secondary aerosol particles
(diameter < 1µm)

uptake of
water

uptake of water

growth by uptake of
gas phase
molecules

growth by uptake of
gas phase
molecules

condensation

nucleation

emission

primary particles with
surface covering

thermodynamically
stabile cluster
(size about 1 nm)

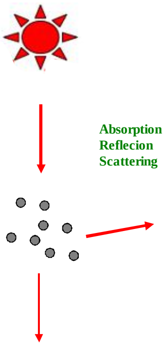
● *primary particles* ▫▫▫▫ *gas phase molecules*
(e.g. H_2SO_4, NH_3, org. substances, water)

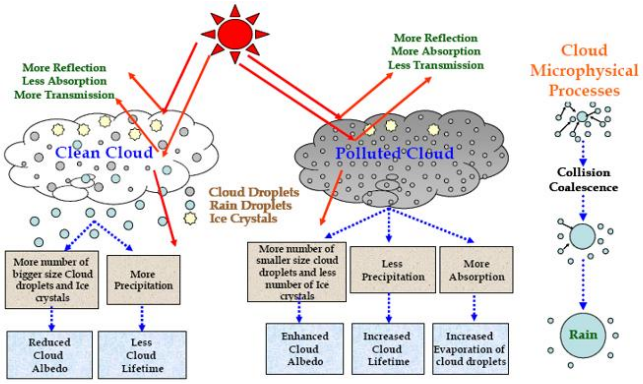
Introduction and Fundamentals

Effects

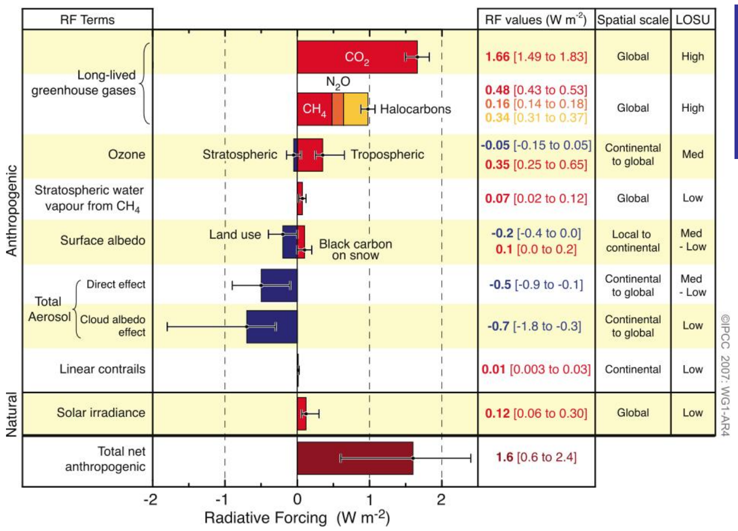
Direct and Indirect (Cloud Albedo)

effect of atmospheric aerosol particles





Esitmation of the global, average climate forcing (Wm^{-2}) of different atmospheric components



Quantification natural / anthropogenic contributions

Intergovernmental Panel on Climate Change (2007)

Summary: Effects I

Visibility reduction:

– Form haze (especially under high RH conditions) that reduces visibility

– Economical concerns (tourism)

Climate effects:

– Absorb and scatter solar radiation and outgoing IR radiation

– Act as CCN (cloud condensation nuclei), affecting cloud formation and properties

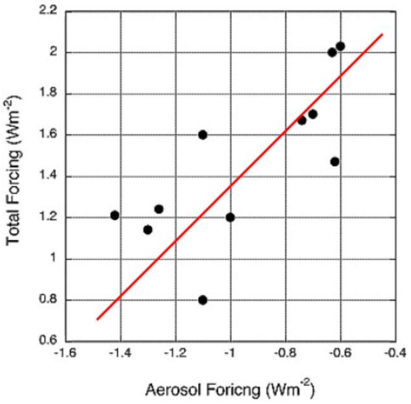
– LARGEST sources of uncertainty in assessments of anthropogenic climate change (IPCC)

- Differences in forcing are mainly due to differences in aerosol forcing

Effects of Atmospheric Aerosols - Influence atmospheric chemistry

– Reaction media

– Heterogeneous & surface reactions (e.g., polar stratospheric clouds and the ozone)



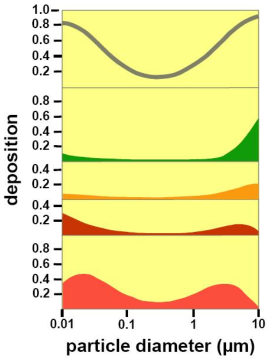
Summary: Effects II

Health effects:

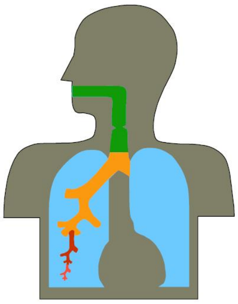
– Epidemiological evidence: affect cardiorespiratory system, cause cancer, impair lung development of children

Ecological hazards:

– Acid and nutrient deposition: damage ecosystems and ecological components, disturb nutrient balance

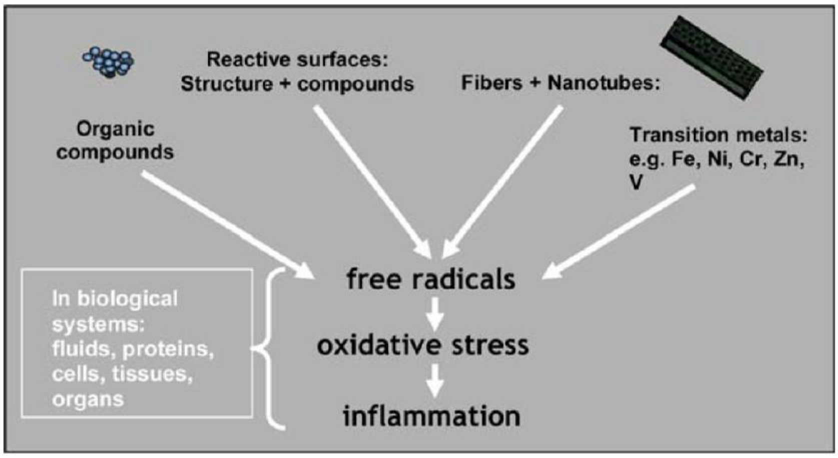


ICRP 66 (1994); MPPDep (2000): based on experimental data



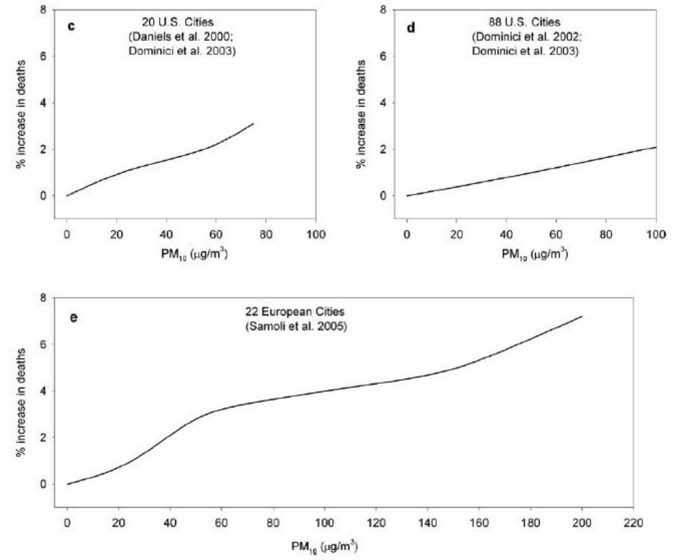
particle density: 1 g cm^{-3}
respiratory flow rate: 300 cm^3 s^{-1}
breathing cycle period : 5 s

Parameters of ultrafine particles, which are considered to be involved in the initiation of oxidative stress and inflammatory processes



Kreyling et al., Journal of Nanoparticle Research, 2006

Selected concentration-response relationships estimated from various multi-city daily time series mortality studies

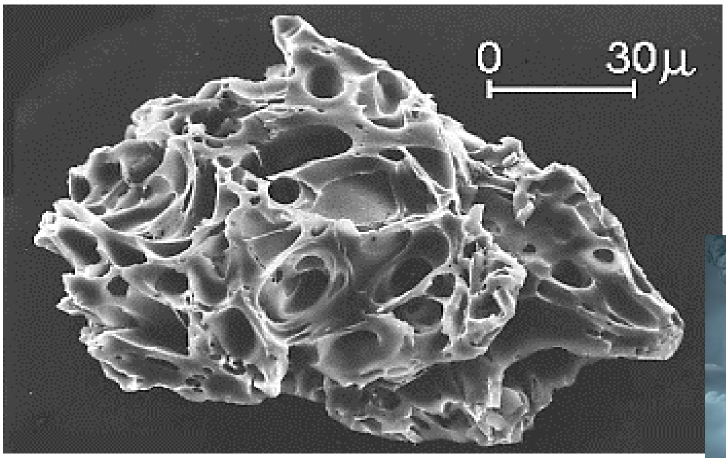


Pope and Dockery, Journal of the Air & Waste Management Association, 2006

Introduction and Fundamentals

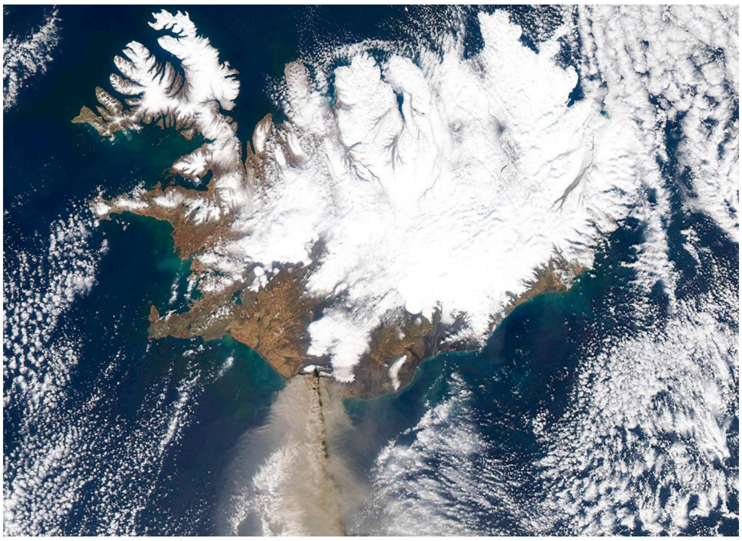
Morphology and shape

Volcanic ash Mt. St. Helens



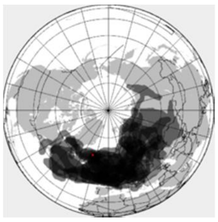
http://volcanoes.usgs.gov/Products/Pglossary/ash.html

Eyjafjallajokull volcano plume (satellite image April, 2010)



http://www.youtube.com/watch?v=DPchWu5GB4M

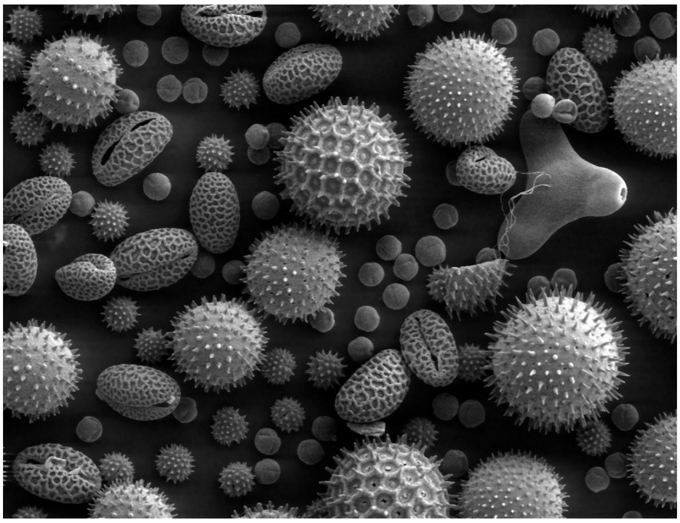
Eyjafjallajokull volcano (April, 18, 2010)



Composite map of the volcanic ash cloud spanning 14–25 April 2010

The Airport Operators Association (AOA) estimated that airports lost £80 million over the six-and-a-half days. Over 95,000 flights had been cancelled all across Europe during the six-day travel ban, with later figures suggesting 107,000 flights cancelled during an 8 day period, accounting for 48% of total air traffic and roughly 10 million passengers (source Wikipedia).

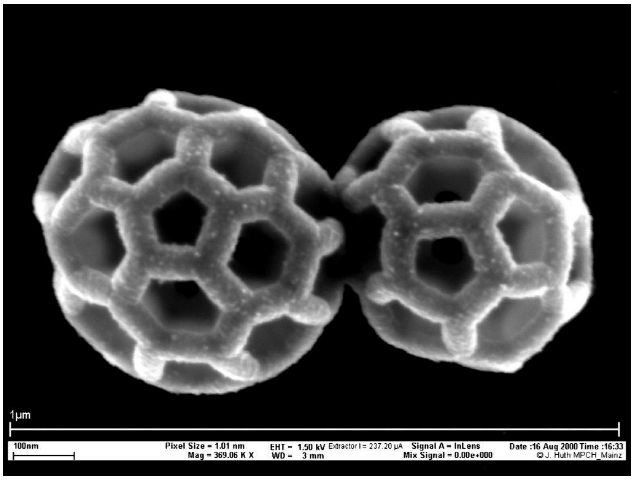
Pollen – airborne biological particles I



Pollen from a variety of common plants: sunflower (*Helianthus annuus*), morning glory *Ipomea purpurea*, hollyhock (*Sildalcea malviflora*), lily (*Lilium auratum*), primrose (*Oenothera fruticosa*) and castor bean (*Ricinus communis*).
http://en.wikipedia.org/wiki/Image:Misc_pollen.jpg

Brochosomes – airborne biological particles II

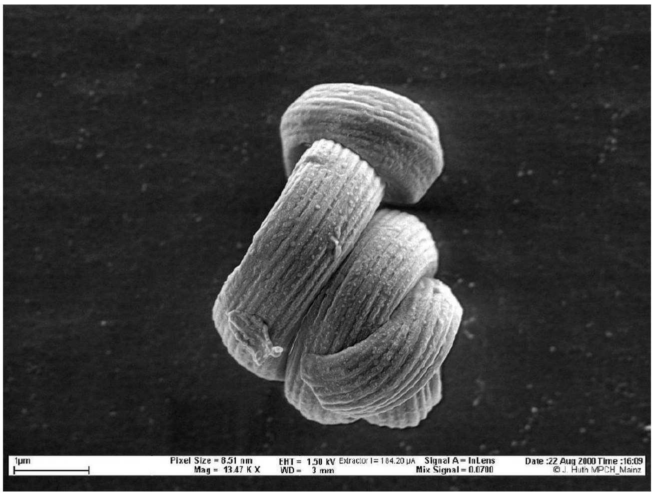
Leafhoppers secrete intricately structured microscopic granules, which probably function as a water repellent



http://www.mpch-mainz.mpg.de/~kosmo/remgallery/medsea/medsea.htm

Plant fiber ? - airborne biological particles III

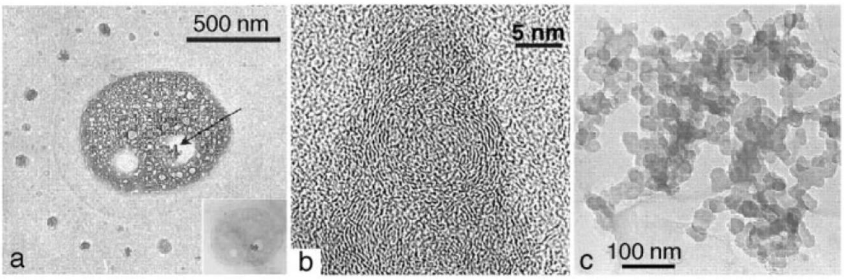
(mechanical erosion (wind driven) of plant material)

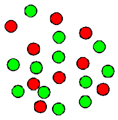


http://www.mpch-mainz.mpg.de/~kosmo/remgallery/medsea/medsea.htm

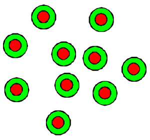
Ammoniumsulfate and soot

Buseck and Posfai, 1999, PNAS





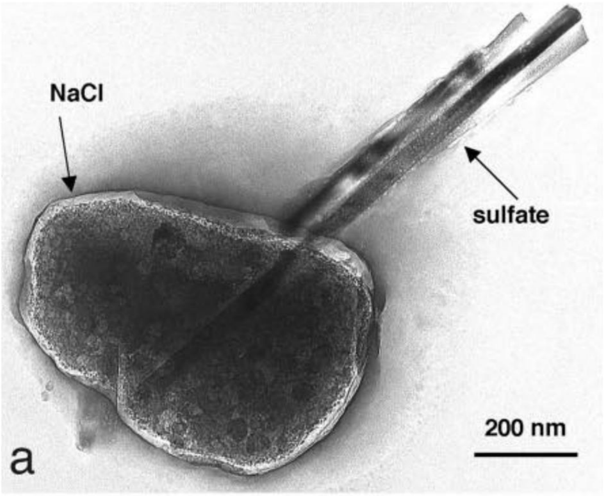
externally mixed aerosol



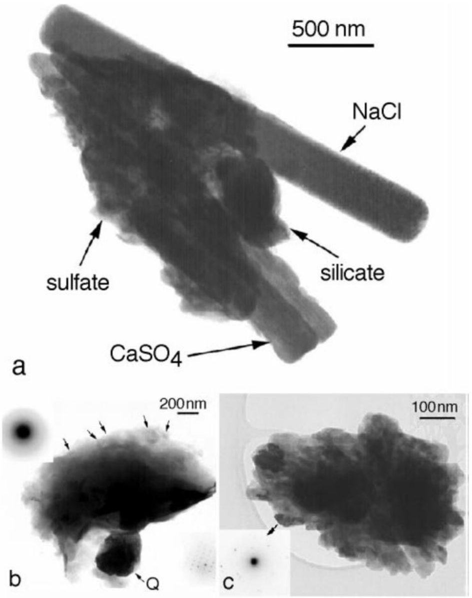
internally mixed aerosol

FIG. 2. TEM images of an internal mixture of $(NH_4)_2SO_4$ and soot. (*a*) The halo is similar to those in Fig. 1. The arrow points to a soot aggregate. (Southern Ocean, ACE-1); (*b*) High-resolution image of the arrowed tip of the soot aggregate in *a*. A degree of ordering is evident in the onion-like graphitic layers, seen edge on. (*c*) A large branching soot aggregate; such aggregates are typical of combustion processes (95). (Southern Ocean, ACE-1.)

Sea salt particle internally mixed with sulfate



Buseck and Posfai, 1999, PNAS



Mineral dust particles

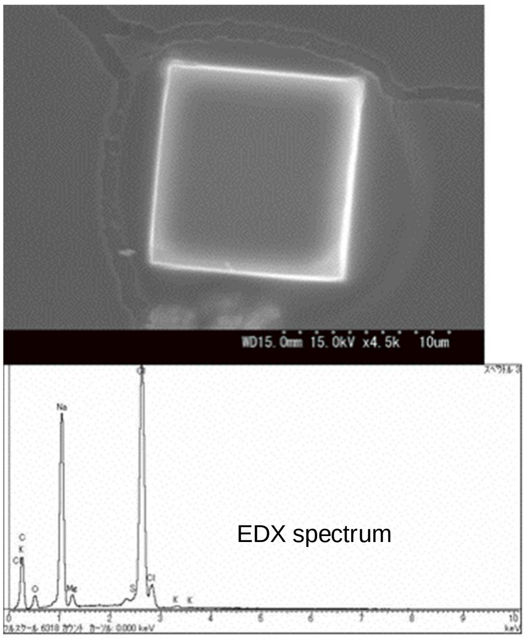
TEM images of mineral dust collected from the marine troposphere.

(a) Internal mixture of presumably terrestrial silicate and anhydrite with sea salt (Azores, North Atlantic)
(b) smectite (clay) and quartz (Q)
(c) TEM image of goethite, FeO(OH), collected 2,600 m above sea level. Fe-bearing minerals like this could be important nutrient sources in remote oceans. (Canary Islands, North Atlantic, ACE-2.)

Buseck and Posfai, 1999, PNAS

Mineral dust particles

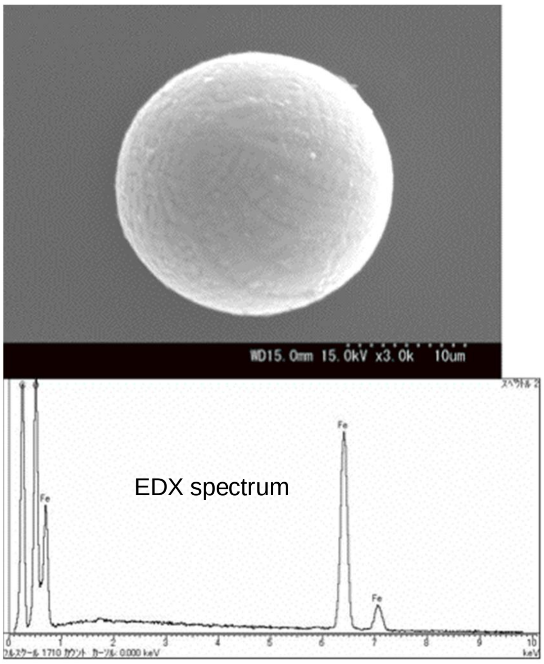
(asbestos)



EDX spectrum

Sea salt particle

cubic shape



EDX spectrum

Cosmic dust particle

Cosmic dust particles

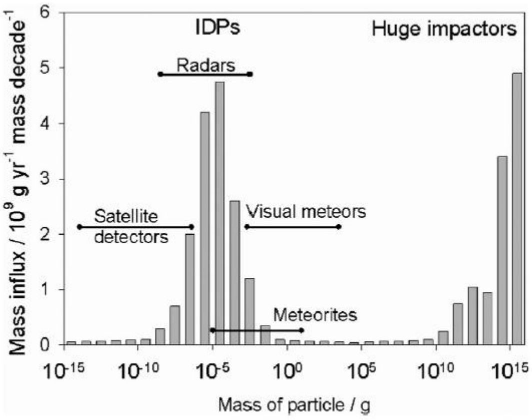


Fig. 2 Mass influx (per decade of mass) plotted against particle mass [data taken from Flynn[21]].

