Lecture 4: Chemical Transport in the Atmosphere

Suggested Reading: SP Chapter 17

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Brian Toon (PAOS)

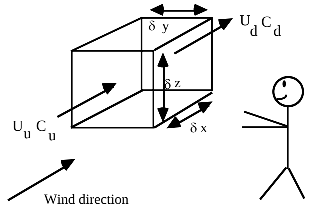
The Aerosol Continuity Equation
A. transport

- The change in the concentration of a chemical often can be written as

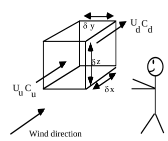
$$\frac{\partial C}{\partial t} = P - LC$$

- Here L is the loss rate, P is the production rate, and C is the species concentration (per unit volume).

How do we account for the effects of transport on C?



- **An observer standing at a fixed point in space measures changing concentrations. The observer must account for the chemical sources and sinks as well as for the motion of the air. This is called an Eulerian measurement since it is at a point.**



•**The flux of material into the upwind side of the box is $U_u C_u$** **(particles per cm^2 per sec.)**

•**The total number of particles being added per second is $U_u C_u$dydz (particles per second), where dydz is the area of the open face of the box.**

•**Therefore, considering that material is also leaving the box on the downwind side, the total amount of material added to the box per second, divided by the volume of the box so that we have the particles added cm^{-3} s^{-1}, is**

$$\frac{\partial C}{\partial t} = (\mathbf{U}_u \mathbf{C}_u - \mathbf{U}_d \mathbf{C}_d) / \mathbf{dx} = -\mathbf{dUC} / \mathbf{dx}$$

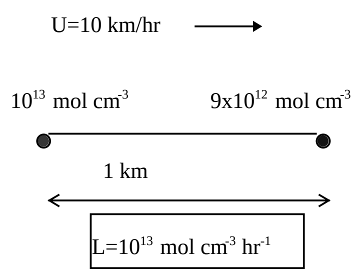
Considering all three directions and adding the sources and sinks, we arrive at the flux form of the continuity equation

$$\frac{\partial C}{\partial t} = -\frac{\partial (UC)}{\partial x} - \frac{\partial (VC)}{\partial y} - \frac{\partial (WC)}{\partial z} + \text{P-LC}$$

This is often called the total derivative in

$$\frac{dC}{dt} = P - LC$$

Example of flux based Eulerian transport:



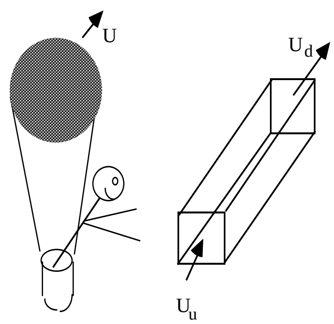
- **Assume the wind speed is constant at 10 km hr^{-1}.**
- **Assume the concentration declines by 10^{12} molecules cm^{-3} km^{-1} in the wind direction.**
- **Assume the concentration declines by 10^{13} molecules cm^{-3} hr^{-1} due to a chemical sink.**

The rate of change in the concentration at the fixed downwind position is

$$\frac{\partial C}{\partial t} = -10^{13}\frac{\text{mol}}{\text{hr}} - (10\frac{\text{km}}{\text{hr}})(\frac{9\text{x}10^{12} - 10^{13}}{1}\frac{\text{mol}}{\text{km}}) = 0$$

Hence, in this example the advection by the wind completely masks the ongoing chemical loss of the material.