Input of cosmic dust:

50-300 tons / day

Plane (2012) Cosmic dust in the earth's atmosphere, Che. Soc. Rev. 41, 6507-6518 DOI: 10.1039/c2cs35132c

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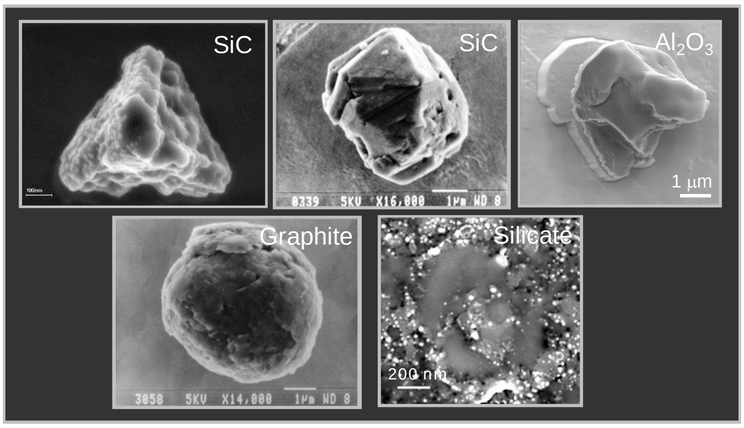
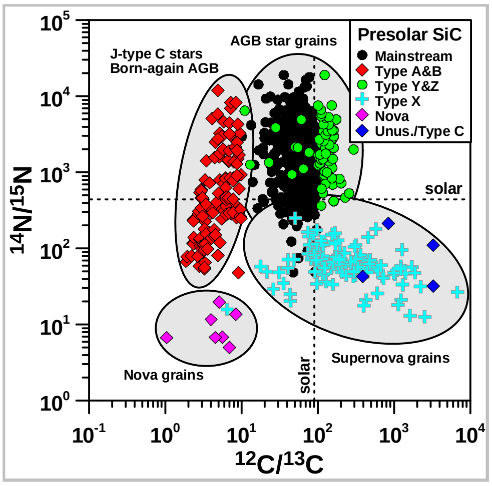
Stardust in meteorites



from: Peter Hoppe, MPI Chemistry, Mainz, 2010

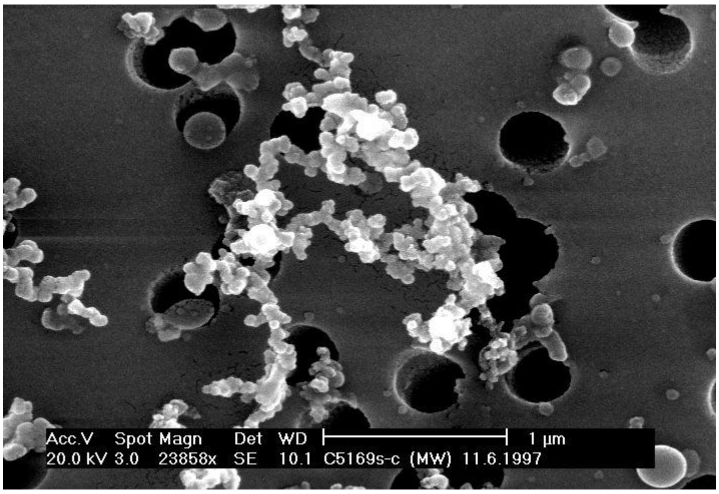
Stardust in meteorites



Eagle nebula

from: Peter Hoppe, MPI Chemistry, Mainz, 2010

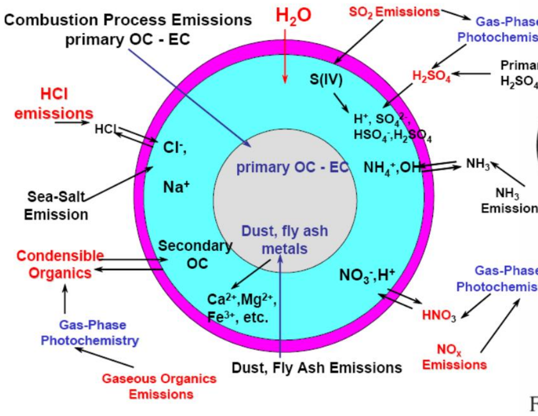
Soot particles



Soot often appears as chains of spherules with diameters close to 10 nm.
The particles were deposited on Nuclepore® filters whose pores can be seen.
http://www.mpch-mainz.mpg.de/~gth/soot_aerosol.htm

Chemical composition

Chemical composition of atmospheric aerosols



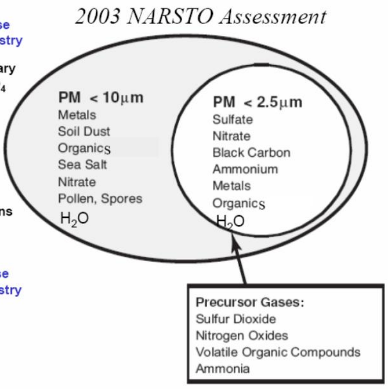
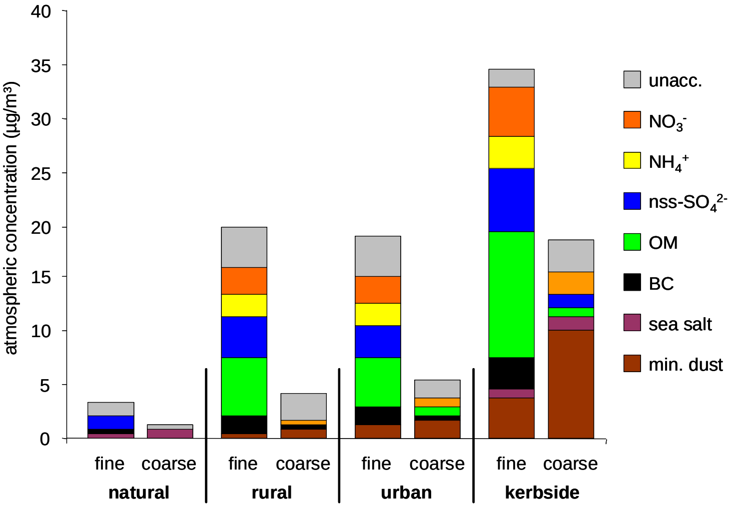


Figure 1.2. Representative Composition of PM.

Chemical composition reflects the sources and processes of particles:
- Metals/crustal materials (e.g., Al, Fe, Ca, Si): soil erosion, dust
- Na, Cl-: Sea-salt
- Black carbon: Fusil fuel / biomass combustion
- Sulfate, nitrate, ammonium: secondary formation
- Organics: a complex mixture of many individual organic compounds
- H_2O

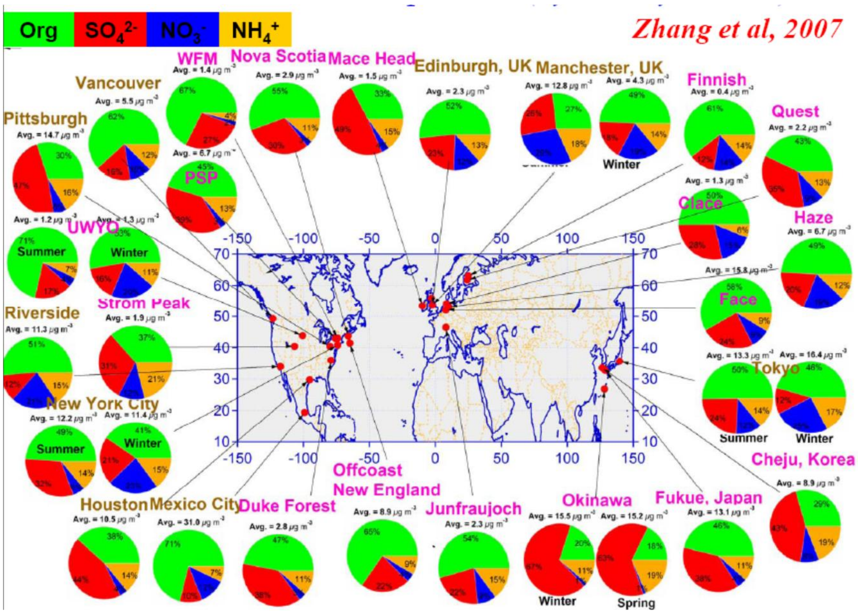
Jose Jiminez Atmospheric chemistry lecture CHEM-5151/ATOC-5151

Chemical composition of atmospheric aerosols



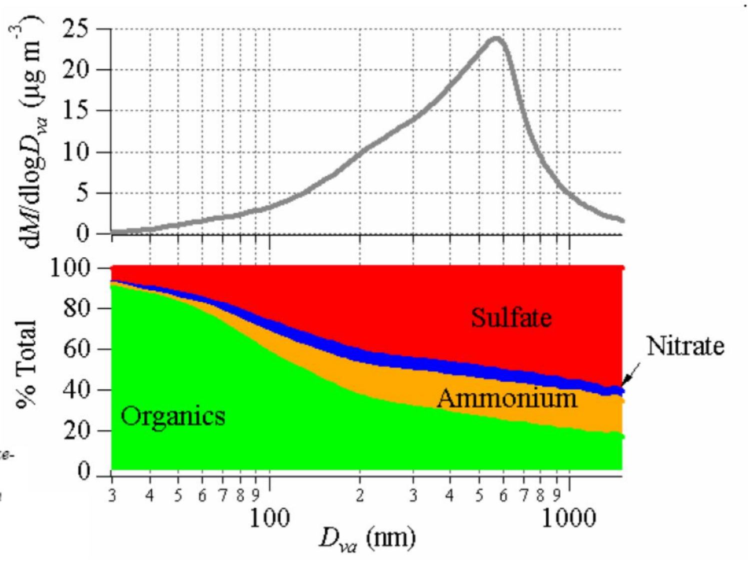
Annual mean composition of fine (PM2.5) and coarse (PM2.5 – PM10) aerosol fraction at a natural (Sevettijarvi (FIN)), rural (Illmittz (A)), urban (Zuerich (CH)) and kerbside (Barcelona (E)) site. Abbreviations: unacc. = unacccounted mass, nss = non-sea-salt, OM = organic matter, BC = black carbon, min. dust = mineral dust.

Submicron Aerosol Composition (by Aerodyne Aerosol MS)



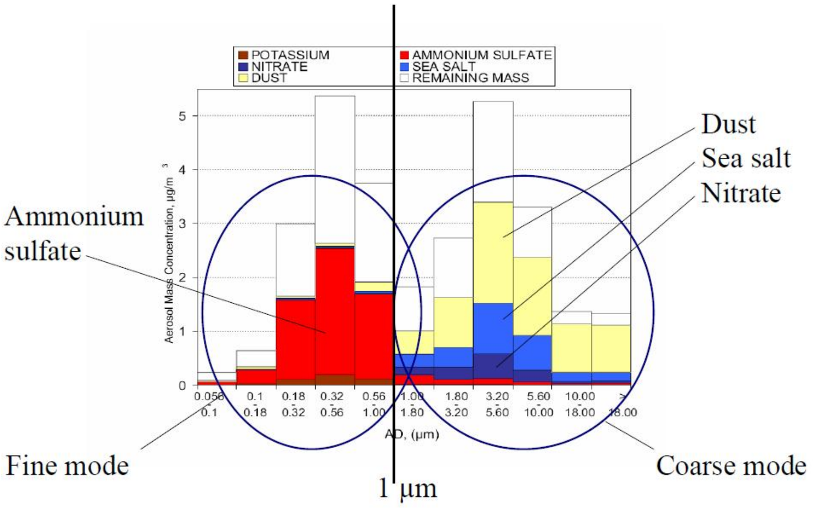
Qi Zhang et al., GRL, 2007

Size resolved ambient aerosol composition (Pittsburgh)
(by Aerodyne Aerosol MS)



Zhang et al., Time and size-resolved chemical composition of submicron particles in Pittsburgh - Implications for aerosol sources and processes, J. Geophys. Res., 110 (D07S09), 2005.

Size resolved ambient aerosol composition (Crete, August 2001) – Impactor sampling



Chemical composition

Organic aerosols (carbonaceous aerosols)

Elemental and Organic Carbon (EC/OC)

EC: elemental carbon, i.e., black carbon (BC)
OC: organic carbon
Soot: by-product of the combustion, contain both EC and OC. Present as chain agglomerate of small roughly spherical elementary carbonaceous particles.
$\rho \approx 2$ g /cm^3

Atmospheric organic compound classes:

Aliphatics (e.g., alkanes, alkenes)
Aromatics
Aliphatic and aromatic acids
Aliphatic and aromatic carbonyls (i.e., aldehydes & ketones)
Aromatic polycarboxylic acids
Polycyclic aromatic hydrocarbons (PAH)
Peroxides
Nitrogen containing organic compounds (e.g., amines, amides, nitro compounds, nitrates, heterocyclics) …
Thousands of compounds, extremely complex

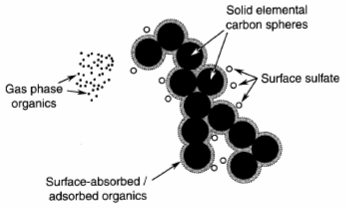


FIGURE 10.1 Schematic of a diesel soot particle consisting of an agglomeration of elemental carbon spheres (0.01- to 0.08-μm diameter). Its surface is covered with absorbed/adsorbed particle-phase organics, including 5-ring (e.g., BaP) and 6-ring PAHs. Gas-phase organics include all of the highly volatile 2-ring PAHs (e.g., naphthalene and methylnapthalenes). Semivolatile 3-ring (e.g., phenanthrene and anthracene) and 4-ring PAHs (e.g., pyrene (**II**) and fluoranthene (**V**)) are distributed between both phases. Sulfate is also associated with diesel particles. (Adapted with permission from Johnson *et al.*, 1994, SAE Paper 940233 © 940233 Society of Automotive Engineers, Inc.; see also Schauer *et al.*, 1999.) *Finlayson-Pitts & Pitts*

Definitions Andreae and Gelencser, ACP, 2006

"Soot carbon" : Carbon particles with the morphological and chemical properties typical of the soot aerosol from combustion: Aggregates of spherules made of graphene layers, consisting almost purely of carbon, with minor amounts of bound heteroelements, especially hydrogen and oxygen. This definition does not include the organic substances (oils, etc.) frequently present in or on combustion soot particles.

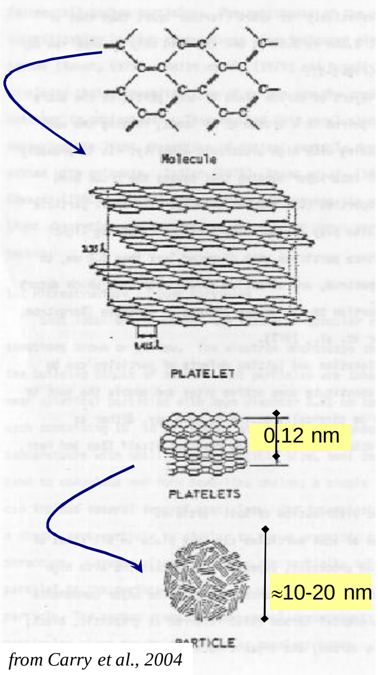
"Brown carbon" : Light-absorbing organic matter in atmospheric aerosols of various origins, e.g., soil humics, HULIS, tarry materials from combustion, bioaerosols, etc. Light-absorbing carbon (LAC): General term for light-absorbing carbonaceous substances in atmospheric aerosol.

"Elemental carbon" ("EC"): Used here (always in quotes) in the sense that is conventionally and carelessly used in the literature, usually implying a near-elemental soot-carbon-like composition, and usually referring to the fraction of carbon that is oxidized above a certain temperature threshold, and only in the presence of an oxygen containing atmosphere.

"Apparent elemental carbon" (ECa): Operationally defined as the fraction of carbon that is oxidized above a certain temperature threshold in the presence of an oxygen containing atmosphere. May be corrected for charring, depending on the technique used.

"Black carbon" ("BC"): Used here (always in quotes) in the sense that is conventionally and carelessly used in the literature, generally implied to have optical properties and composition similar to soot carbon. In the climate science and in pollutant inventory communities this is the most commonly used term, without consideration of its unclear definition. Also commonly used for the result of a LAC measurement by an optical absorption technique.

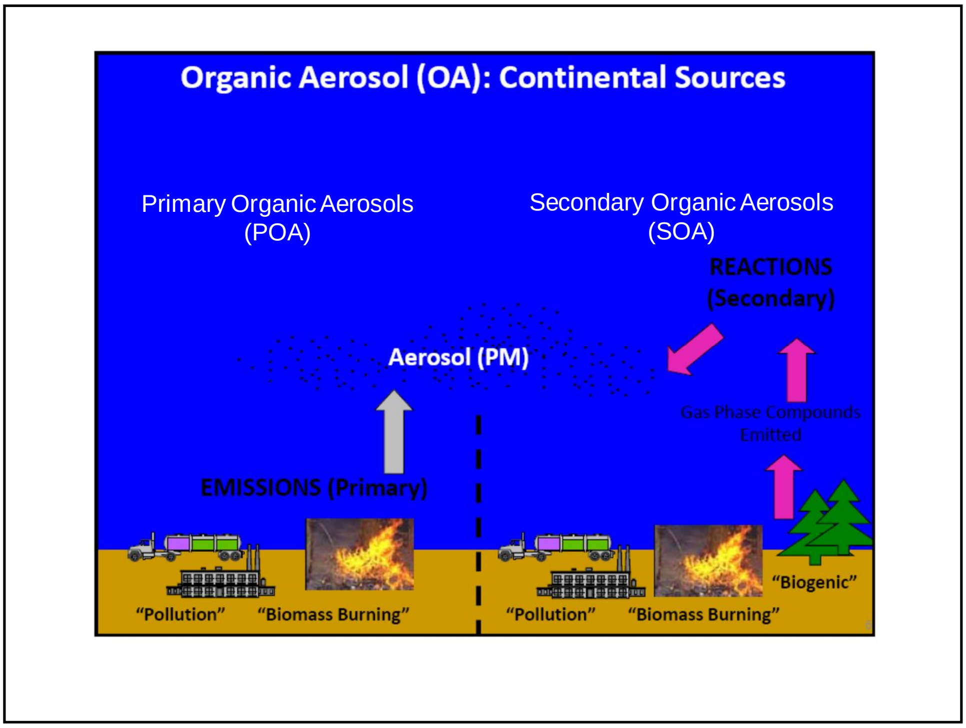
"Equivalent black carbon" (BCe): Operationally defined as the amount of strongly light-absorbing carbon with the approximate optical properties of Csoot that would give the same signal in an optical instrument (e.g., the aethalometer) as the sample.



from Carry et al., 2004

Chemical composition

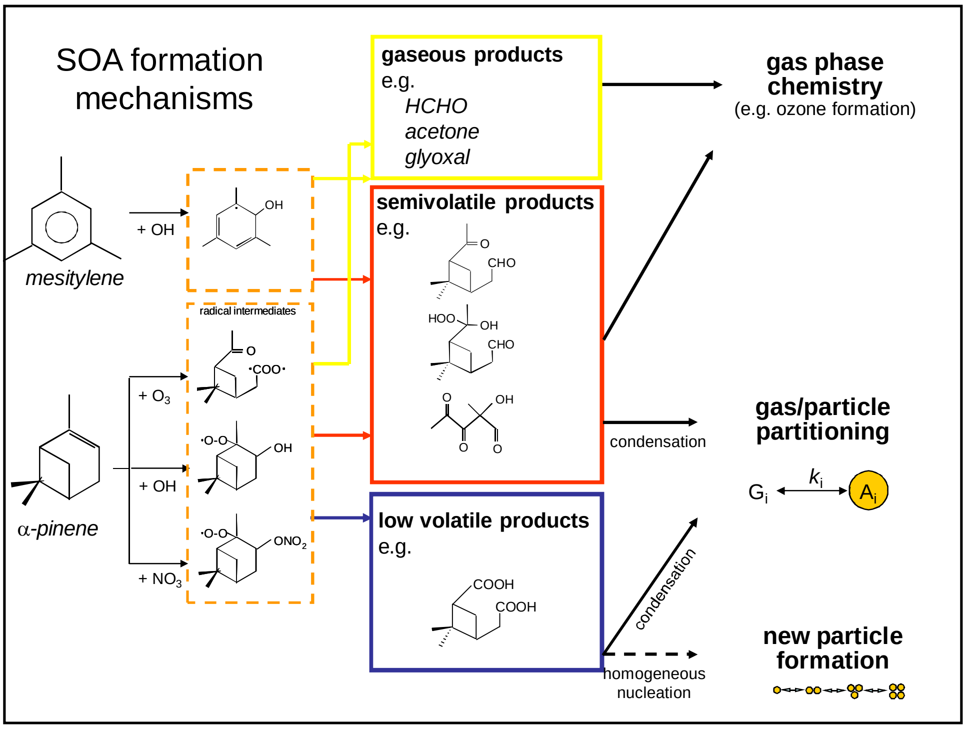
Continental organic aerosols (primary and secondary)



Organic Aerosol (OA): Continental Sources

Primary Organic Aerosols (POA)

Secondary Organic Aerosols (SOA)



SOA formation mechanisms

gaseous products
e.g.
HCHO
acetone
glyoxal

semivolatile products
e.g.

low volatile products
e.g.

gas phase chemistry
(e.g. ozone formation)

gas/particle partitioning

new particle formation

Source contributions to POA (Eastern US)

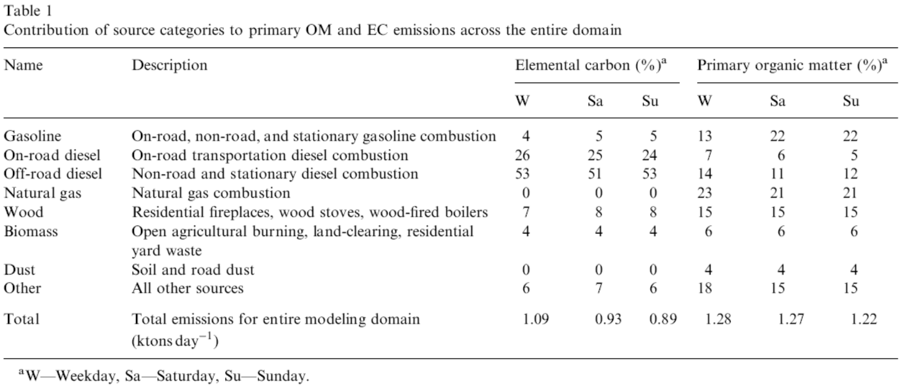


Table 1
Contribution of source categories to primary OM and EC emissions across the entire domain

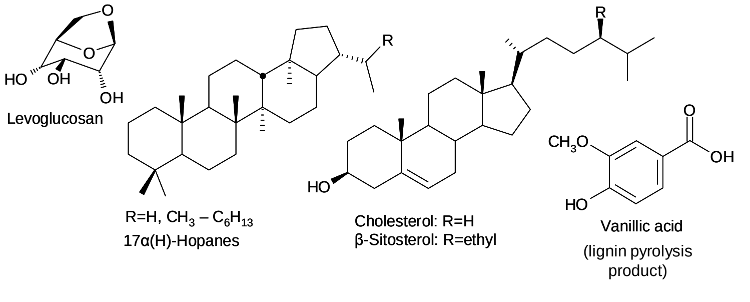
Name	Description	Elemental carbon (%)[a]			Primary organic matter (%)[a]		
		W	Sa	Su	W	Sa	Su
Gasoline	On-road, non-road, and stationary gasoline combustion	4	5	5	13	22	22
On-road diesel	On-road transportation diesel combustion	26	25	24	7	6	5
Off-road diesel	Non-road and stationary diesel combustion	53	51	53	14	11	12
Natural gas	Natural gas combustion	0	0	0	23	21	21
Wood	Residential fireplaces, wood stoves, wood-fired boilers	7	8	8	15	15	15
Biomass	Open agricultural burning, land-clearing, residential yard waste	4	4	4	6	6	6
Dust	Soil and road dust	0	0	0	4	4	4
Other	All other sources	6	7	6	18	15	15
Total	Total emissions for entire modeling domain (ktons day^{-1})	1.09	0.93	0.89	1.28	1.27	1.22

[a] W—Weekday, Sa—Saturday, Su—Sunday.

Lane et al. 2007, Atmospheric Environment

Tracers utilised for petroleum use, biomass burning and cooking
(tracers for POA)

Alkanes (combustion, lubricants, plant waxes)
PAH (combustion)
Alkoholes + aldehydes + fatty acids (plant waxes, microorganisms)
Aromatic acids + diacids (combustion, secondary sources)
Sugars (plants, microorganisms)
Anhydrosugar (biomass burning)
Steroids (cooking)
…



Levoglucosan

R=H, $CH_3 – C_6H_{13}$
17α(H)-Hopanes

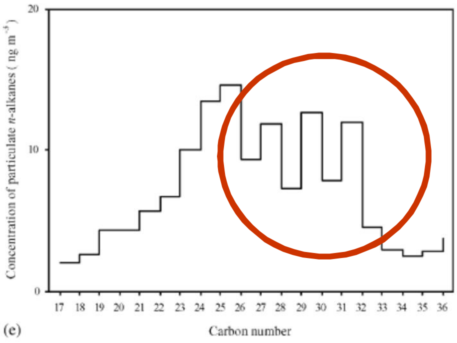
Cholesterol: R=H
β-Sitosterol: R=ethyl

Vanillic acid
(lignin pyrolysis product)

Hoffmann and Warnke, 2007, in: Volatile Organic Compounds in the Atmosphere

n-Alkanes as source tracers (tracer for POA)

Plant abrasion is mainly induced by wind-driven mechanical force, like the rubbing of leaves against each other (Rogge et al. 1993a). Identified substances in aerosols from plant abrasion (green and dead leaves) are mainly constituents of the epicuticular plant waxes: n-alkanes, n-alkanals, n-alkanols, n-alkanoic acids (fatty acids). These compound groups are not very specific for biological sources but, due to their biosynthesis, specific patterns in carbon numbers of plant-derived wax components can be observed. Leaf wax alkanes have a strong odd carbon number predominance with the dominant carbon numbers C_{29}, C_{31} and C_{33}, whereas alkanoic acids, alkanals and alkanols have a predominance of even carbon numbers. Fossil fuel constituents are showing no predominance in carbon numbers.



$$[\text{Plant wax } C_m] = [C_m] - \frac{[C_{m+1}] + [C_{m-1}]}{2},$$

Hoffmann and Warnke, 2007, in: Volatile Organic Compounds in the Atmosphere

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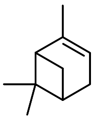
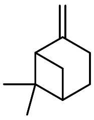
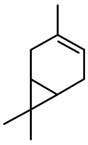
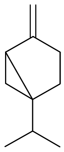
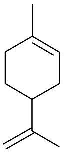
Important monoterpenes and some of their products from atmospheric oxidation (tracer for SOA)

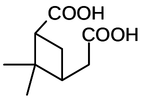

α-Pinene


β-Pinene

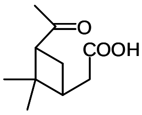

3-Carene


Sabinene

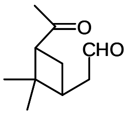

Limonene



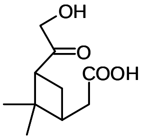
Pinic acid



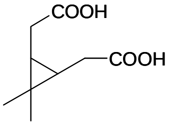
Pinonic acid



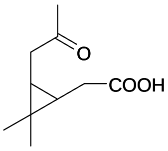
Pinonaldehyde



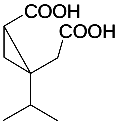
10-Hydroxypinonic acid



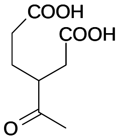
Caric acid



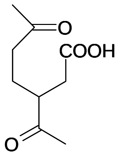
Caronic acid



Sabinic acid



Ketolimonic acid

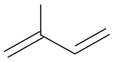


Ketolimononic acid

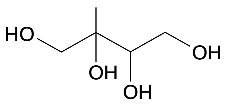
Hoffmann and Warnke, 2007, in: Volatile Organic Compounds in the Atmosphere

Isoprene and selected products from its atmospheric oxidation

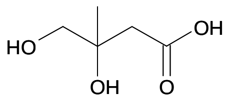
(tracer for SOA)



Isoprene



Methyltetrol
(erythro- and threo-)



2,3-Dihydroxy-4-oxobutanoic acid

Hoffmann and Warnke, 2007, in: Volatile Organic Compounds in the Atmosphere

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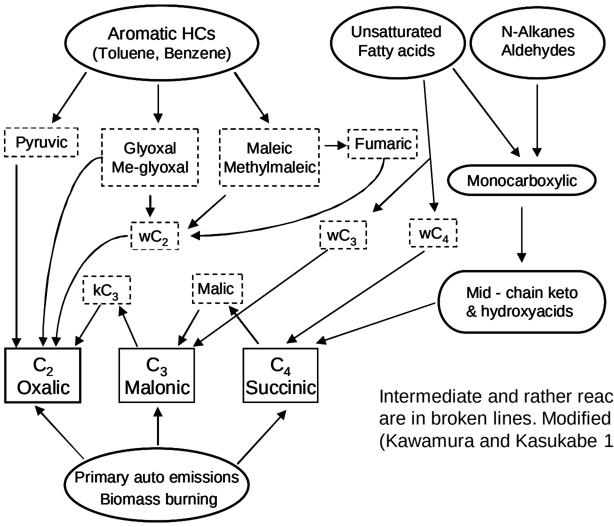
Primary and secondary sources for oxalic, malonic and succinic acid



Aromatic HCs
(Toluene, Benzene)

Unsatturated
Fatty acids

N-Alkanes
Aldehydes

Pyruvic

Glyoxal
Me-glyoxal

Maleic
Methylmaleic

Fumaric

Monocarboxylic

wC_2

wC_3

wC_4

kC_3

Malic

Mid - chain keto
& hydroxyacids

C_2
Oxalic

C_3
Malonic

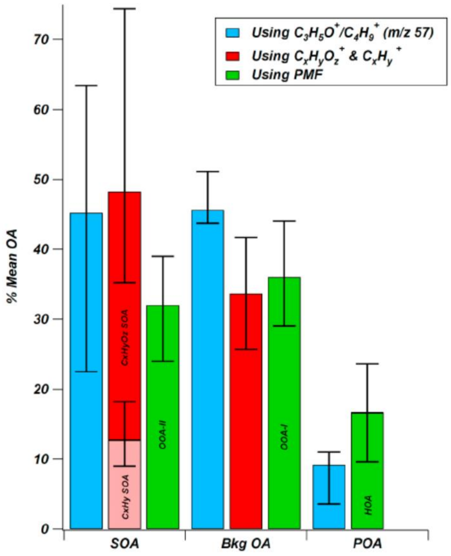
C_4
Succinic

Primary auto emissions
Biomass burning

Intermediate and rather reactive products are in broken lines. Modified figure after (Kawamura and Kasukabe 1996).

Hoffmann and Warnke, 2007, in: Volatile Organic Compounds in the Atmosphere

Primary and secondary organic aerosols in urban air masses intercepted at a rural site in Canada



Blue bars show the average fractional contribution of OA components to the mean urban influenced OA at Egbert using **$C_3H_5O^+/C_4H_9^+$** of Figure 5b.

Red bars show the average fractional contribution of OA components to the mean urban influenced OA at Egbert using **$C_xH_yO_z^+/C_2H_2$** and **$C_xH_y^+$ /C_2H_2** data.

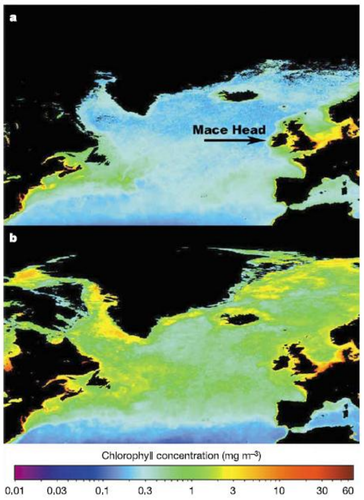
Green bars show the average fractional contribution of OA components to the mean OA based on **PMF** analysis. Ranges represent the 25th to 75th percentiles of the computed quantity.

Liggio et al. 2010, JGR

Chemical composition

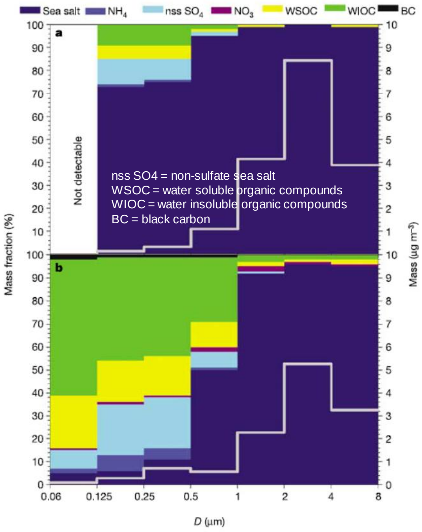
Marine organic aerosols (primary and secondary)

Biogenically driven organic contribution to marine aerosol



Organic matter at the sea surface. SeaWiFS-derived seasonal average (5-year) sea-surface chlorophyll concentrations in winter (a) and spring (b)

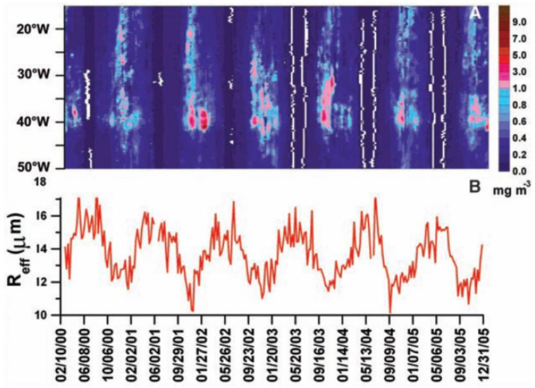
O‘Dowd et al., 2004, Nature



nss SO4 = non-sulfate sea salt
WSOC = water soluble organic compounds
WIOC = water insoluble organic compounds
BC = black carbon

Chemical composition of marine aerosols. Shown are average size-segregated chemical compositions and absolute mass concentrations for North Atlantic marine aerosols sampled with a Berner Impactor, for low biological activity (a) and high biological activity (b).

Biogenically driven organic contribution to marine aerosol

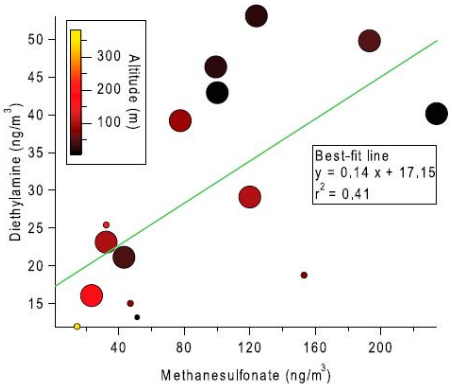


The 8-day averaged (A) SeaWiFS-observed chlorophyll a and (B) MODIS-retrieved cloud effective radius (Southern Ocean)

“We propose that secondary organic aerosol, formed from the oxidation of phytoplankton produced isoprene, can affect chemical composition of marine cloud condensation nuclei and influence cloud droplet number. Model simulations support this hypothesis, indicating that 100% of the observed changes in cloud properties can be attributed to the isoprene secondary organic aerosol.”

Meskhidze and Nenes, 2006, Science

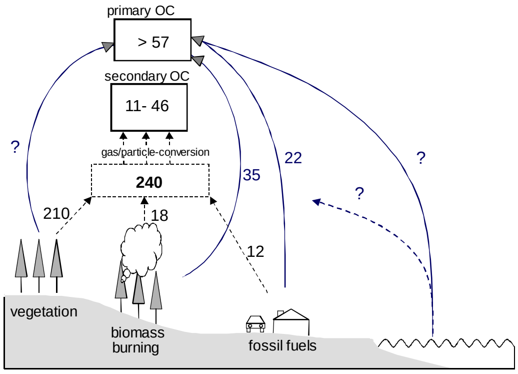
Biogenically driven organic contribution to marine aerosol



Relationship between particulate diethylamine (DEA) and methanesulfonate (MSA) in the marine boundary layer off the central California coast.

Sorooshian et al., 2009, Global Biochem. Cycles

Estimated global annual contribution to primary (POA) and secondary (SOA) organic aerosols

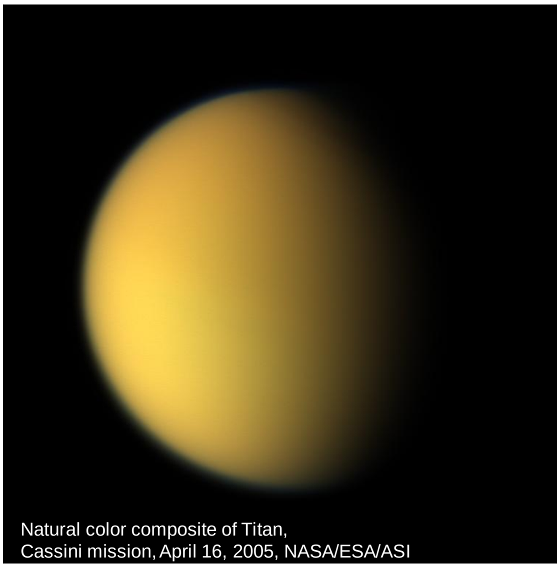


numbers in Tg/a

Organic aerosols in other atmospheres

SOA in Titan's atmosphere

Orange haze from VOC oxidation



Natural color composite of Titan,
Cassini mission, April 16, 2005, NASA/ESA/ASI

Titan’s haze layers

Detached
stratospheric haze layer
Cassini mission NASA/ESA/ASI

Aerosol forming chemistry on Titan (I)

$CH_4 \rightarrow CH_3 + H$ (homolytical dissociation induced by UV or energetic particles)

$CH_3 + CH_3 \rightarrow C_2H_6 + (h\cdot\nu) \rightarrow C_2H_4 + H_2 + (h\cdot\nu) \rightarrow C_2H_2 + 2\,H_2$

$C_2H_2 + C_2H \rightarrow C_4H_2 + H$

This process can continue, forming ever-larger successive polyacetylenes C_6H_2, C_8H_2 etc. [Wilson and Atreya, 2003].

$C_{2n}H_2 + C_2H \rightarrow C_{2n+2}H_2 + H, \quad n = 1,2,3,\ldots.$

$H-C\equiv C-C\equiv C-C\equiv C-H$ Polyynes

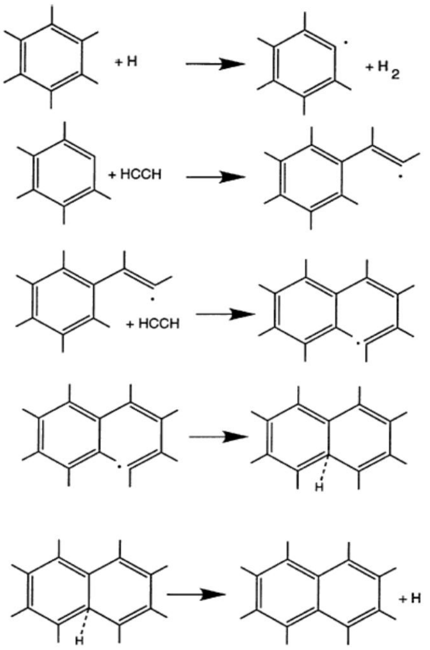
Similar reactions involving HCN can form nitrogen containing copolymers

$N\equiv C-C\equiv C-C\equiv N$ dicyanoacetylene

⇒ formation of ‚Tholins‘

Aerosol forming chemistry on Titan (II)

⇒ mid-infrared spectroscopic measurements from Titan's atmosphere show gaseous benzene [Coustenis et al., 2003]



Bittner-Howard mechanism
[Bauschlicher and Ricca, 2000]

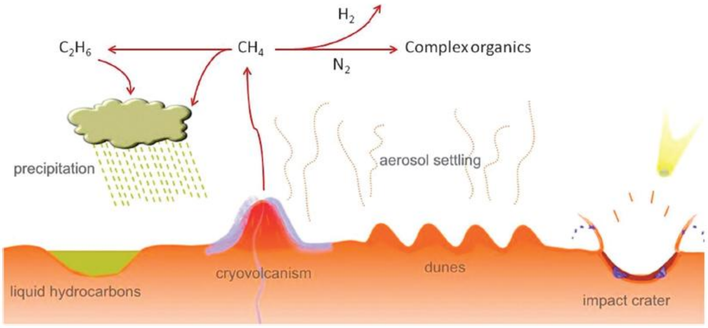
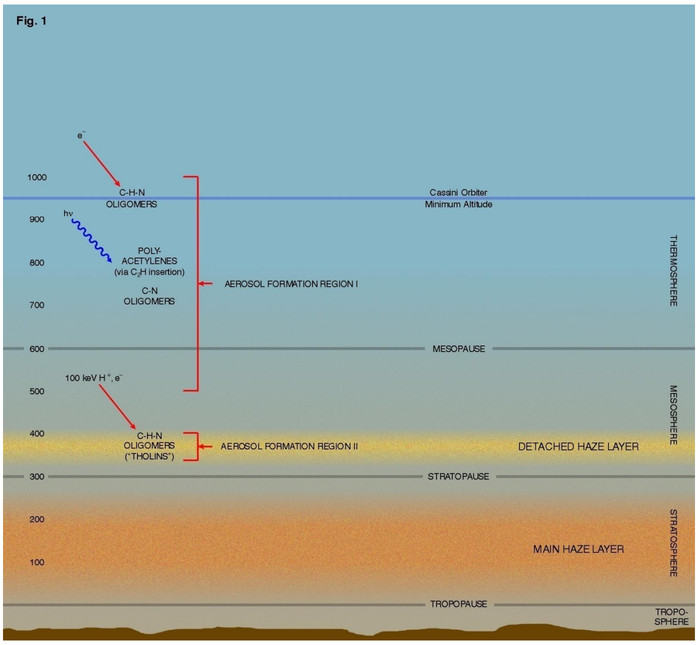
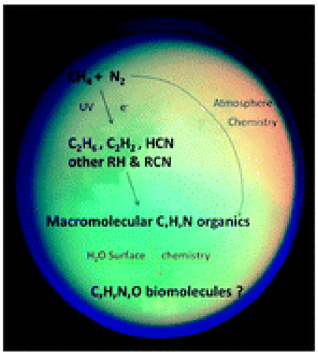


Fig. 10 Methane cycle and variety of surface features able to participate in surface chemistry (adapted from *Planetary and Space Science*, 2012, **61**, 114–123; O. Poch *et al.*). Production yields of organics of astrobiological interest from H_2O–NH_3 hydrolysis of Titan's tholins (ref. 64) (Copyright 2011, with permission from Elsevier)

Fig. 1





HUYGENS		
Gas chromatograph-mass Spectrometer (GCMS)	H. Niemann	USA
Aerosol collector & pyrolyser (ACP)	G. Israël	France
Huygens atmospheric structure instrument	M. Fulchignoni	Italy
Descent imager/spectral radiometer (DISR)	M. Tomasko	USA
Doppler wind experiment (DWE)	M. Bird	Germany
Surface science package (SSP)	J. Zamecki	UK
Interdisciplinary program		
Aeronomy	D. Gautier	France
Atmosphere–surface interactions	J.I. Lunine	USA
Chemistry and exobiology	F. Raulin	France

Motivation to understand organic particle formation in Titan's atmosphere

Titan as model for a primordial Earth

early faint sun paradox
(20% fainter 3 billon years ago – geological evidence liquid water – CO_2 concentrations too low to counteract)

other greenhouse gases that can counteract the temperature effects of the faint sun (e.g. NH_3)
would be rapidly photodissociated by the solar UV continuum

↓

presence of high altitude organic aerosols (40-75 km) may have shielded ammonia sufficiently that the supply rates were able to maintain surface temperature above freezing [*Sagan and Chyba*, 1997]

[*Kasting and Siefert (2002)*] : Early life forms like anaerobic bacteria produce atmospheric methane

↓

CH_4 would accumulate to very high concentrations in the atmosphere,
this time with temperatures too high to favour development of life

↓

formation of organic aerosols (at a critical CH_4/CO_2 ratio)

↓

removes methane from the atmosphere and creates an „anti-greenhouse effect"

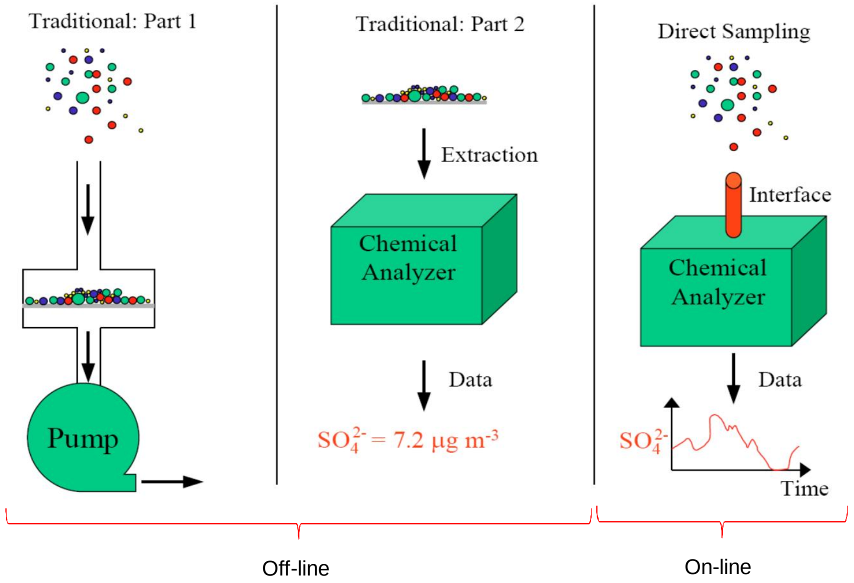
↓

formation and the thickness of an organic haze layer in the early Earth atmosphere would serve as a negative feedback loop thus stabilizing the Earth temperature

---

Analysis of Organic Aerosols

Principles of chemical aerosol characterization



Off-line analysis

Aerosol sampling

Probenahme

Die meisten Verfahren zur chemischen Analyse von Aerosolbestandteilen erfordern eine Trennung von Gas- und Partikelphase:

- Anreicherung
- Möglichkeit zur chemischen Vorbehandlung der Partikelphase
- Einbringen in Analysegeräte

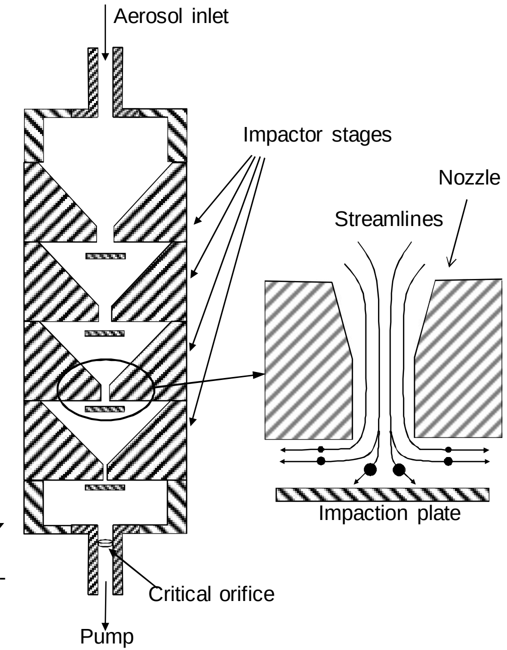
aber auch:
- Abtrennung störender Gasphasenkomponenten bei Partikelprobenahme (→ Probenahmeartefakte)
- Abtrennung störender Partikelphasenkomponenten bei Gasphasenanalytik

Probenahme-Techniken

- Filter: Abscheidung der gesamten Partikelphase, Vorabscheider für bestimmte Größenklassen (PM10, PM2.5, PM1)
- Kaskaden-Impaktoren: Sammlung der Partikel in verschiedenen Größenklassen
- Steam Jet Aerosol Collector (SJAC): Aufkondensieren von Wasser in übersättigter Dampfatmosphäre, danach Abscheidung praktisch aller Partikel durch Zyklon.