The Lagrangian form of the continuity equation

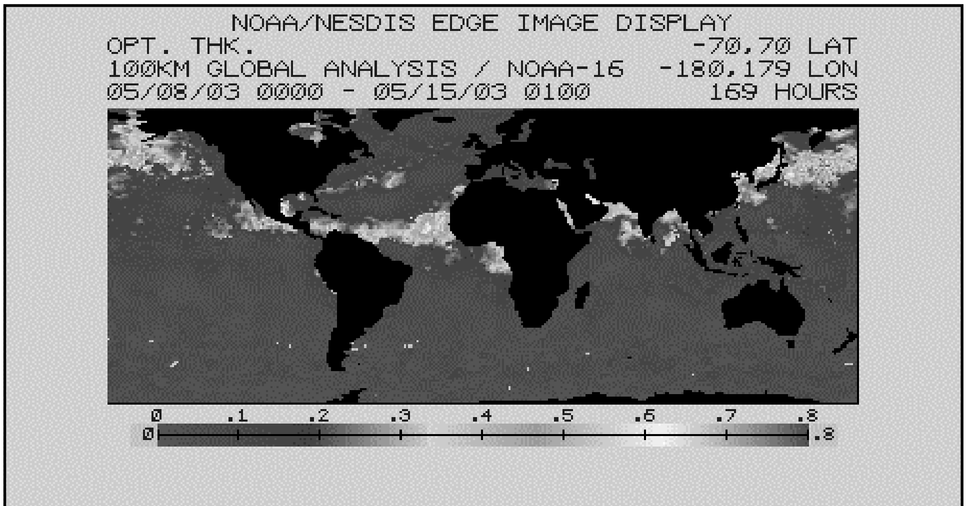


An observer moving with the wind, so that the same air parcel is always observed, only has to account for physical and chemical changes within the air parcel, and not for air motions, to understand how the mixing ratio varies.

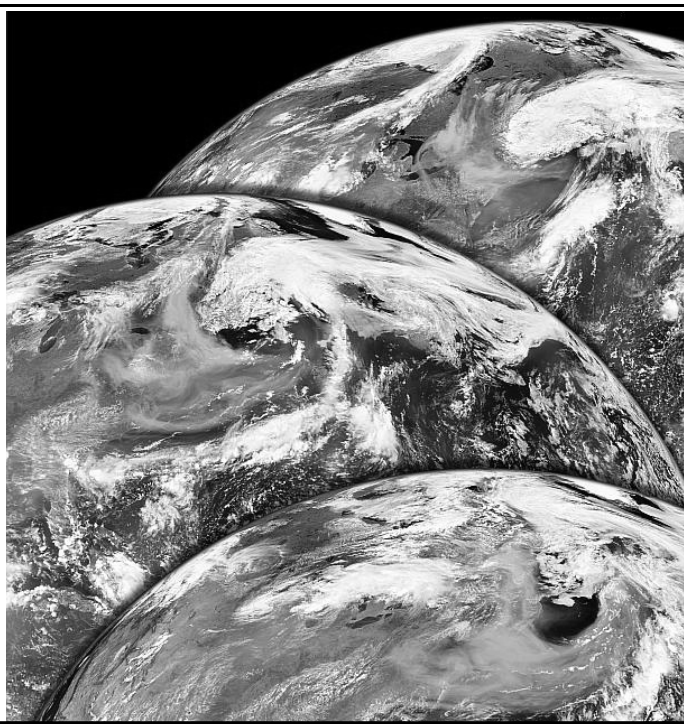
The Lagrangian form of the continuity equation

Since neither air molecules, nor the species being observed can be lost from within the parcel, the ratio of the species concentration to the air density is not changed no matter how winds distort the volume of the air parcel.

$$\frac{d(C/\rho)}{dt} = (P - LC)/\rho$$

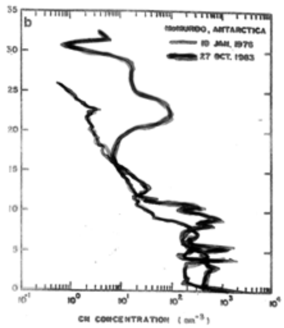


A view of aerosol transport,
There were large fires in Russia prior to this time period,
and dust storms in Africa. Can you tell the source and sink regions just by glancing at the distributions and knowing the winds?