Kaskadenimpaktoren

Impaktor:
- Ausnutzung der Massenträgheit der Partikel
- Abscheidung von Partikeln in Größenklassen
- Substrate für die Abscheidung: Al-, Tedlar-Folien (z.B. Berner-Impaktor), Filter (z.B. Battelle-Impaktor)
- Oberflächen der Substrate oft gefettet oder geölt, um ein Abprallen der Partikel zu vermeiden (bounce off) → Problem bei Spurenanalytik !!!
- Verwendung von Filtern, um sehr kleine Partikel nach der letzten Stufe aufzufangen



Battelle-Impaktor. Normalerweise 5- oder 6-stufig.

Foto: AK Hoffmann

5 (6)-stufiger Berner-Impaktor. Cutoffs: D_{50} /µm: 10.0, 5.9, 2.0, 0.71, 0.25, 0.085. Die erste Stufe ist zum Abscheiden der groben Partikel, sie werden nicht für eine Analyse genutzt.

Weiter Impaktoren:

LPI (Low pressure impactor)

MOUDI (Micro orifice uniform deposit impactor)
Rotating impaction plates for uniform loading (XRF-analysis)

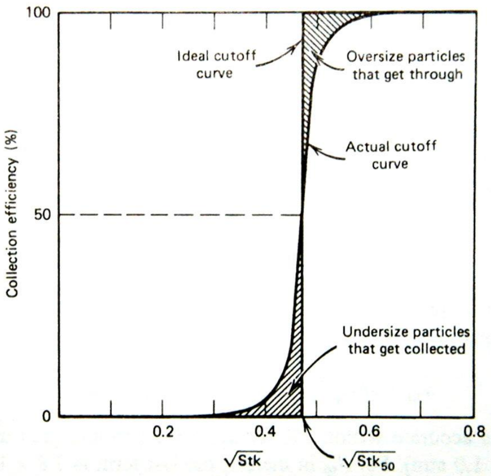
MOUDI

Impaktor - Abscheidekennlinie

Abscheide-Eigenschaften werden beschrieben durch die Stokes-Zahl (Stk):

$$Stk = \frac{2\tau U}{D_j} = \frac{\rho_p d_p^2 U C_c}{9\eta D_j}$$

U	Geschwindigkeit in Düse
D_j	Düsendurchmesser
ρ_p	Partikeldichte
d_p	Partikeldurchmesser
η	Viskosität der Luft
C_c	Cunningham Slip Korrektur



- 50 % der Partikel werden abgeschieden bei Stk ≈ 0.49

- Stufenförmige Abscheidekurve (theoretisch) ist in Realität abgeflacht

---

Kaskadenimpaktor

Erreichbarer Abscheidebereich:
50 µm (1. Stufe) bis ca. 5 nm - mit extrem kleinene Düsen ("MOUDI) und/oder Niederdruck ("LPI" - low pressure impactor)

Typische Sammelzeiten:
für chemische Analytik zwischen 1 und 24 Stunden → Information über chemische Zusammensetzung abhängig von Partikelgröße mit 1-24 h Zeitauflösung.
aber: man erhält jeweils "nur" Mittelwerte, optimale Info nur, wenn meteorolog. Bedingungen während Sammelzeit konstant

Probleme:

- Abprallen von impaktierenden Partikeln (Bounce off) → Transport in nächste Impaktorstufe (Vermeidung durch Beschichten der Prallplatten mit Ölen, Fetten, kann aber nachfolgende Analyse stören)
- Verlust von leichtflüchtigen Aerosolkomponenten während der Sammelzeit (vor allem in LPIs)
- Verluste von Partikeln zwischen den Stufen (interstage losses)

Impaktoren als Einlass-Systeme

Viele Aerosolsammler (z.B. Filtersammler, Impaktoren) besitzen einen größenselektiven Einlass (Inlet) nach dem Impaktor-Prinzip
→ Vorabscheidung größerer Partikel (z.B. für PM10, PM2.5 - Messung)

Vorabscheider

- Einstufige Impaktoren
- Filterprobenahme bestimmter Größenklassen (PM10, PM2.5, PM1)

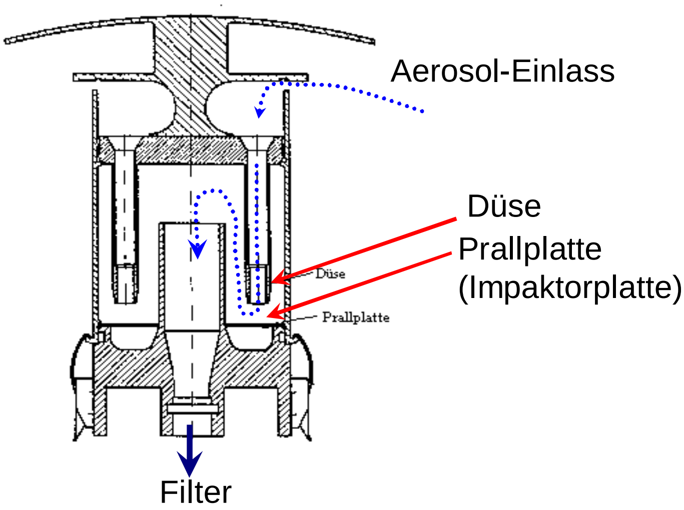
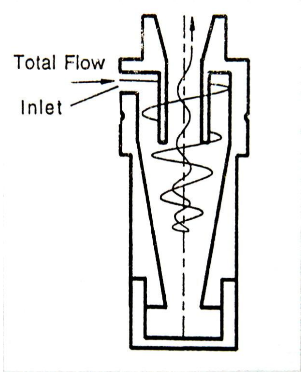


Foto: AK Hoffmann

Sonderform eines Impaktors: Cyclone



Aerosol strömt tangential in Zylinder – Absenken der Strömung in konischen Teil – Umkehrung der Strömung – Strömung verlässt Cyclone auf der inneren Achse

→ Partikel impaktieren während der zyklonischen Bewegung auf Innenwand und fallen in Sammelbehälter

Beispiel: URG-Cyclone

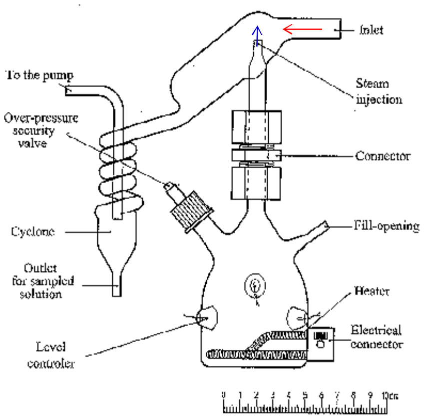
- Abscheidekennlinie nicht so scharf wie in Impaktor
- Druckabfall wesentlich geringer als bei Impaktor

→ Anwendung zur Abscheidung von Partikeln aus industriellen Prozessen

→ Anwendung als Vorabscheider für Aerosol-Messinstrumente ($PM_{2.5}$, PM_{10} – Cyclones)

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Steam Jet Aerosol Collector



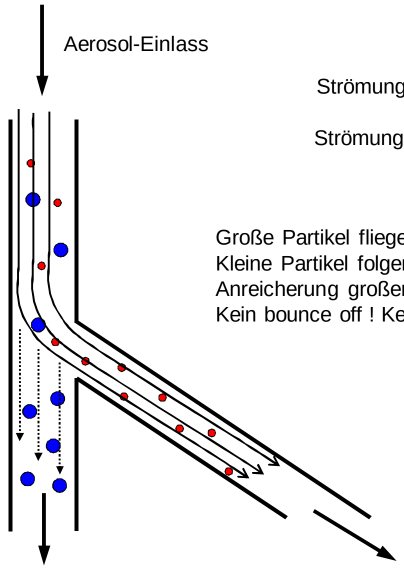
Abscheidung der Aerosolpartikel in einer wässrigen Lösung durch Einbringen von Wasserdampf in den Probenahmestrom:

- Wasserdampfübersättigung
- Aktivierung
- Wachstum der Partikel

nachfolgende Abscheidung der (nun großen im wesentlichen aus Wasser bestehenden Tröpfchen) durch Cyclone

http://www.ecn.nl/sf/products/env_air/sjac.en.html

Virtuelle Impaktoren



Aerosol-Einlass

Strömungsgeschwindigkeit Hauptstrom
größer als
Strömungsgeschwindigkeit Nebenstrom

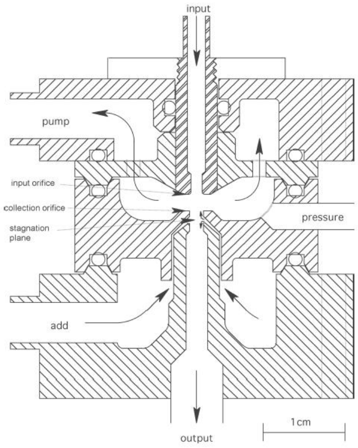
Große Partikel fliegen aufgrund ihrer Trägheit geradeaus.
Kleine Partikel folgen dem Luftstrom.
Anreicherung großer Partikel im Nebenstrom.
Kein bounce off ! Kein Druckabfall !

Nebenstrom

Hauptstrom

Counterflow virtual impactor

Boulter et al. 2006, Aerosol Sci. Technol.



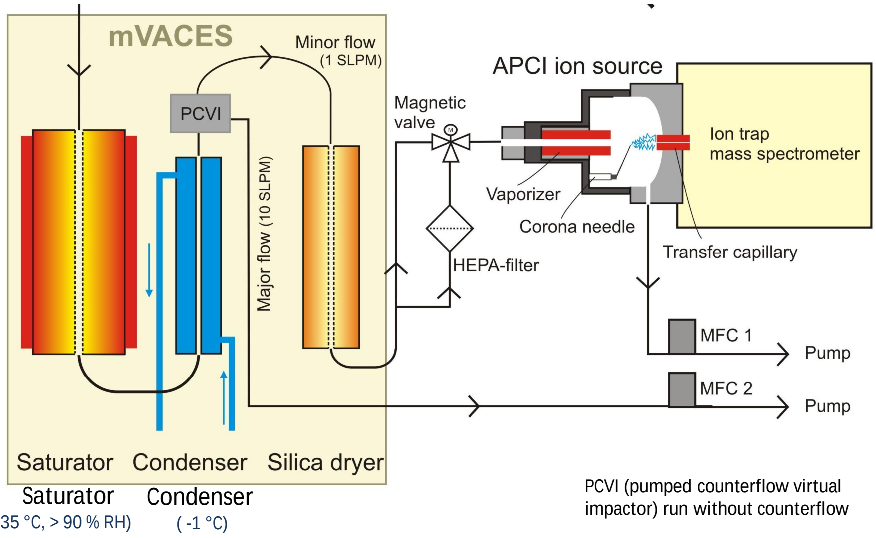
Counterflow virtual impaction uses a flow of gas in a direction opposite the motion of the particles to separate them from gas and smaller particles

Design of a Pumped Counterflow Virtual Impactor

Instrumental setup

Vogel *et al.* (2012) *Atmos. Measurement Techniques*

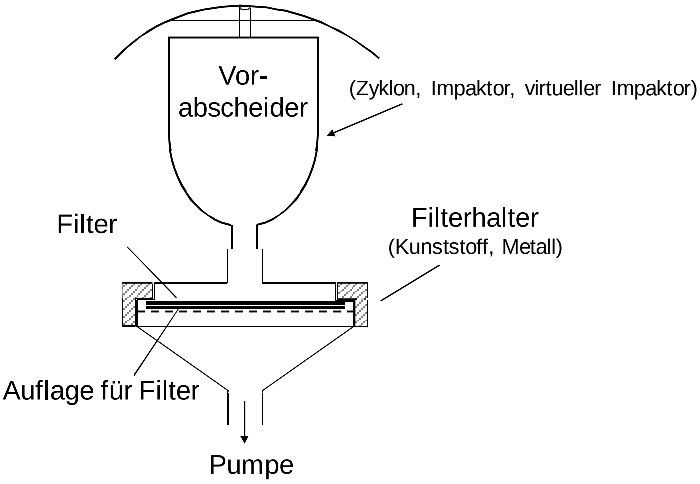
mVACES - miniature Versatile Aerosol Concentration Enrichment System



PCVI (pumped counterflow virtual impactor) run without counterflow

mVACES Geller *et al.* (2005) *J. Aerosol Sci*

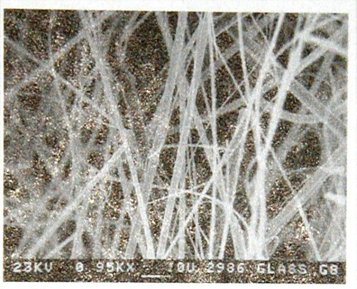
Filterprobenahme



Wichtig: konstanter, auf den Vorabscheider abgestimmter Luftdurchsatz

Auch Probenahme ohne Vorabscheider (TSP – total suspended particulate matter)
aber mit standardisiertem Einlass!

Filtertypen : Faser-Filter



- Faser-Matte aus Cellulose-, Glas-, Quarz- oder Kunststofffasern

- Hohe Porosität (70 bis > 99% Luft)

→ Niedriger Druckverlust verglichen mit anderen Filtertypen bei sonst vergleichbaren Eigenschaften

- Partikelabscheidung im ganzen Filtervolumen → nicht für mikroskopische Untersuchungen geeignet

- Cellulose-Filter: ungeeignet für gravimetrische Messungen (Cellulose sehr hygroskopisch); Vorteil: billig

- Glasfaser-Filter und Quarz-Filter (auch Teflon beschichtet) : Oft verwendet für chemische Analyse (inert, ausheizbar, hoher Durchfluss möglich → große Partikelmenge), seltener: Massenbestimmung

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filtertypen : Membran-Filter

- Komplexe Poren-Struktur aus PVC, Celluloseester, gesinterten Metallen, Teflon und anderen Kunststoffen

- geringere Porosität (50 bis 90 %)

→ höherer Druckverlust; effektivere Abscheidung kleinerer Partikel

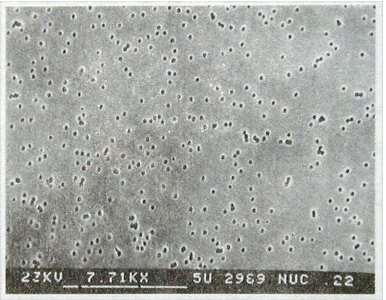
- Partikelabscheidung im ganzen Filtervolumen → nicht für mikroskopische Untersuchungen geeignet

- Teflon-, PVC- und Polykarbonat-Filter meist für gravimetrische Messungen verwendet (geringe Hygroskopizität, hohe Sammeleffizienz auch kleiner Partikel)

- Da nicht ausheizbar, nur eingeschränkt für chemische Analyse verwendet; z.B. Teflonfilter für XRF-Analyse (geringer Untergrund)

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filtertypen : Kernporen-Filter



- Auch: Kapillarporen- oder Nuclepore-Filter; 10 µm dicke Polykarbonat-Folie mit zylindrischen Poren, hergestellt durch Ätzen nach Beschuss mit Kernspaltprodukten

- geringe Sammeleffizienz für kleine Partikel (< Porengröße), geringe Porosität (5-10%) → hoher Druckabfall

- glatte Oberfläche → gut geeignet für mikroskopische Verfahren

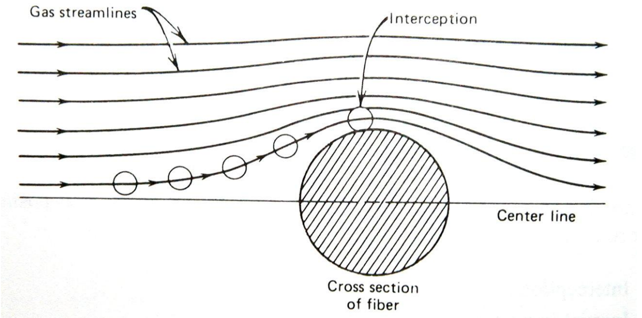
- Für oberflächenempfindliche Methoden verwendet: Lichtmikroskopie, Elektronenmikroskopie, XRF, PIXE

- Da nicht ausheizbar, geringe Beladungskapazität → nicht für (nass-)chemische Analyse geeignet

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filter-Abscheidemechanismen

Abscheidung an einzelner Faser durch *Interzeption*:

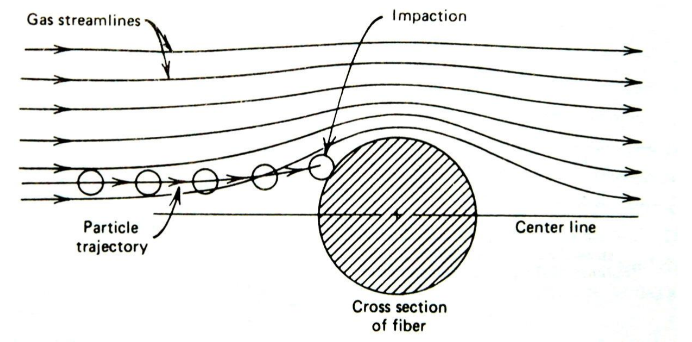


Partikel folgt Stromlinie → Wenn kleinster Abstand der Stromlinie von der Faser < Partikelradius, dann berührt das Partikel die Faser und kann dort hängen bleiben → Effizienter für große Partikel

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filter-Abscheidemechanismen

Abscheidung an einzelner Faser durch *Impaktion*:

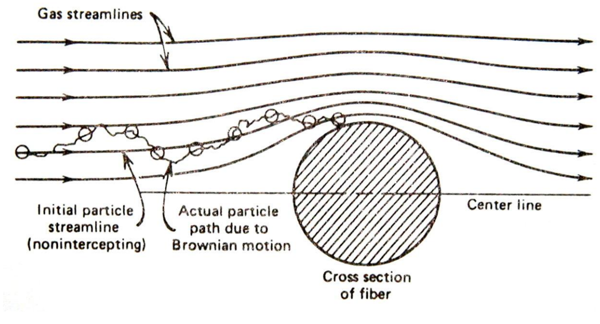


Aufgrund seiner Trägheit kreuzt das Partikel Stromlinien und kann dann ggf. auf eine Faser prallen und dort hängen bleiben, obwohl die Stromlinien um sie herum verlaufen → Effizienter für große Partikel

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filter-Abscheidemechanismen

Abscheidung an einzelner Faser durch *Diffusion*:



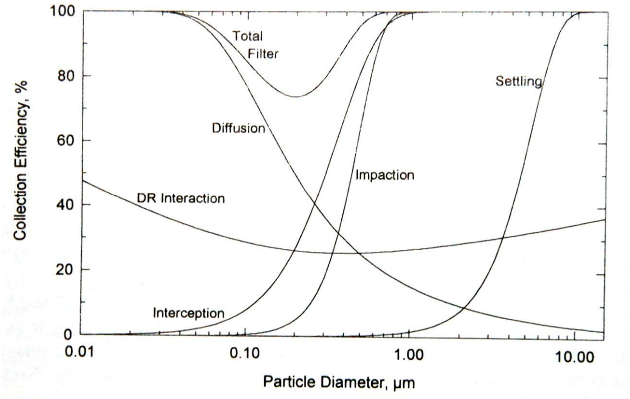
Durch Diffusion kreuzt das Partikel Stromlinien und kann dann ggf. auf eine Faser prallen und dort hängen bleiben, obwohl die Stromlinien um sie herum verlaufen → Effizienter für kleine Partikel

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Filter-Abscheideeffizienz

Gesamt-Abscheideeffizienz: Summe der Einzelfaser-Effizienzen für alle Fasern und alle Prozesse (Interzeption, Impaktion, Diffusion, Sedimentation, [elektrostatische Deposition])

DR Interaction: Korrekturterm für Gesamteffizienz, beschreibt Interzeption bei Diffusion

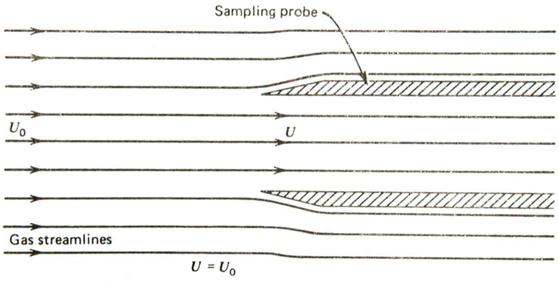


→ Minimum der Abscheideeffizienz bei einigen 100 nm

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Isokinetische Probenahme

U = U_0:



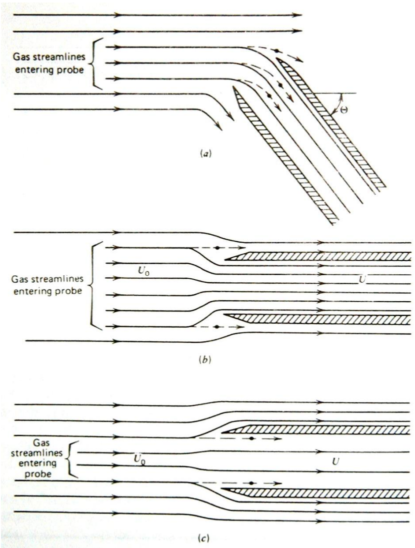
Die Stromlinien der äußeren Luftströmung werden nicht verbogen

→ Keine An- oder Abreicherung von Partikeln im Probenvolumen

wichtig bei der Probenahme großer Partikeln!