Transport of forest fire smoke in July 2002 from Seawifs

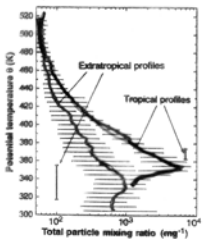
Evidence for sulfuric acid nucleation in the stratosphere



Polar nucleation layer

Hofmann and Rosen GRL 12, 13, 1985

Mixing ratios can identify source and sink regions



Tropical nucleation

Brock et al Science, 270, 1650, 1995

The diffusion approximation in the continuity equation

- **Brownian Diffusion occurs due to the relative random motions of air molecules.**

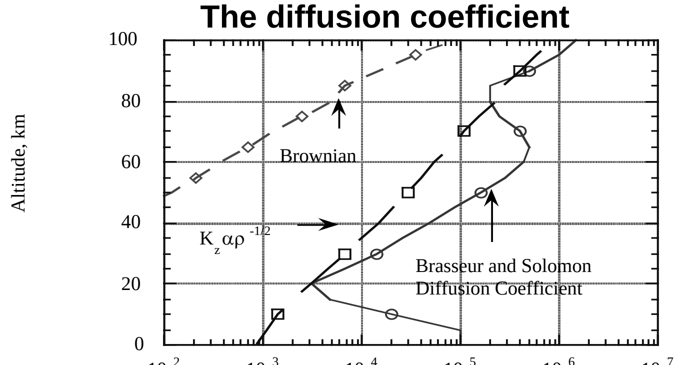
- **The Brownian diffusion equation can be derived from THE KINETIC THEORY OF GASES.**
- **In fluid mechanics turbulent motions can be approximated using equations similar to those from Brownian diffusion.**
- **Therefore, atmospheric chemists have developed an approximate theory which is referred to as eddy diffusion.**
- **Eddy diffusion is not real, often is misleading, and usually is not used to represent turbulence, but instead the large scale circulation. Still it is widely used.**

The diffusive flux, in analogy to thermodynamics is

$$-\rho K_X \frac{\partial(\frac{C}{\rho})}{\partial x}$$

- There is no diffusive flux if the mixing ratio is independent of location.
- The diffusive flux is often referred to as being "down the gradient", which means diffusion causes a positive flux in the direction of decreasing mixing ratio.
- Hence diffusion produces a uniform mixing ratio by transporting material from regions where the mixing ratio is high into regions where the mixing ratio is low

The diffusion coefficient

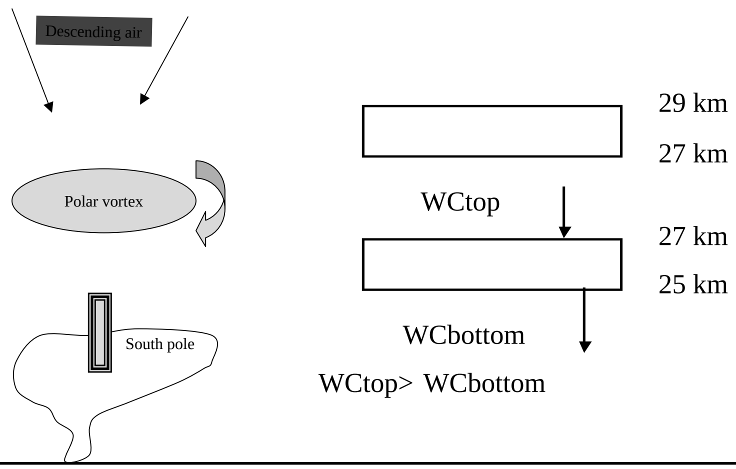


- A typical eddy diffusion coefficient used in one -dimensional models of the atmosphere.
- The Brownian diffusion coefficient is much smaller than the eddy diffusion coefficient below 100 km