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Nicht-isokinetische Probenahme



a) Probenahme-Strömung nicht in Richtung der äußeren Strömung (nicht-isoaxiale Probenahme)

→ Abreicherung großer Partikel

b) Super-isokinetische Probenahme (U > U_0)

→ Abreicherung großer Partikel

c) Sub-isokinetische Probenahme (U < U_0)

→ Anreicherung großer Partikel

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

Transportverluste

Das in den Einlass eingesaugte Aerosol unterliegt verschiedenen Transportverlust-Mechanismen:

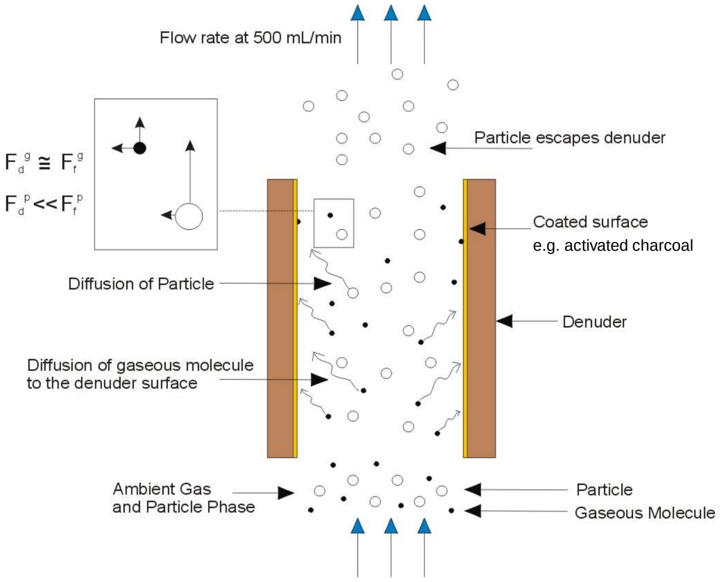
- *Diffusion* von kleinen Partikeln auf Oberflächen
- *Impaktion* von großen Partikeln an Krümmungen und Kanten
- *Sedimentation* von großen Partikeln auf horizontalen Strecken
- *Interzeption* von großen Partikeln bei Vorbeiströmen an Oberflächen
- *Thermophorese* und *Elektrophorese* von kleinen Partikeln auf Oberflächen

→ Transportverluste können nur minimiert werden; v.a. durch kurze, gerade, senkrecht verlaufende Rohre, ohne Änderungen des Innendurchmessers, thermisch isoliert und elektrisch geerdet, und Auswahl einer geeigneten Strömungsgeschwindigkeit

Folie aus: Dr. Frank Drewnik, Aerosolmesstechnik II

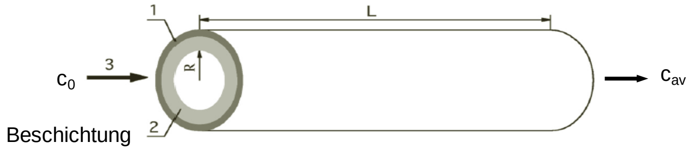
Denuder (Diffusionsabscheider)

z.B. zur (Abtrennung oder Anreicherung) von Gasphasenkomponenten



aus: Hongwei Chen, Dissertation, Mainz 2005

Denuder (Diffusionsabscheider) – Gormley-Kennedy Eq.



Gormley-Kennedy (GK) solution [Gormley 1949]:

$$\frac{c_{av}}{c_0} = 0.819\exp(-14.63\Delta) + 0.0976\exp(-89.22\Delta) + 0.0325\exp(-227.8\Delta) + \cdots$$

c_{av}: average concentration of analyte A in the gas stream leaving the denuder;
c_0: concentration of analyte A in the gas stream at denuder inlet;
Δ: equivalent length (dimensionless) given by equation:

$$\Delta = \frac{\pi}{4} \times \frac{D_A L}{V}$$

D_A – diffusion coefficient of component A in air [cm·s-1];
L – length of the cylinder [cm];
V – volume air flow rate [$cm^3 \cdot s^{-1}$] through the denuder, accounting for the actual conditions in the device

aus: Hongwei Chen, Dissertation, Mainz 2005

Artefakte bei der Probenahme

Artefakte: Physikalische, physikochemische und chemische Veränderungen / Fehlerquellen, die zu einer Änderung der Zusammensetzung führen.

Schon behandelt: Partikelverluste bei der Probenahme in Impaktoren und Filtern.

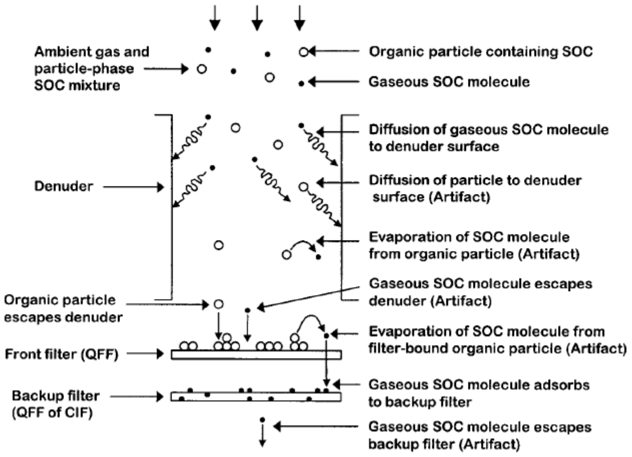
Wenn man von Artefakten in Zusammenhang mit org. Aerosolen spricht, sind meistens Adsorptions- und Verdunstungsprozesse (evtl. Kondensation) bei Filtern und Impaktoren gemeint (positive / negative Artefakte).

Positive Artefakte: Filtermaterialien mit hoher Oberflächenaktivität führen zur Adsorption von Gasphasenkomponenten (besonders Quarzfaserfilter!)

Negative Artefakte: Verdunstung von Aerosolbestandteilen aufgrund von Druck- und Temperaturänderungen.

Chemische Artefakte: Änderungen der Zusammensetzung durch Reaktionen z.B. mit Oxidantien.

Important processes occurring in a denuder/filter sampler



Mader, Flagan, Seinfeld (2001). Environ. Sci. Technol., 35, 4857-4867

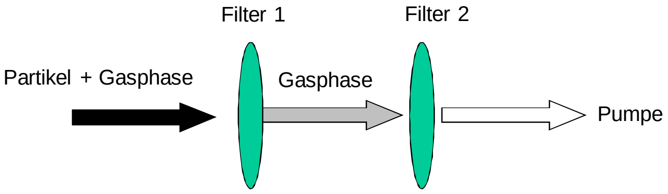
Besonders häufig: positive Artefakte durch Quarzfilter

Gegenmaßnahmen:

- Wechsel des Filtermaterials (Teflon) → aber: es gibt z.B. bei OC/EC-Messungen keine Alternative zu Quarzfiltern
- Verwendung von Backup-Filtern
- Verwendung von Denudern → aber Achtung: Störung des Gleichgewichts von Gas- und Partikelphase!

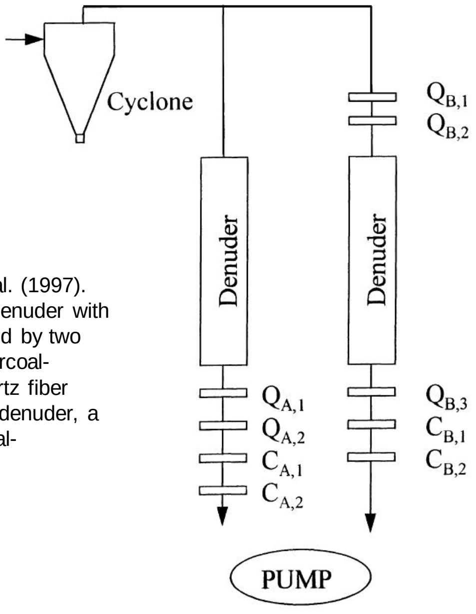
Für eine möglichst Artefaktfreie Probenahme werden oft komplizierte Kombinationen von Denudern/Filtern/Backup-Filtern in verschiedenen Probenahme-Linien verwendet.

Einfache Möglichkeit zur Korrektur pos. Artefakte von Quarzfiltern (!)


Filter 1
Filter 2
Partikel + Gasphase
Gasphase
Pumpe

Filter1: Partikel+adsorbierte Gasphase, Filter 2: adsorbierte Gasphase
Partikelphase (korrigiert)= Filter 1 – Filter 2

The BOSS sampler



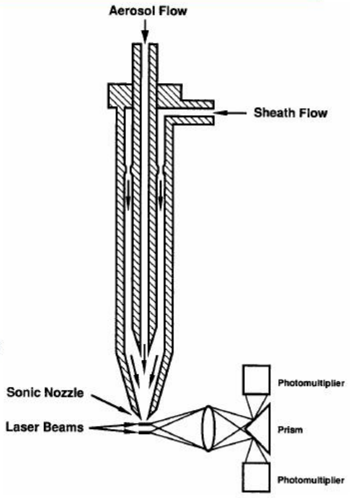
Denuder-based collection system of Cui et al. (1997). Port A contains an aluminum parallel plate denuder with charcoal-impregnated filter surfaces, followed by two quartz fiber filters (QA,1, QA,2) and two charcoal-impregnated filters. Port B contains two quartz fiber filters (QB,1, QB,2) followed by an identical denuder, a third quartz fiber filter and finally two charcoal-impregnated filters.

Turpin, B. J., P. Saxena, et al. (2000). "Measuring and simulating particulate organics in the atmosphere: problems and prospects." Atmospheric Environment 34: 2983-3013.

Exkurs: Messmethoden zur Partikelgrößenverteilung (phys. Charakterisierung)

Aerodynamic Particle Sizer (APS) (I)

- Time-of-flight instruments can provide real-time, high resolution measurement of aerodynamic particle size.
- Flow is accelerated through a nozzle, and small particles (< 0.3 μm) keep up with the acceleration while larger particles accelerate more slowly.
  - Particle size is obtained from measuring the transit time for particles between two laser beams.

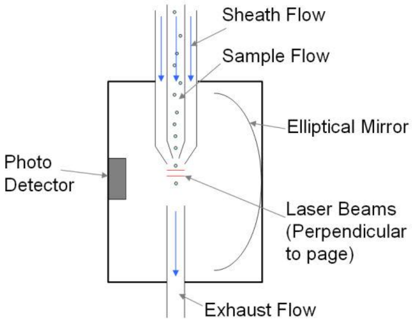


Aerodynamic Particle Sizer (APS) (II)

In this instrument the particle and sheath flow are constricted through a nozzle, accelerating the airflow. Particles within the airflow are also accelerated, but by different amounts depending on particle surface area and mass, thus particles exiting the jet have a velocity related to their aerodynamic diameter. Aerodynamic diameter is defined assuming spherical particles and unity density.

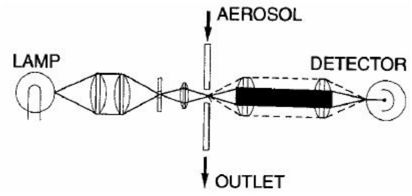
The APS measures particle velocity by passing the particles through two laser beams separated by about 200microns. An elliptical mirror collects scattered light onto a photodetector. A particle passing through both beams produces two pulses of scattered light, the time delay between the pulses being related to the velocity and hence aerodynamic diameter of the particle. The APS also records the height of the peaks allowing a secondary calculation of particle size based on optical scattering.

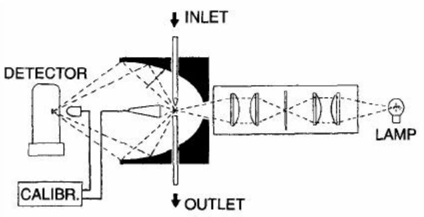
- size range 0.3-20 μm aerodynamic diameter
- about 50 size bins
- Measurement frequency 10Hz



Optical Particle Counters (I)

- Schematic of a simple light scattering instrument
  - small collection angle

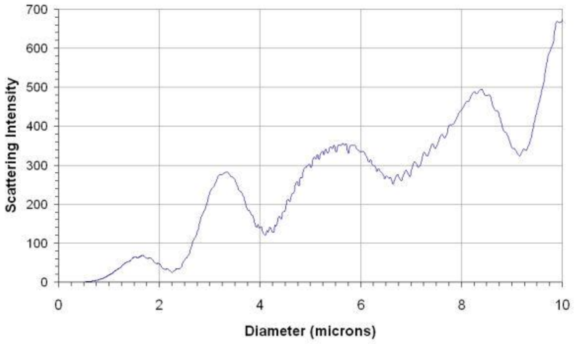




- Schematic of a CLIMET light scattering instrument
  - larger collection angle
  - Greater signal strength for the same aerosol size

Optical Particle Counters (II)

Particle measurements using optical instruments are based on the fact that when a particle passes through a beam of light, some of the light is scattered. Detection of this scattered light is the basis of all such instruments. Particle number can be determined simply by counting the pulses of scattered light reaching the detector. The intensity of scattered light is related to the size of the scattered particle and this relationship can be used to make measurements of particle size (Mie theory). Spatial scattering pattern is also dependant on particle shape.



Electrical mobility sizing

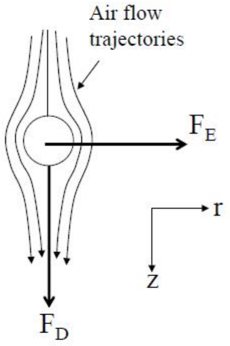
- Particles injected into the region with an applied electric field experience force in the r and z directions
  - z-direction force
    - Stokes drag due to flow around the particle

$$F_D = 3\pi\eta V d_p$$

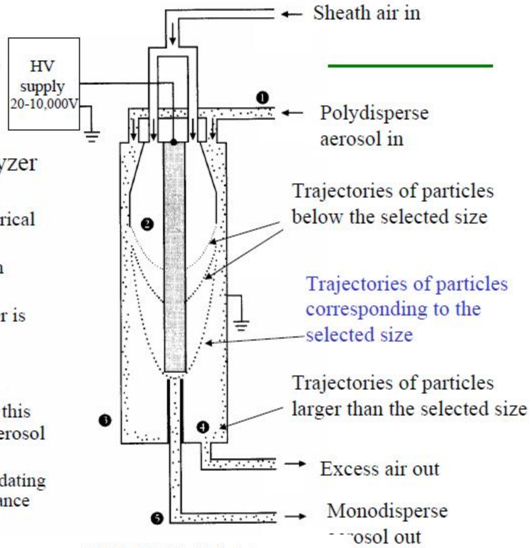
      - Where η is the gas viscosity, V is the gas velocity and d_p is the particle diameter.
  - r-direction force
    - Due to the applied electric field

$$F_E = neE$$

      - Where n is the number of charges on a particle, e is the charge on an electron, E is the applied electric field



Electrical mobility sizing
The DMA



TSI 3080 DMA

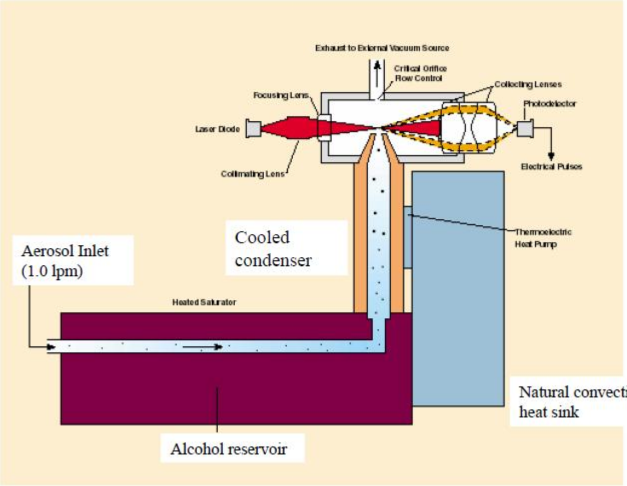
Differential Mobility analyzer (DMA)

- Sizes particles by their electrical mobility
- Usually very high resolution measurements are possible
- Downstream particle counter is required for particle size distribution measurements
  - Usually a CNC
- Due to the high accuracy of this instrument it is a standard aerosol instrument
  - Used for testing and validating new instrument performance

Particle counting

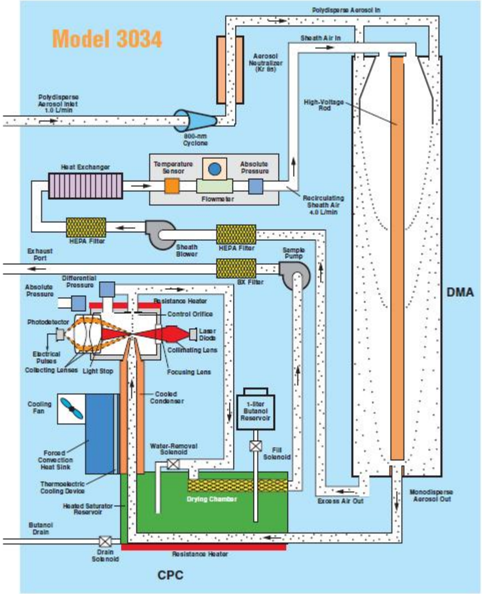
- Condensation nucleus counter
  - Particles are grown by condensation
    - Usually a high vapor pressure liquid like Butanol is used
  - Particles are counted as they pass through a light scattering region
  - Popular instrument to measure total aerosol concentration
  - Can count particles of sizes > 2nm
    - Upper limit is dependent on particle transport through the instrument

CNC



SMPS systems (Scanning Mobility Particle Sizer)

- combination between DMA and CNC
- Particle size range 3 – 1000 nm
- Time resolution 30 s – 1 min

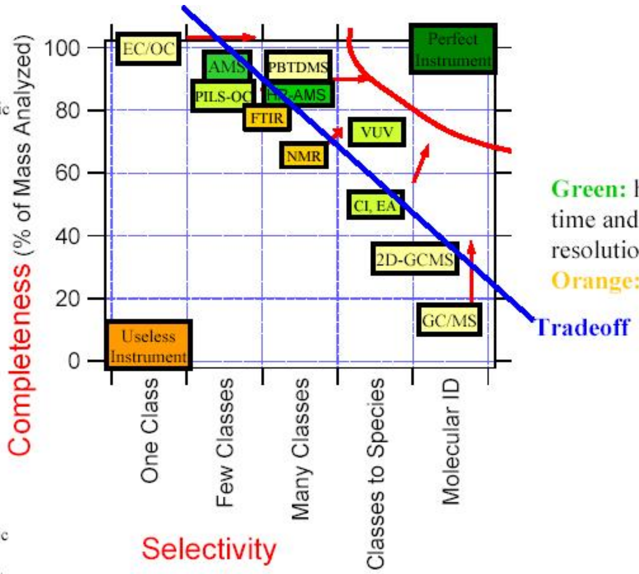


Off-line analysis

Measurement techniques for organic aerosol characterization

13:44

AMS=Aerosol Mass Spectrometer
CI=Chemical Ionization
EA= Electron Attachment
EC/OC=Elemental/Organic Carbon
FTIR=Fourier Transform Infrared Spectroscopy
GC/MS=Gas Chromatography/Mass Spectrometry
2D-GCMS=Two-Dimensional Gas Chromatography/Mass Spectrometry
HR-ToFAMS=High-Resolution Time-of-Flight Mass Spectrometer
NMR=Nuclear Magnetic Resonance
PBTDMS=Particle Beam Thermal Desorption Mass Spectrometer
PILS-OC= Particle-Into-Liquid-Sampler for Organic Carbon
VUV= Vacuum Ultraviolet

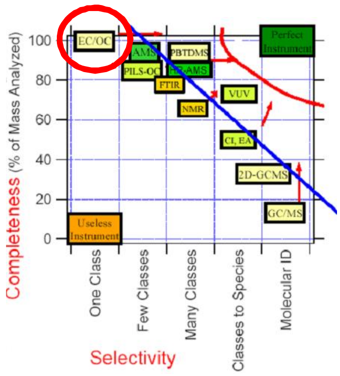


Green: higher time and size resolution
Orange: lower

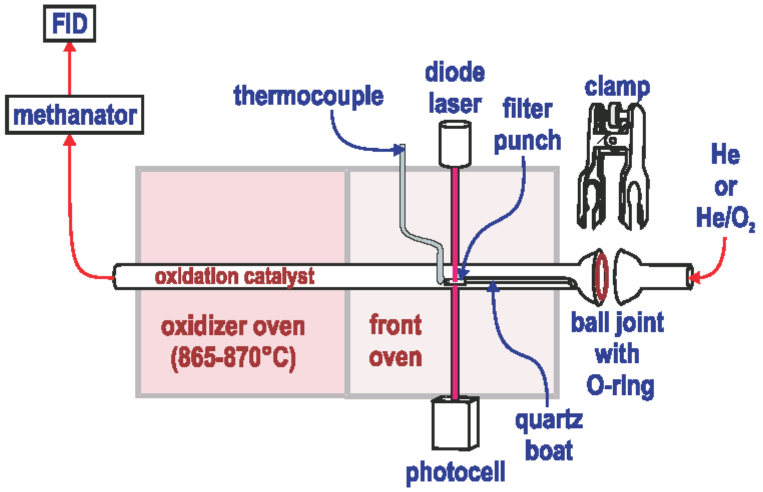
Produced by J. Jimenez

OC/EC-Determination

Thermal-optical analyzer

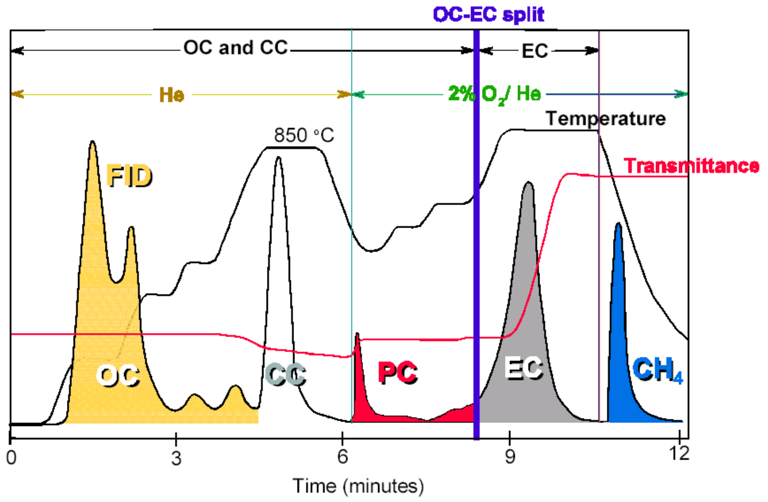


Evolved gas analysis (EGA) by thermal-optical analyzer



Max R. Peterson and Melville H. Richards, **2002**

Evolved gas analysis (EGA) by thermal-optical analyzer

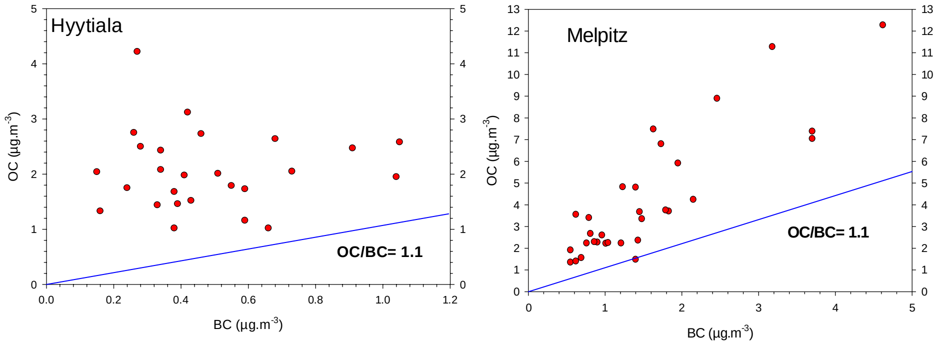


Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak.

⇒ time resolution about 30 min
⇒ no species information but a lot of data available

NIOSHmethod 5040, **1999**

Evolved gas analysis (EGA) by thermal-optical analyzer



⇒ OC/BC ratio at the remote site is higher and more variable than at the urban site

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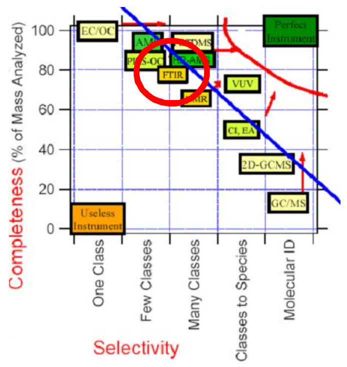
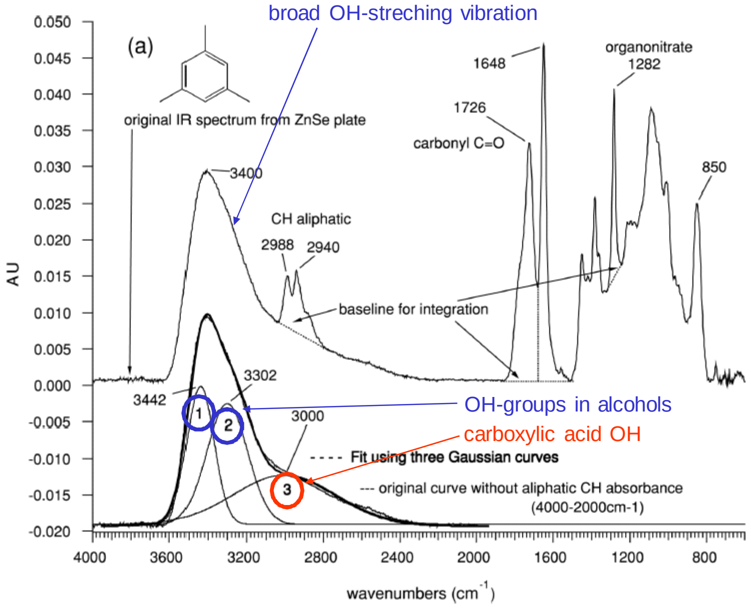
Fourier-Transform Infrared Spectroscopy (FTIR)

- FTIR spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an IR light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule.
- For example, the C=O stretch of a carbonyl group appears at around 1700cm^{-1} in a variety of molecules.
- ⇒ correlation of the band wavenumber position with the chemical structure is used to identify and quantify functional groups
- ⇒ Impaction of size segregated particles (multistage impactor) on Zinc-selenide plates, (25 mm * 2 mm)





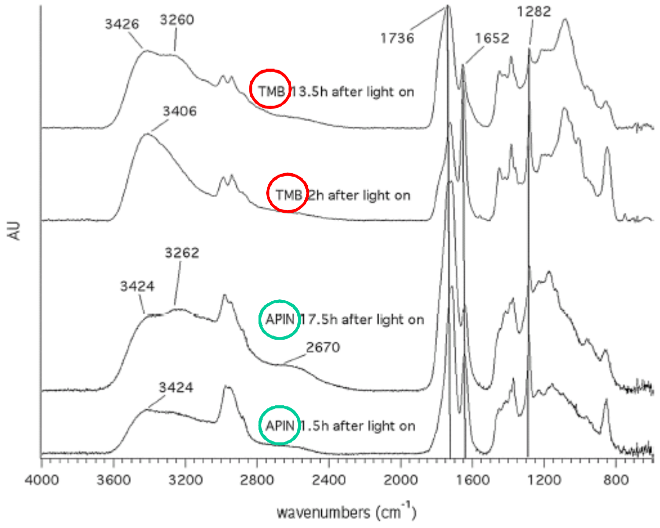
broad OH-streching vibration

OH-groups in alcohols

carboxylic acid OH

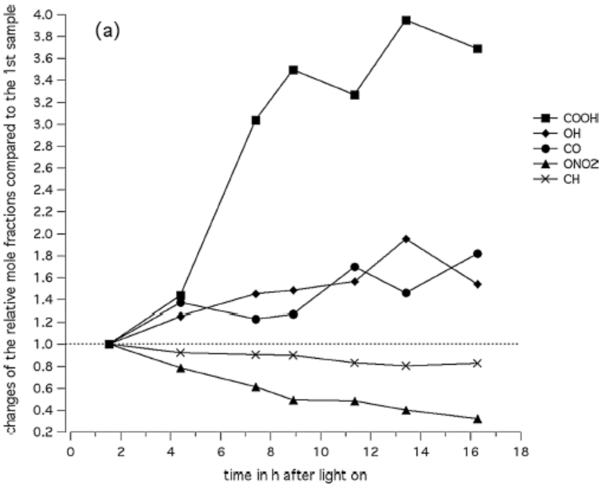
Sax et al., **2005**, *Aerosol Sci. Technol.*

Comparison of TMB (upper two traces) and APIN-IR spectra at the beginning of the experiment and after 13.5 h and 17.5 h



Sax et al., **2005**, *Aerosol Sci. Technol.*

Time-resolved changes of mole fractions of five functional groups present in SOA from TMB

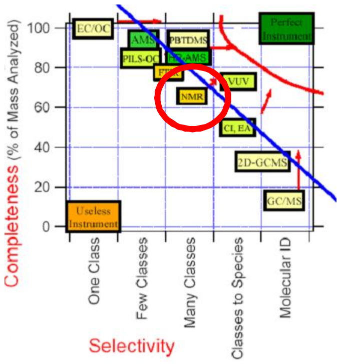


⇒ especially interesting for functional group analysis
⇒ no thermal stress for the analytes (thermally unstables compounds)

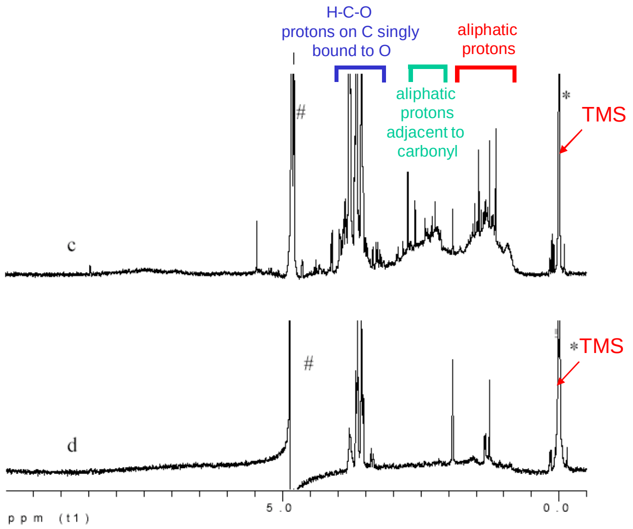
Sax et al., **2005**, *Aerosol Sci. Technol.*

Nuclear Magnetic Resonance Spectroscopy (^{1}H- or ^{13}C-NMR)

- Nuclear magnetic resonance (NMR) is a physical phenomenon based upon the magnetic property of an atoms‘s nucleus. The individual nuclei are surrounded by orbiting electrons, which will partially shield the nuclei. The amount of shielding depends on the exact local environment.
- ⇒ resonance frequency depends from the chemical structure and can be used to identify and quantify molecular structures
- ⇒ filter sampling and extraction

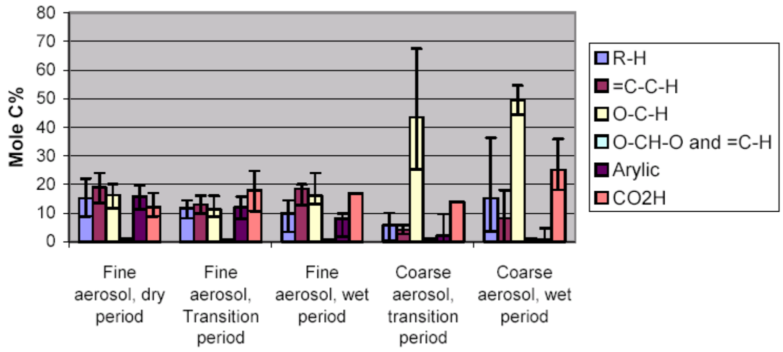


Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)



Descari et al., **2000,** J. Geophy. Res.; Tagliavini et al., **2005**, ACPD

Comparison of functional groups of different aerosol samples from SMOCC campaign (Amazon, Brasil)

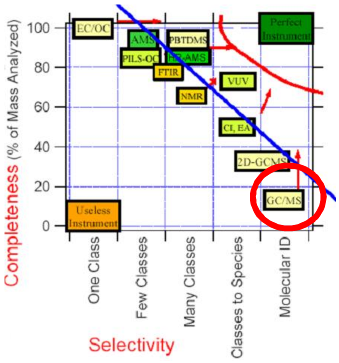


- ⇒ used for source apportionment
- ⇒ processes such as aging might be observable
- ⇒ analysis of non-volatile compounds
- ⇒ 1 mg of OC necessary
- ⇒ long sampling times (1-3 days)

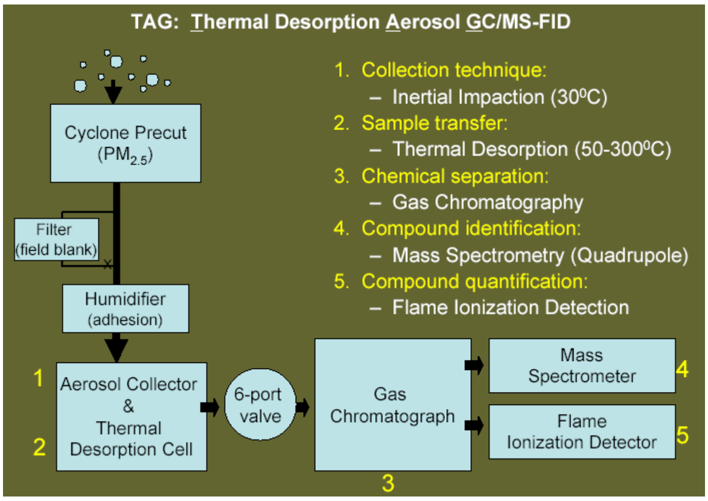
Tagliavini et al., **2005**, ACPD

Off-line techniques based on chromatography

GC and LC



Thermal Desorption Aerosol GC/MS-FID (TAG)

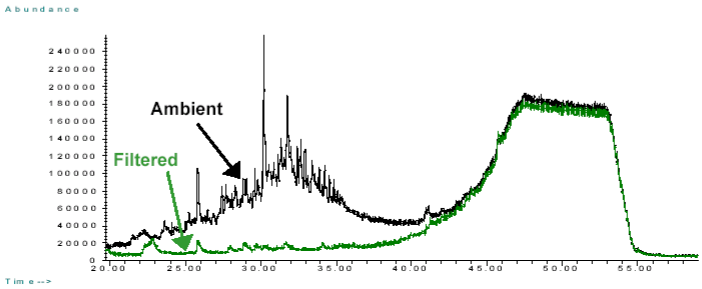


TAG: Thermal Desorption Aerosol GC/MS-FID

1. Collection technique:
   - Inertial Impaction (30^{0}C)
2. Sample transfer:
   - Thermal Desorption (50-300^{0}C)
3. Chemical separation:
   - Gas Chromatography
4. Compound identification:
   - Mass Spectrometry (Quadrupole)
5. Compound quantification:
   - Flame Ionization Detection

Williams et al. **2005**, www.al.noaa.gov/csd/2004/chptdata/17williams.pdf

Thermal Desorption Aerosol GC/MS-FID (TAG)



Chebogue Point, Nova Scotia. August 7, 2004

Sample time: 0.5 hour
Sample Volume: 0.25 m^3
Thermal Desorption: 50-300^{0}C
GC oven temp. range shown here: ~ 45^{0}C to 300^{0}C

Total Organic Aerosol = (Resolved Compounds + Unresolved Compounds + Non-Eluting Compounds)

Williams et al. **2005**, www.al.noaa.gov/csd/2004/chptdata/17williams.pdf

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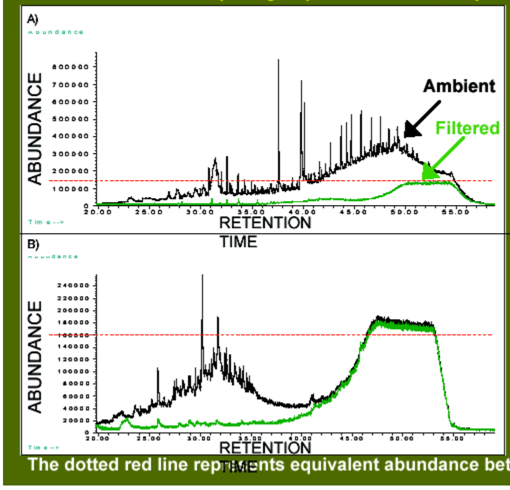
Thermal Desorption Aerosol GC/MS-FID (TAG)

ASIDE: -Compounds collected in Nova Scotia are extremely oxygenated
-Difficult to identify using only **NIST** database, may not be in database



Berkeley, CA
Winter Evening 2004

Resolved Compounds Matched by NIST library: **80%**

Nova Scotia, Canada
Summer Evening 2004

Resolved Compounds Matched by NIST library: **35%**

The dotted red line represents equivalent abundance between graphs A and B.

Williams et al. **2005**, www.al.noaa.gov/csd/2004/chptdata/17williams.pdf

Thermal Desorption Aerosol GC/MS-FID (TAG)

⇒ relatively fast technique
⇒ very good for unpolar, thermally stable techniques with intermediate volatility
⇒ existing MS libraries can be used for compound identification
⇒ not suitable for very polar compounds (e.g. most SOA products)

Williams et al. **2005**, www.al.noaa.gov/csd/2004/chptdata/17williams.pdf

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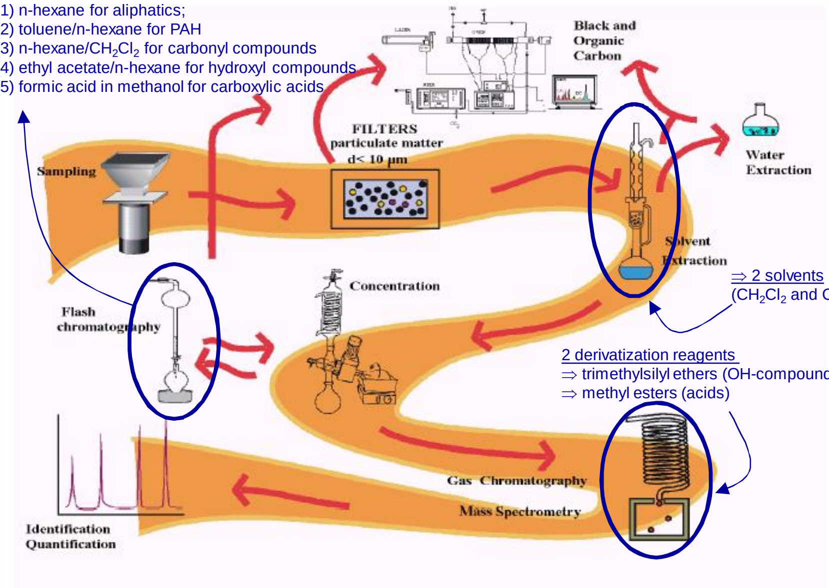
Extraction/derivatisation GC/MS



5 solvents for elution
(1) n-hexane for aliphatics;
(2) toluene/n-hexane for PAH
(3) n-hexane/CH_2Cl_2 for carbonyl compounds
(4) ethyl acetate/n-hexane for hydroxyl compounds
(5) formic acid in methanol for carboxylic acids

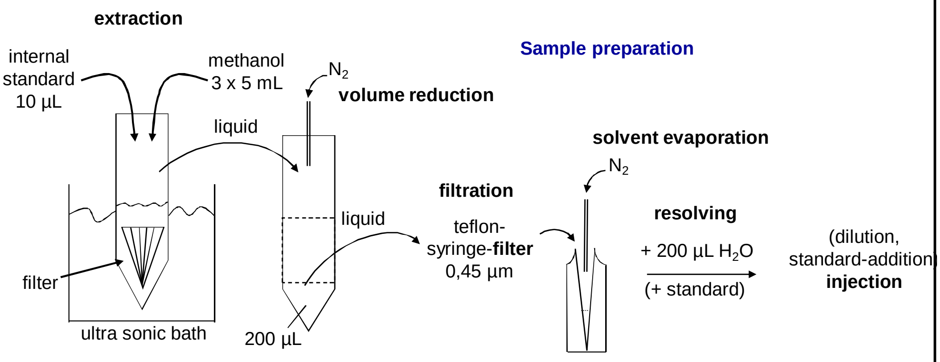
⇒ 2 solvents
(CH_2Cl_2 and CH_3OH)

2 derivatization reagents
⇒ trimethylsilyl ethers (OH-compounds)
⇒ methyl esters (acids)

⇒ Hundrets of compounds
⇒ Used for tracer analysis (often to characterize POA)
⇒ very time consuming

Gogou, Apostolaki, Stephanou **1998**
J. Chromatog. A, 1998, 799, 215.

Organic Aerosol characterization by LC/MS techniques



Sample preparation

extraction

internal standard 10 µL

methanol 3 x 5 mL

liquid

filter

ultra sonic bath

N_2

volume reduction

liquid

200 µL

filtration

teflon-syringe-**filter** 0,45 µm

solvent evaporation

N_2

resolving

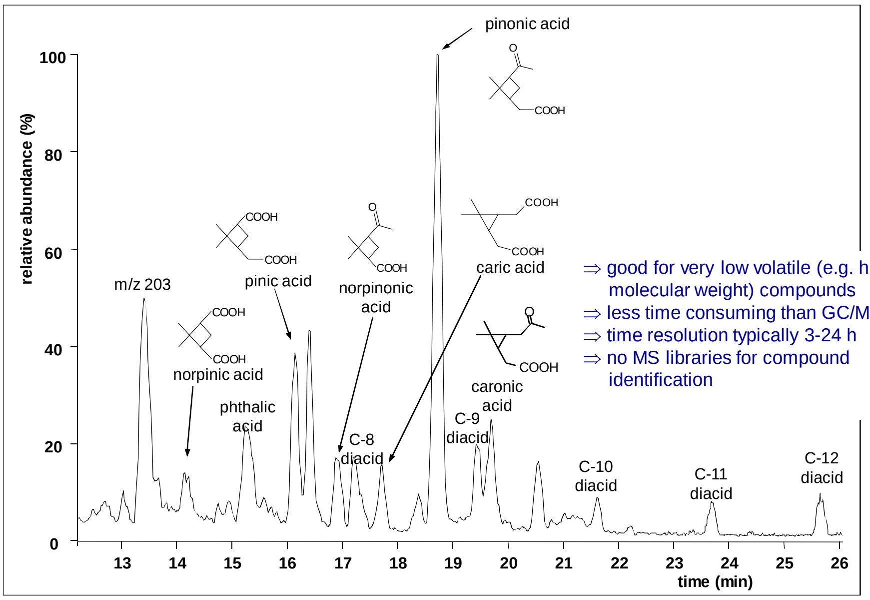
+ 200 µL H_2O

(+ standard)

(dilution, standard-addition)

injection

Base peak chromatogram of an aerosol sample from Hyytiälä



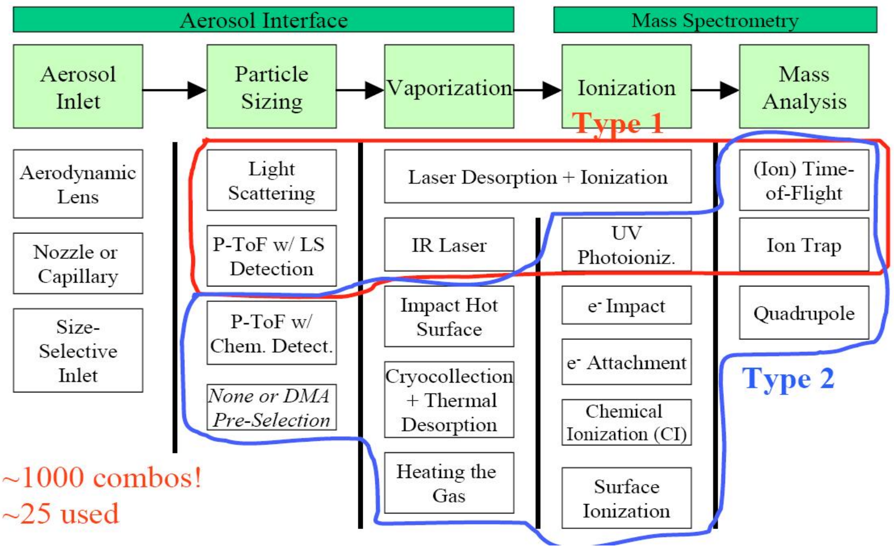
- ⇒ good for very low volatile (e.g. high molecular weight) compounds
- ⇒ less time consuming than GC/MS
- ⇒ time resolution typically 3-24 h
- ⇒ no MS libraries for compound identification

On-line analysis

Aerosol mass spectrometry

13:44

Bausteine von Aerosolmassenspektrometern



Aerosol Interface | Mass Spectrometry

Aerosol Inlet → Particle Sizing → Vaporization → Ionization → Mass Analysis

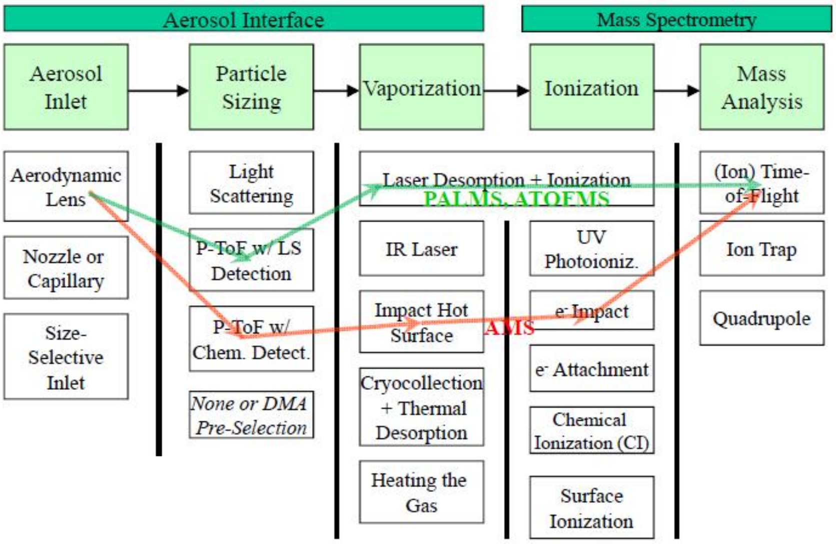
- Aerosol Inlet: Aerodynamic Lens; Nozzle or Capillary; Size-Selective Inlet
- Particle Sizing: Light Scattering; P-ToF w/ LS Detection; P-ToF w/ Chem. Detect.; *None or DMA Pre-Selection*
- Vaporization: Laser Desorption + Ionization; IR Laser; Impact Hot Surface; Cryocollection + Thermal Desorption; Heating the Gas
- Ionization: UV Photoioniz.; e^- Impact; e^- Attachment; Chemical Ionization (CI); Surface Ionization
- Mass Analysis: (Ion) Time-of-Flight; Ion Trap; Quadrupole

Type 1

Type 2

- ~1000 combos!
- ~25 used

Bausteine von Aerosolmassenspektrometern

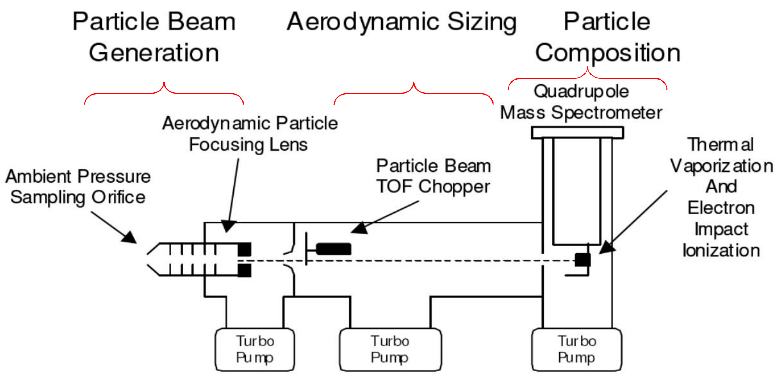


Aerosol Interface			Mass Spectrometry	
Aerosol Inlet	Particle Sizing	Vaporization	Ionization	Mass Analysis
Aerodynamic Lens	Light Scattering	Laser Desorption + Ionization		(Ion) Time-of-Flight
Nozzle or Capillary	P-ToF w/ LS Detection	IR Laser	UV Photoioniz.	Ion Trap
Size-Selective Inlet	P-ToF w/ Chem. Detect.	Impact Hot Surface	e^- Impact	Quadrupole
	None or DMA Pre-Selection	Cryocollection + Thermal Desorption	e^- Attachment	
		Heating the Gas	Chemical Ionization (CI)	
			Surface Ionization	

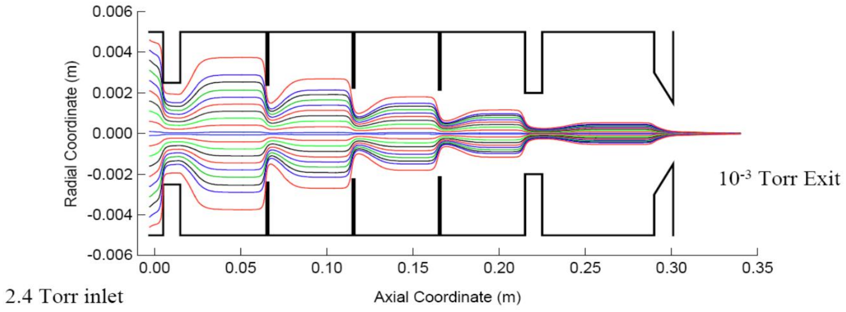
On-line analysis

Thermal Desorption Aerosol MS
z.B. Aerodyne AMS

Genereller Aufbau eines Aerodyne AMS



Aerodynamische Linsen (*particle beam generation*)



Calculated Particle Trajectories, 100 nm (Fluent ver 4.47)
Diameter Unit Density Spheres

Original lens design:
- Liu, P., Ziemann, P. L., Kittelson , D. B., and McMurry, P. H. (1995a). Aerosol Sci. Technol. 22:293–313.
- Liu, P., Ziemann, P. L., Kittelson, D. B., and McMurry, P.H. (1995b). Aerosol Sci. Technol. 22:314–324.