Three views of transport

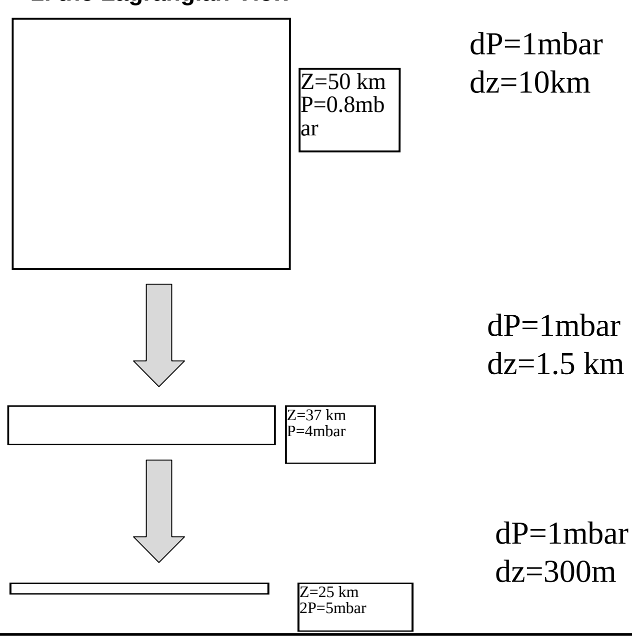
- **Example descent into the polar vortex. During polar night air descends from the mesopause into the lower stratosphere. How can we think about this process?**

1. The Eulerian view



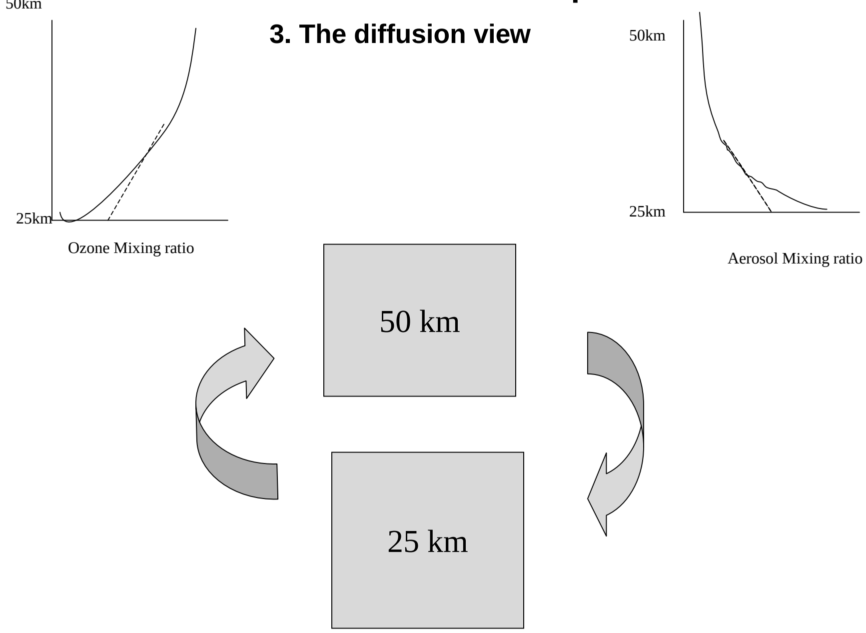
Three views of transport

2. the Lagrangian View



Three views of transport

3. The diffusion view



The ADVANTAGE OF THE DIFFUSION EQUATION IS

THAT IT CAN BE SOLVED RELATIVELY EASILY.

CONSIDER THE FOLLOWING SIMPLE TRANSPORT AND CHEMISTRY PROBLEM

1. ASSUME THAT THE CONCENTRATION OF A MATERIAL IS HELD CONSTANT AT THE SURFACE

2. ASSUME THAT VERTICAL TRANSPORT BY EDDY DIFFUSION ACTS AGAINST A CONSTANT, ALTITUDE INDEPENDENT CHEMICAL LOSS RATE

3. THE STEADY STATE EQUATION TO BE SOLVED IS

$$\frac{\partial\left(\rho K_z \frac{\partial(C/\rho)}{\partial z}\right)}{\partial z} = LC$$