CFD Simulations:
- Zhang, X., Smith, K.A., Worsnop, D.R., Jimenez, J.L., Jayne, J.T., and Kolb, C.E. Aerosol Science and Technology, 36: 617, 2002.
- Zhang, X., Smith, K.A., Worsnop, Jimenez, J.L., Jayne, J.T., D.R., Kolb, C.E., Morris, J. & Davidovits, P., Aerosol Sci. Tech., 38: 619, 2004.

Aerodynamische Linsen II

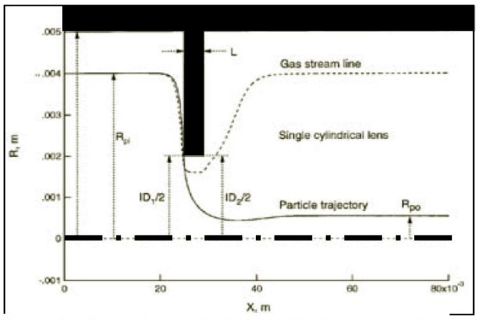


Figure 2. Schematic of a single thin cylindrical lens showing a gas streamline and the trajectory of a 500 nm particle. $Q = 60$ sec/min, $L = 4$ mm, $ID_1 = ID_2 = 2$ mm, $OD = 10$ mm, $\mathrm{Re}_0 = = 12.5$, $P_{\mathrm{up}} = 280$ Pa, $R_{pi} = 4$ mm, $R_{po} = 0.5$ mm.

Note: original lens design by Liu, Ziemann, and McMurry (1995).

Xuefeng Zhang, Kenneth A. Smith, Douglas R. Worsnop, Jose Jimenez,
John T. Jayne, and Charles E. Kolb. A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System: Part I. An Individual Lens or Nozzle Aerosol Science and Technology 36: 617–631 (2002)

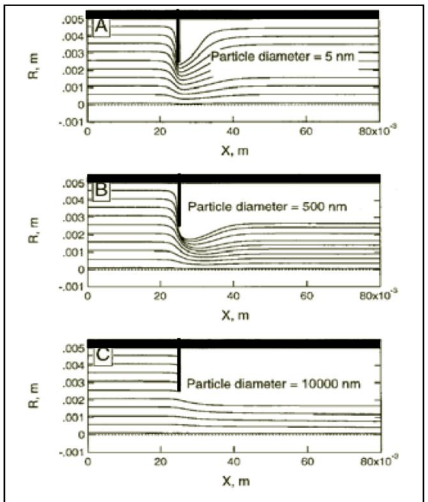


Figure 3. Particle trajectories through a single thin cylindrical lens ($D_p = 5{,}500$, 1000 nm). $L = 0.5$ mm, $ID_1 = ID_2 = 5$ mm, $OD = 10$ mm, $Q = 60$ scc/min, $\mathrm{Re}_0 = 12.5$, and $P_{\mathrm{up}} = 280$ Pa.

Aerodynamische Linsen III

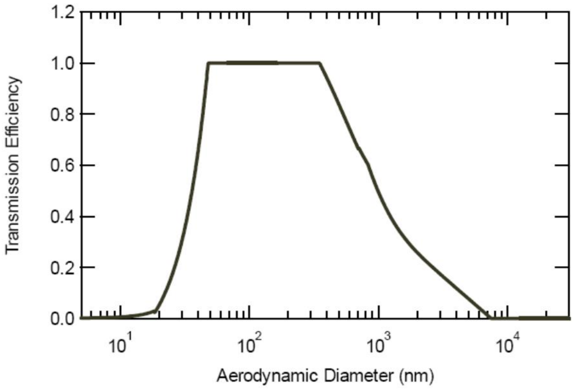


Figure 3.5: Aerodynamic lens transmission efficiency as a function of particle size (Jayne et al., 2000)

Partikelstrahlbreite - Aerodynamische Linsen

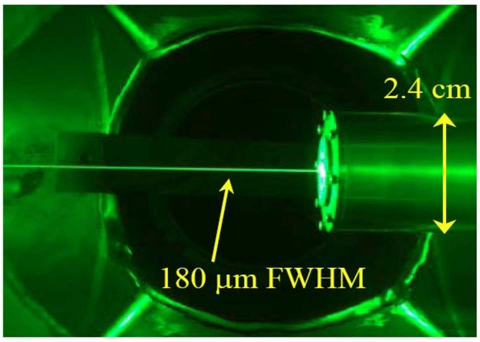


Figure courtesy of Guiseppe Petrucci, Univ. Vermont
http://www.uvm.edu/~gpetrucc/ams/particleinlet.htm

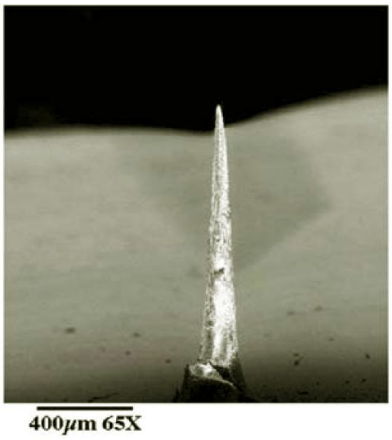
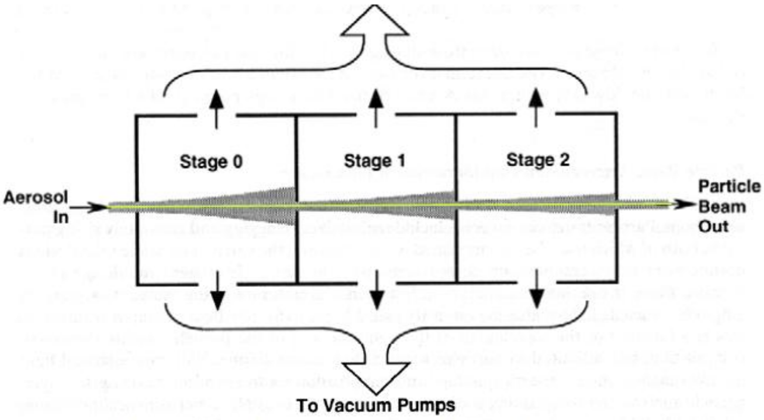


Fig. 6. SEM image of a silicon carbide 'tower' deposited by a focused nanoparticle beam [18].

Heberlein, J., O. Postel, S. Girshick, P. McMurry, W. Gerberichc, D. Iordanoglou, F.D. Fonzo, D. Neumann, A. Gidwani, M. Fan, and N. Tymiakc, *Thermal plasma deposition of nanophase hard coatings.* Surface and Coatings Technology, 2001. **142-144**: p. 265-271.

Differentielles Pumpen – Anreicherung der Partikelphase

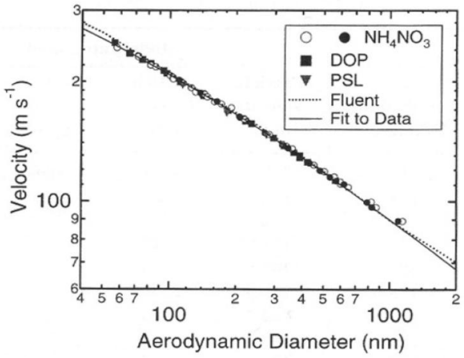


- E.g. in AMS: particles concentrated by 10^7 with respect to gas

Wexler, A. S., and Johnston, M. V. (2001). "Real-time single-particle analysis." Aerosol Measurement: Principles, Techniques, and Applications, P. A. Baron and K. Willeke, eds., Wiley-Interscience, New York, 365-386.

Größenklassifizierung
(aerodynamic sizing - particle time-of-flight)

- Upon expansion into vacuum, particles acquire size-dependent velocity
- It's there, so you may as well use it to measure particle size

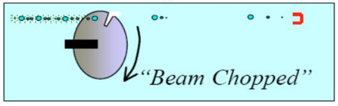


Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

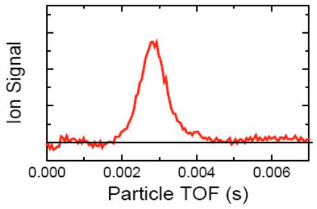
Möglichkeit des AMS-Betriebs

Size Distribution

(limited composition info)

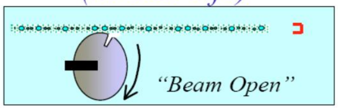


Spectrometer Setting is Fixed
(small subset of 0-300 amu)

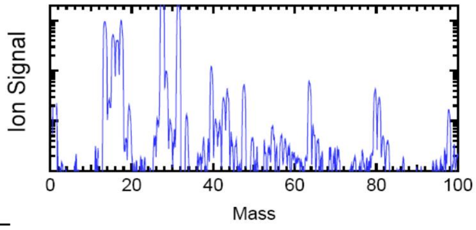


Average Composition

(no size info)



Spectrometer is Scanned
(0-300 amu)



Verdampfung und Ionisation (*particle composition*)

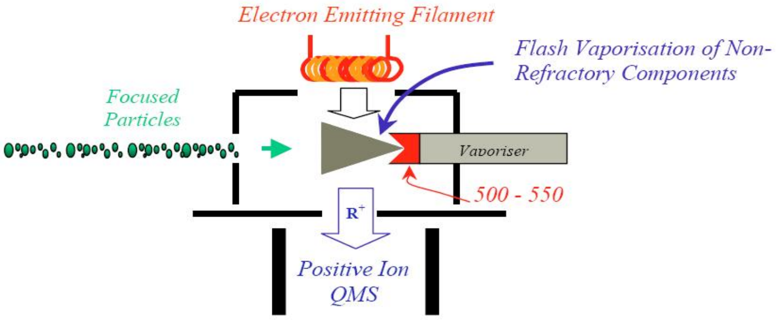


Figure 3.6: Particle vaporisation and ionisation cell

EI-Massenspektren eines AMS

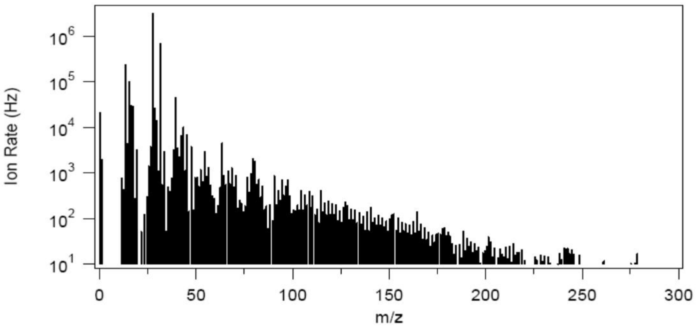
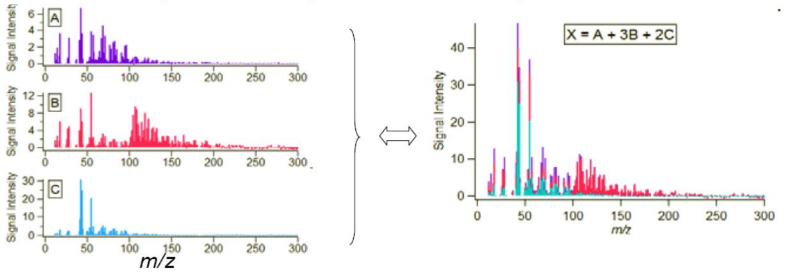


Figure 3.7: An example mass spectrum calculated from the difference between two spectra recorded in the 'open' and 'blocked' beam positions.

Dekonvolution der AMS Daten

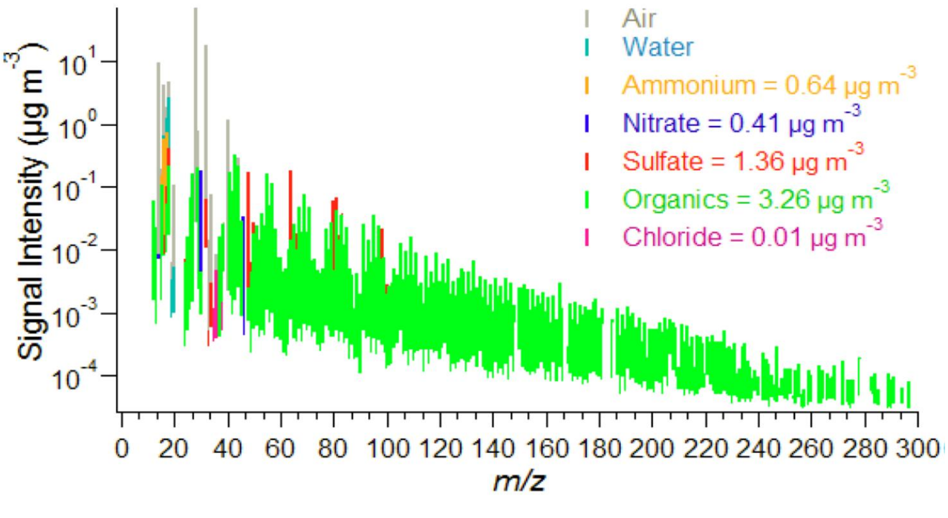
A measured AMS mass spectrum is essentially the linear superposition of the distinctive mass spectra of components in the analyte:



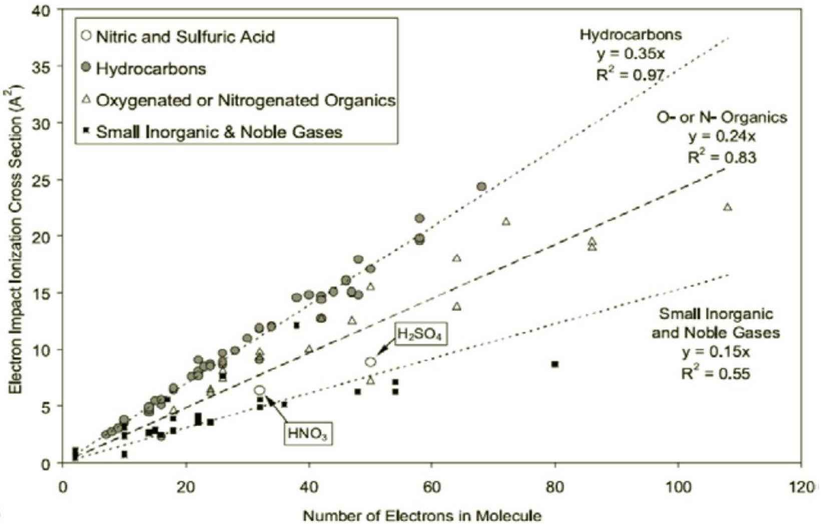
$$\mathbf{ms}_t = c_1 \cdot \mathbf{ms}_1 + c_2 \cdot \mathbf{ms}_2 + \ldots + c_n \cdot \mathbf{ms}_n + \varepsilon_i$$

$\mathbf{ms}_t$ – observed mass spec vector
$\mathbf{ms}_n$ – mass spec vector of component n
c_n – concentration of component n
ε_i – residual vector

AMS Ambient Mass Spectrum



Ionisationseffizienz und Quantifizierung



On-line analysis

Laser Ablation Aerosol MS
z.B. Aerosol-Time-of Flight MS (ATOFMS)

ATOFMS (Hinz et al. Prather et al.)

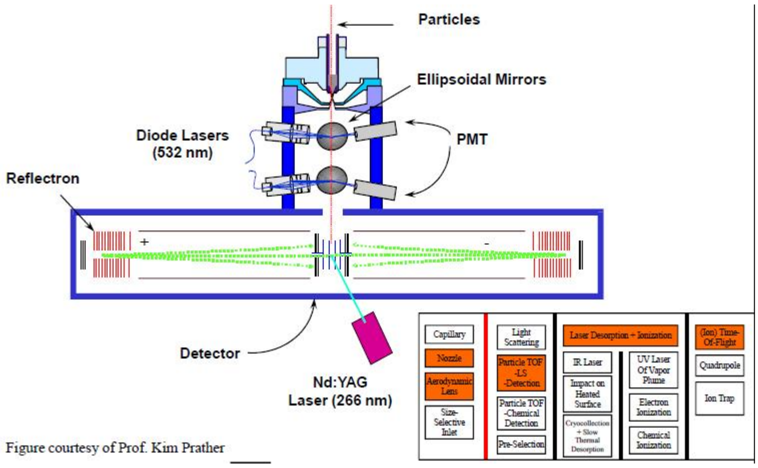


Figure courtesy of Prof. Kim Prather

Andere Namen/Abkürzungen:
ATOFMS - Aerosol Time-of-Flight Mass Spectrometer
PALMS - Particle Analysis by Mass Spectrometry
SPLAT - Single-Particle Laser Ablation Mass Spectrometer:

⇒ charakteristisch für Laser Ablations-Systeme – starke Fragmentierung

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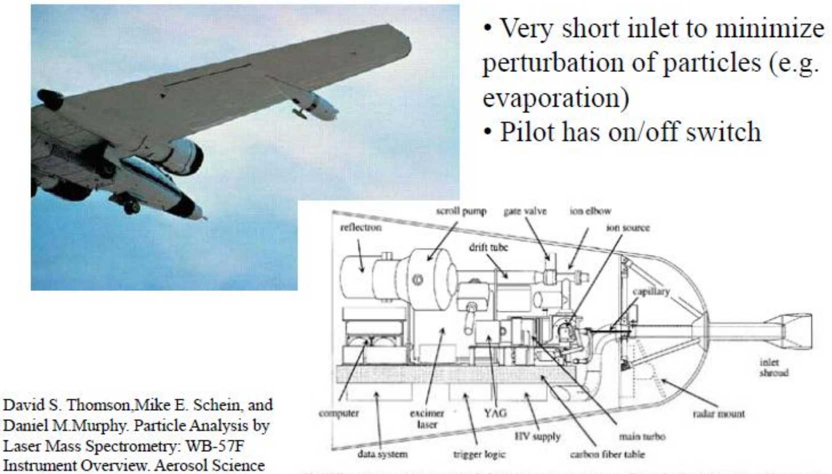
Online Aerosol MS



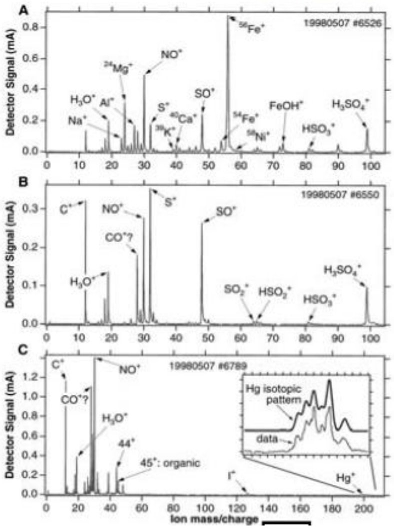
- Very short inlet to minimize perturbation of particles (e.g. evaporation)
- Pilot has on/off switch

FIGURE 3. Schematic layout of the PALMS instrument components. For scale, the carbon fiber table is 122 cm (48") long.

David S. Thomson,Mike E. Schein, and Daniel M.Murphy. Particle Analysis by Laser Mass Spectrometry: WB-57F Instrument Overview. Aerosol Science and Technology 33:153-169 2000.