•The LOSS RATE IS THE INVERSE OF THE CHEMICAL LIFETIME

$$\tau_C = 1/L$$

- The AIR DENSITY IS A SIMPLE FUNCTION OF ALTITUDE IF THE ATMOSPHERE IS ISOTHERMAL

$$\rho = \rho_o \exp(-\frac{z}{H})$$

SO WE CAN REWRITE THE EQUATION AS

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{H}\frac{\partial C}{\partial z} - \frac{C}{K\tau} = 0.$$

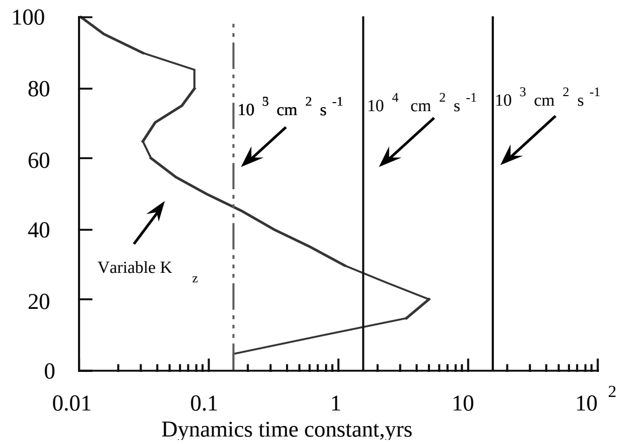
THE SOLUTION TO THE EQUATION IS

$$\frac{C}{\rho} = \frac{C_0}{\rho_0} \exp - \frac{z}{H}(\sqrt{0.25 + \frac{H^2}{K\tau_c}} - 0.5)$$

- The chemical time constant appears in a ratio with another time constant for vertical transport.

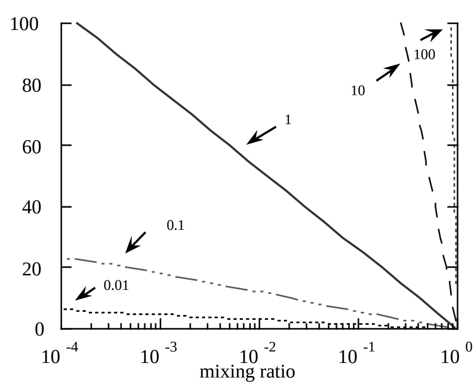
$$\frac{H^2}{K_z} = \tau_d$$

The dynamical lifetime $\tau_d = H^2/K_z$ for several fixed values of diffusion coefficient and for a typical altitude dependent diffusion coefficient



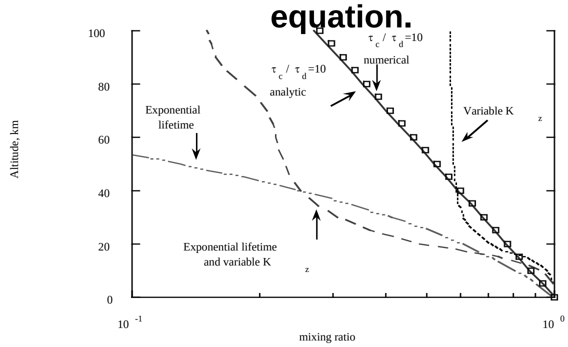
The vertical variation of the mixing ratio (assuming a unit mixing ratio at the surface for simplicity) for various values of the ratio of the chemical lifetime

to the dynamical lifetime.



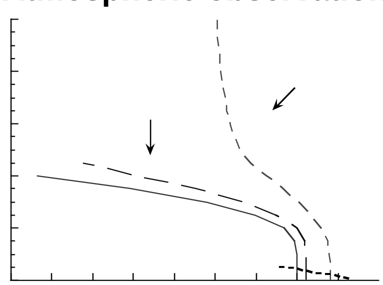
- **When the chemical lifetime is 100 times larger than the dynamical lifetime, materials will have an almost constant mixing ratio to nearly 100 km altitude.**
- **However, when the chemical lifetime is 1% of the dynamical lifetime the mixing ratio falls very rapidly in the troposphere.**

Numerical and analytical solutions of the diffusion equation.