Beispiele für Online Aerosol MS: Stratosphärische Aerosole

Murphy et al. (1998) Science, 282, 1664



- Several common types of positive ion spectra in the stratosphere.
- The most common type contained iron, magnesium, and other metals as well as sulfate (A). About half of the stratospheric spectra had a large Fe peak.
- Between 20 and 40% of the spectra obtained more than 2 km above the tropopause showed little Fe, Hg, K, or other metals (B).
- Some organic material and NO^+ was almost always present.
- Some particles contained mercury (C), usually with a distinctive pattern of other peaks including a large C^+ peak and a peak at $m/z = 127$ that is presumed to be I^+.
- These spectra were obtained within minutes of each other in an otherwise fairly homogeneous air mass at 19 km

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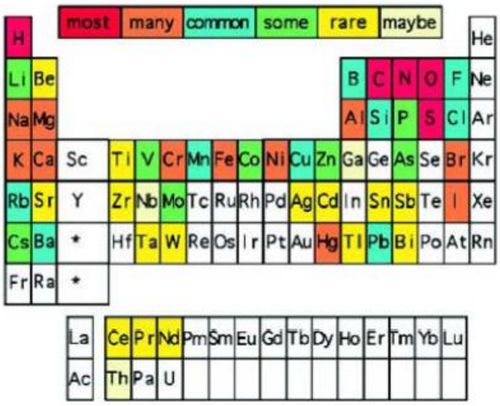
Beispiele für Online Aerosol MS: Stratosphärische Aerosole

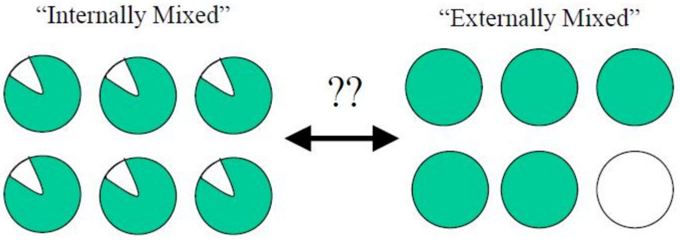
Fig. 9. Elements observed in aerosol particles at altitudes above 5 km. Frequencies are approximate because of differing ionization efficiencies. Elements with a distinctive signature of isotopes are also more likely to be unambiguously observed than those with only one isotope. Certain elements are likely to be undercounted because of spectral interferences. For example, the main isotopes of Si and Ti can be obscured by CO and SO, respectively.



D. M. Murphy*, D. S. Thomson, M. J. Mahoney. In-Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols from 5 to 19 km. Science 282: 1664-1668, 1998.

Ensemble vs. Single particle (AMS vs. ATOFAMS)

For example: 17% of the mass is organics, 83% is sulfate



- Single Particle instruments DIRECTLY detect the mixing state
  - Superior for e.g. ice nucleation studies (also refractory)
  - Ensemble averaging instruments only provide indirect info. on mixing state
- SP also superior for low number density situations

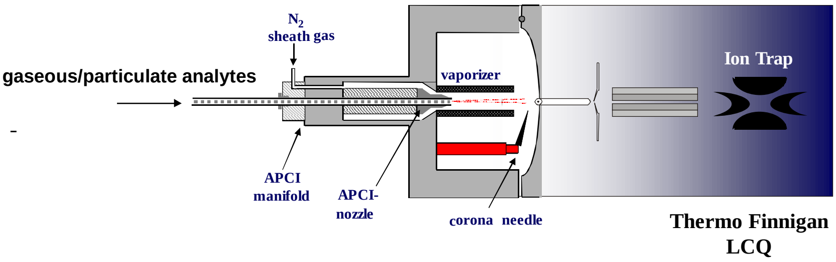
On-line analysis

APCI-MS (Atmospheric Pressure Chemical Ionization)

Atmospheric Pressure Chemical Ionization Ion Trap MS APCI-MS

Atmospheric Pressure Chemical Ionization (APCI)
firstly introduced by Horning and coworkers in 1974 as an ionization technique for LC/MS

⇒ soft ionization technique



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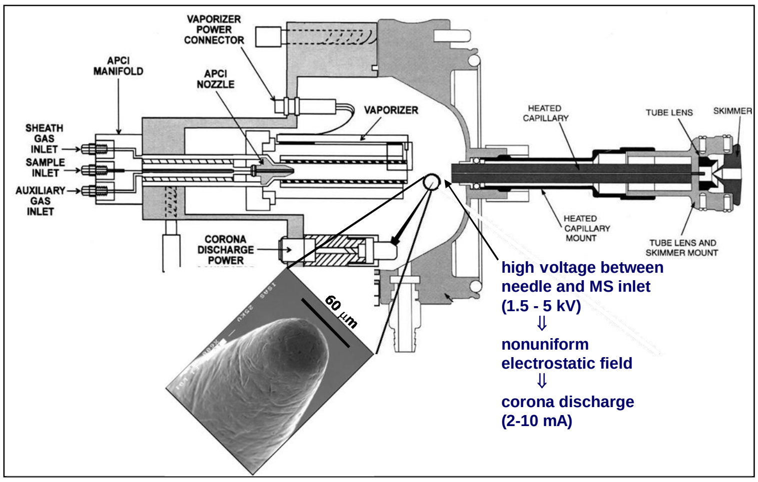
APCI source



high voltage between needle and MS inlet (1.5 - 5 kV)
⇓
nonuniform electrostatic field
⇓
corona discharge (2-10 mA)

Detection of positiv ions:

$N_2 + e^- \rightarrow N_2^{+\cdot} + 2e^-$
$N_2^{+\cdot} + 2N_2 \rightarrow N_4^{+\cdot} + N_2$
$N_4^{+\cdot} + H_2O \rightarrow H_2O^{+\cdot} + 2N_2$
$H_2O^{+\cdot} + H_2O \rightarrow H_3O^+ + OH^\cdot$

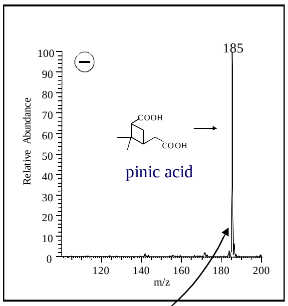
$H_3O^+ + n\,H_2O \rightarrow H_3O^+ \cdot (H_2O)_n$

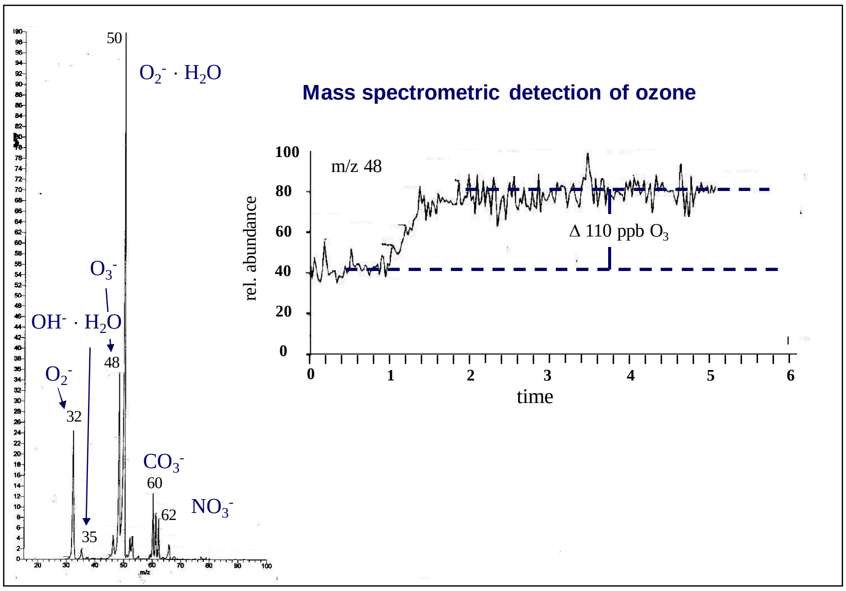
Proton transfer reactions
$H_3O^+ + M \rightarrow [M+H]^+ + H_2O$

Detection of negative ions:

$O_2 + e^- \rightarrow O_2^{-\cdot}$
$O_2^{-\cdot} + n\,H_2O \rightarrow O_2^{-\cdot} \cdot (H_2O)_n$

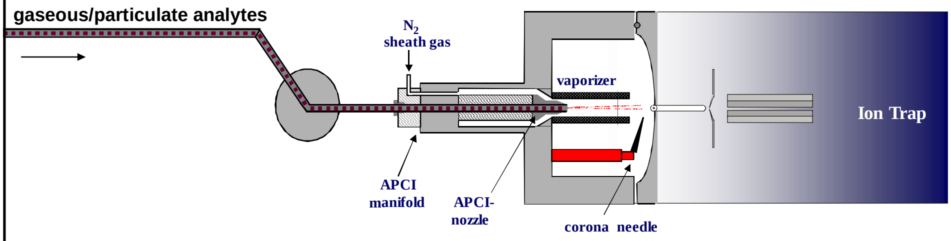
Proton abstraction:
$O_2^{-\cdot} \cdot (H_2O)_n + M \rightarrow [M-H]^- + HO_2 + n\,H_2O$



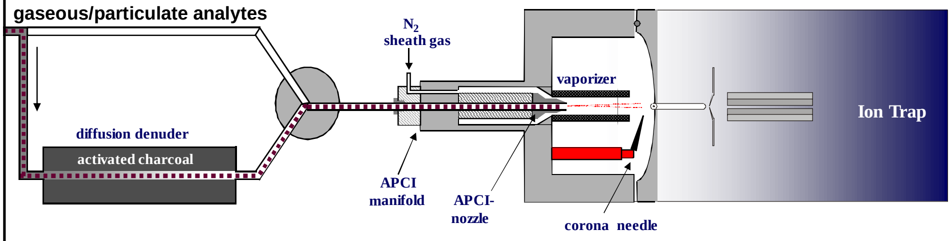


Mass spectrometric detection of ozone

Sample introduction into the APCI source



Sample introduction into the APCI source



gaseous/particulate analytes

N_2 sheath gas

vaporizer

diffusion denuder

activated charcoal

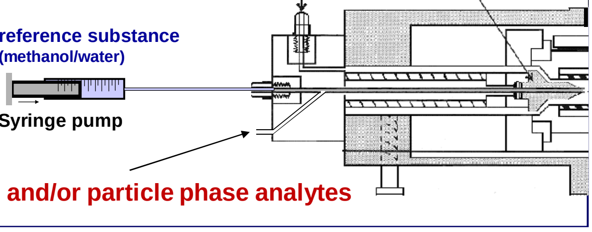
Ion Trap

APCI manifold

APCI-nozzle

corona needle

Quantification on-line APCI-MS



Sheath gas

APCI-nozzle

reference substance
(methanol/water)

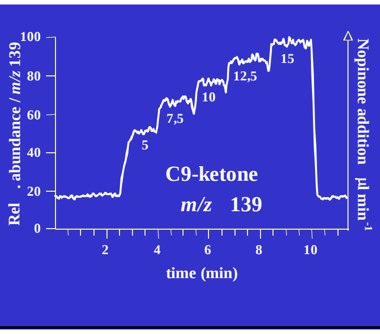
Syringe pump

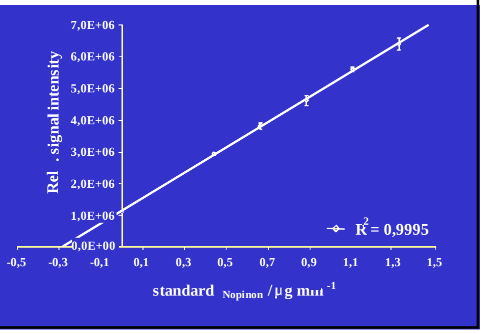
gas- and/or particle phase analytes

Sheath gas: 9 L min^{-1}

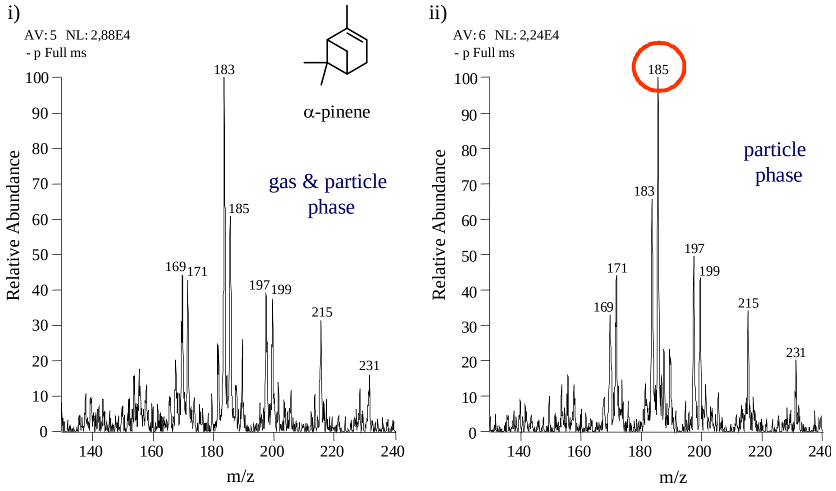
Flow rate: 0-15 ml min^{-1}

$T_{evaporator}$ = 450°C

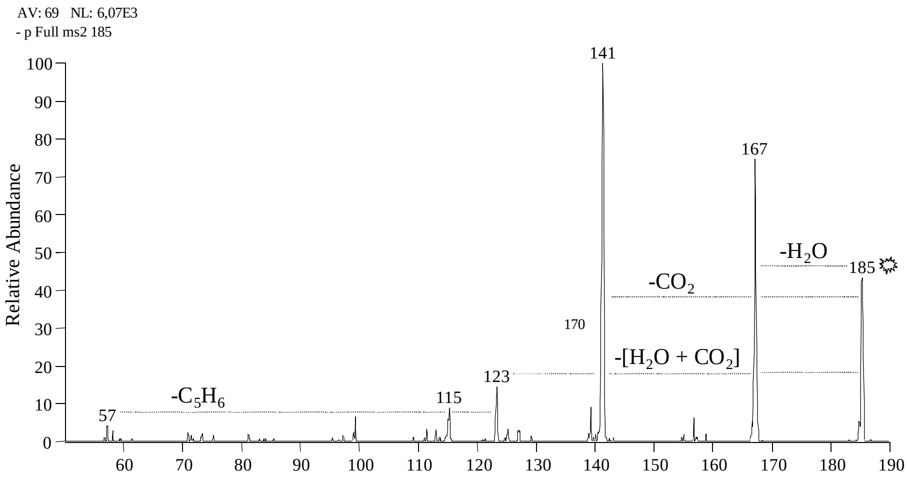




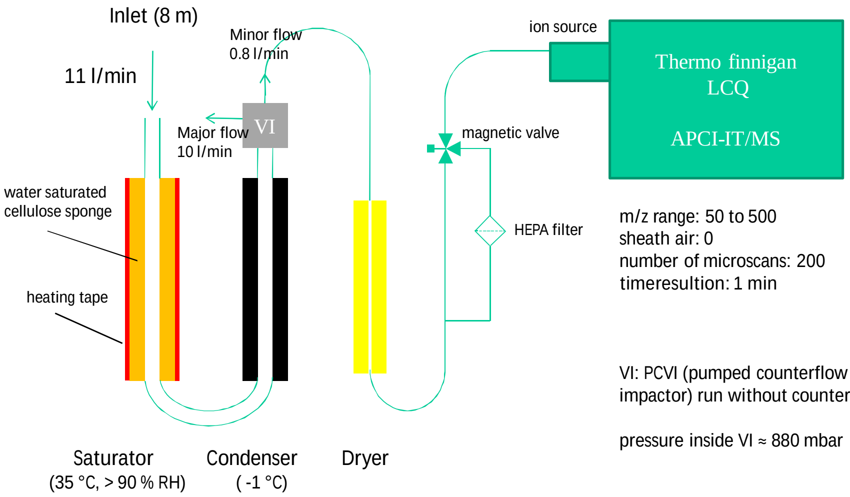
APCI mass spectra of α-pinene/ozone reaction products



Second order negative ion CID mass spectra of m/z 185



APCI-MS in the field

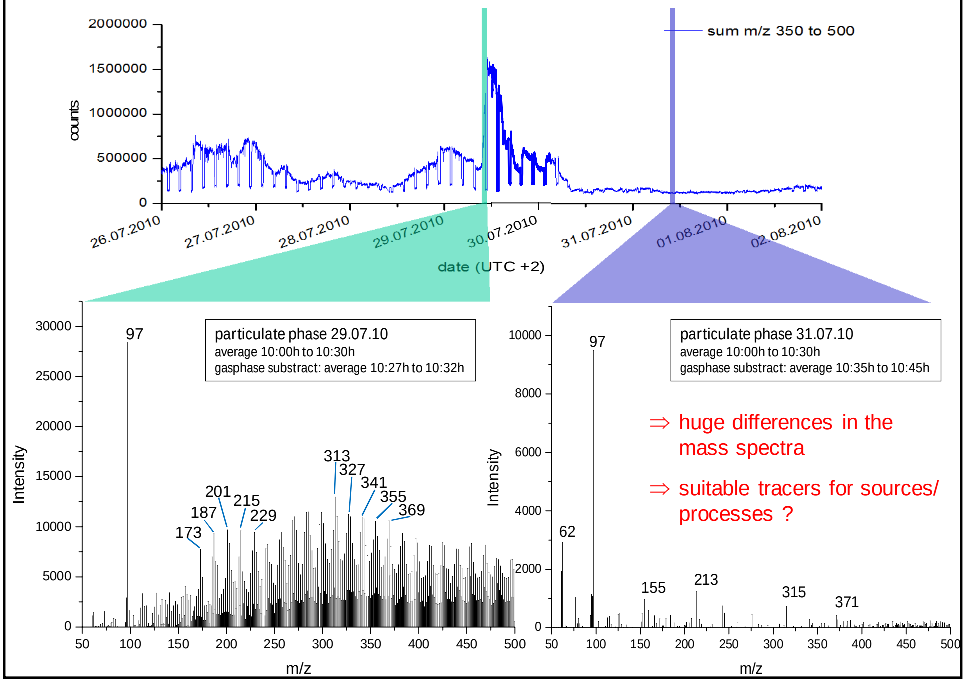


m/z range: 50 to 500
sheath air: 0
number of microscans: 200
timeresultion: 1 min

VI: PCVI (pumped counterflow virtual impactor) run without counterflow

pressure inside VI ≈ 880 mbar

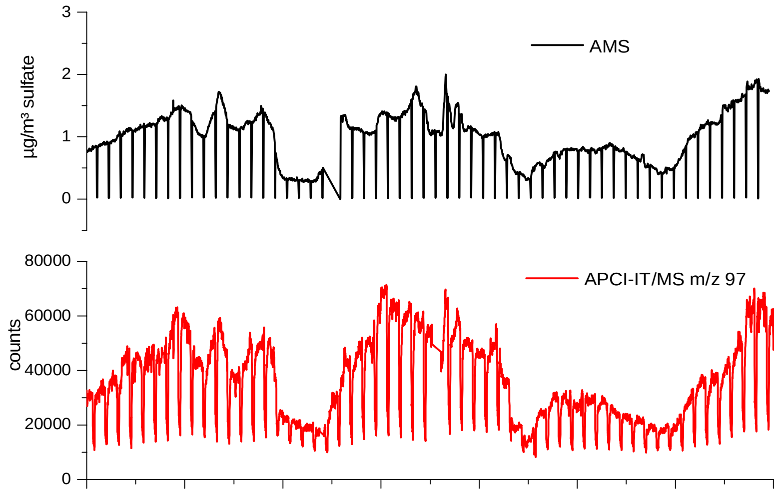
mVACES: Geller et al., *Journal of Aerosol Science*, 2005, 36, p. 1006-1022
VI: Boulter et al., *Aerosol Science and Technology*, 2006, 40, p. 969-976



⇒ huge differences in the mass spectra

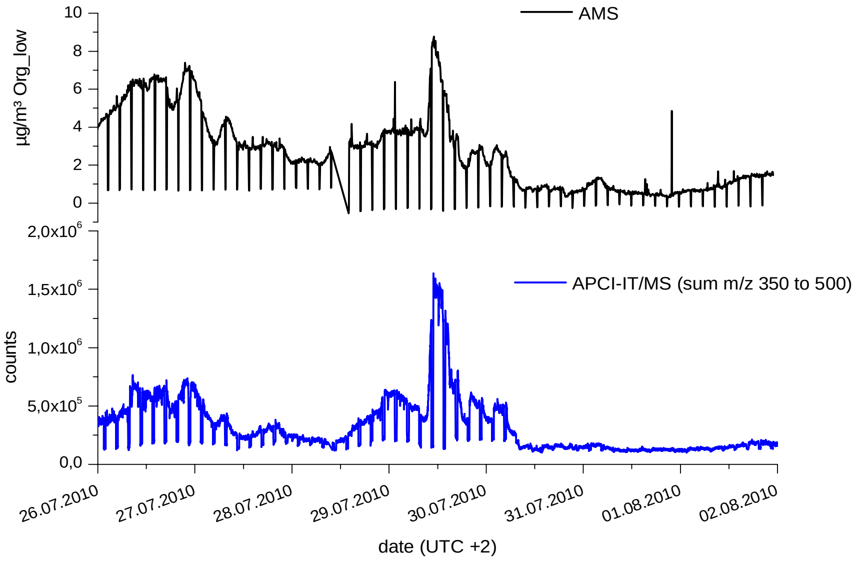
⇒ suitable tracers for sources/ processes ?

Intercomparison between AMS and APCI-IT/MS - sulfate



⇒ very good correlation with AMS data

Intercomparison between AMS and APCI-IT/MS - Organics



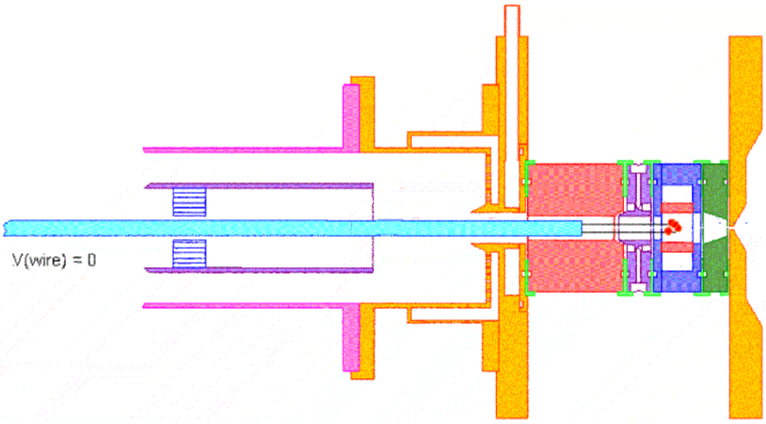
⇒ very good correlation with AMS data

⇒ running both in parallel for quantification

On-line analysis

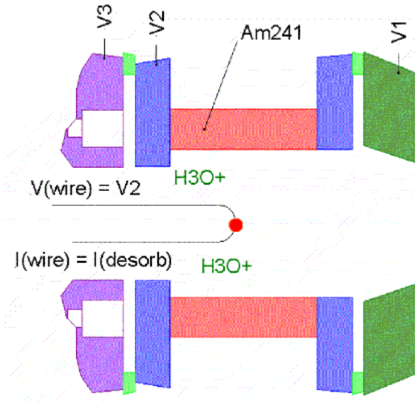
TDCIMS

13:44



- Air with charged particles enters electrostatic precipitator
- Collection filament is biased at a ca. 4 Kvolts with respect to chamber walls.
- Particles cross flow streamlines to collect on metal filament
- After a few minutes, wire is inserted into ion source for sample analysis

Thermo Desorption Chemical Ionization Mass Spectrometry



Desorption

- Wire momentarily heated at temperatures up to 300 °C to desorb sample
- Neutral compounds are ionized using chemical ionization, e.g.: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$
- Reagent ions are created by particles emitted from the source, generating mostly $H_3O^+$and O_2^-
- Ionized analyte injected into a quadrupole mass spectrometer for analysis

⇒ the only aerosol MS for chemical investigation of nm particles
⇒ complicated and bulky instrumentation (e.g. charger)
⇒ ammonium sulfate could account for all of the sampled nanoparticle mass