1. Solid red-chemical lifetime is ten times the dynamical lifetime.
2. Dotted black the chemical lifetime is held constant, but the transport is done with the vertically varying diffusion coefficient .
3. Green- constant diffusion coefficient of 10^4 cm^2 s^{-1}, but the chemical lifetime decreases exponentially with altitude using a scale height of 4H Where H=7 km.
4. Dashed red- the diffusion coefficient varies with altitude, and the chemical lifetime decreases exponentially with altitude.

Atmospheric observations



Lifetimes of some interesting materials

Material	M_b, Abundance (Tg)	P_b, Source (Tg/yr)	t_c, Lifetime (yr)
H_2O	1.3×10^7	5×10^8	0.025
CH_4	5×10^3	515	10
COS	5.2	1.2	4.3
SO_2	0.6-0.9	200	.003-.005
N_2O	2.5×10^3	12-21	120
CFC-11	6.2	0.25	50
CFC-12	10.3	0.37	102
CH_3Cl	5	3.5	1.5
NaCl	3.6	1300	0.003

METEOROLOGICAL TRACERS

IT IS VERY USEFUL TO HAVE METEOROLOGICAL TRACERS SO THAT THE PATHS ALONG WHICH AIR PARCELS MOVE CAN BE IDENTIFIED

CONSIDER THE FIRST LAW OF THERMODYNAMICS REWRITTEN WITH THE IDEAL GAS LAW

$$\frac{1}{T}\frac{dQ}{dt} = c_p \frac{d\ln T}{dt} - \frac{R}{M}\frac{d\ln p}{dt}$$

IF WE CONSIDER ADIABATIC TRANSPORT IN WHICH NO HEATING OCCURS THEN WE CAN INTEGRATE THE TEMPERATURE OVER ALTITUDE AND GET

$$\int_T^{\theta} d\ln T = \int_p^{1000\text{mbars}} \frac{R}{Mc_p} d\ln P$$

YIELDING

$$\theta = T\left(\frac{1000\text{mbars}}{p}\right)^{\frac{R}{Mc_p}}$$

θ IS CALLED THE POTENTIAL TEMPERATURE. IT IS THE TEMPERATURE THAT AN AIR PARCEL WOULD HAVE IF IT WERE TAKEN ADIABATICALLY TO A PRESSURE OF 1000 MBARS.

θ IS A CONSERVED TRACER

TAKING THE LOGARITHM OF θ, DIFFERENTIATING WITH RESPECT TO TIME, AND USING THE FIRST LAW OF THERMODYNAMICS YIELDS THE LAGRANGIAN FORM OF THE CONTINUITY EQUATION FOR THE POTENTIAL TEMPERATURE:

$$\frac{d\theta}{dt} = \frac{\theta}{c_p T}\frac{dQ}{dt}.$$

θ IS CONSERVED BY AIR PARCELS WHICH DO NOT EXPERIENCE ANY EXTERNAL HEATING.

OVER SHORT TIME SCALES, OFTEN SEVERAL DAYS, EXTERNAL HEATING DUE TO RADIATION IS USUALLY SMALL. SO AIR PARCELS WHICH DO NOT PASS THROUGH CLOUDS, APPROXIMATELY MOVE ALONG SURFACES OF CONSTANT POTENTIAL TEMPERATURE. SUCH SURFACES CAN BE FOUND FROM ANALYSES OF THERMAL STRUCTURE. WINDS ON THESE SURFACES ALLOW THE TRAJECTORIES OF AIR PARCELS TO BE CALCULATED. THESE TRAJECTORIES ALLOW STUDIES OF LAGRANGIAN CHEMISTRY. SO THE RECOGNITION OF CONSTANT POTENTIAL TEMPERATURE SURFACES CONVERTS THE THREE-DIMENSIONAL CHEMICAL TRANSPORT

θ MEASURES THE STABILITY OF THE ATMOSPHERE

FROM THE FIRST LAW OF THERMODYNAMICS AND THE CONTINUITY EQUATION FOR θ WE GET

$$dQ = C_p\,dT - \frac{RT}{MP}\,dP = TC_p\,\frac{d\theta}{\theta}$$

USING THE HYDROSTATIC EQUATION AND DIVIDING BY C_pTdz YIELDS

$$\frac{1}{\theta}\frac{d\theta}{dz} = \frac{1}{T}\frac{dT}{dz} - \left(\frac{RT(-\rho g dz}{M\frac{\rho RT}{M}C_p\,Tdz}\right) = \frac{1}{T}\left(\frac{dT}{dz} + \frac{g}{C_p}\right) = \frac{1}{T}\left(\Gamma_d - \Gamma\right.$$

So

$\frac{d\theta}{dz} > 0$ stable

$\frac{d\theta}{dz} = 0$ neutral

$\frac{d\theta}{dz} < 0$ unstable

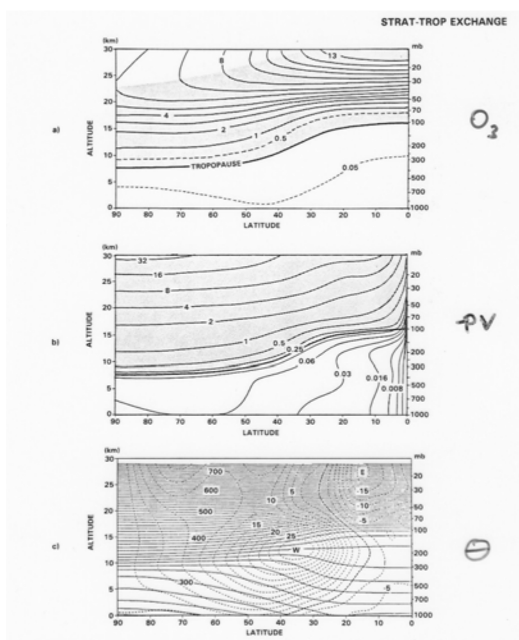
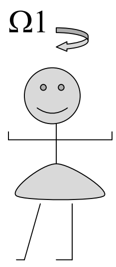
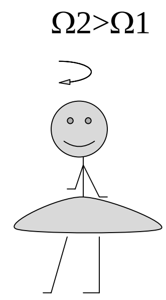


Figure 5-1. Zonal-annual mean distributions of: (a) ozone mixing ratio, ppmv; (b) potential vorticity, 10^{-4} cm^2 s^{-1} K g^{-1}; (c) potential temperature, K, and westerly wind velocity, m s^{-1}.

POTENTIAL VORTICITY

ANOTHER USEFUL METEOROLOGICAL TRACER IS POTENTIAL VORTICITY. IT IS ANALOGOUS TO ANGULAR MOMENTUM $J=\Omega R^2$





THE POTENTIAL VORTICITY PV OBEYS

$$\frac{d[PV]}{dt} = \frac{d[g(\varsigma + f)\frac{\partial\theta}{\partial p}]}{dt} = 0,$$

IF THE FLOW IS ADIABATIC AND FRICTIONLESS (IE DIFFUSION ISN'T IMPORTANT DUE TO SMALL SCALE TRANSPORT). SO PV AND θ ARE CONSERVED UNDER THE SAME CONDITIONS.

PV HAS UNITS OF K CM^2 G^{-1} S^{-1}

$$PV = g(\varsigma + f)\frac{\partial\theta}{\partial p}$$

$f = 2\Omega \sin\phi$

IS A MEASURE OF THE ROTATION OF AN AIR PARCEL DUE TO ITS LOCATION ON THE EARTH, IT HAS S^{-1} UNITS.

ς, IS THE VERTICAL COMPONENT OF THE RELATIVE VORTICITY OF THE FLUID, A MEASURE OF THE MICROSCOPIC TENDENCY OF THE FLUID TO ROTATE DUE TO WINDS AND HAS UNITS OF S^{-1}

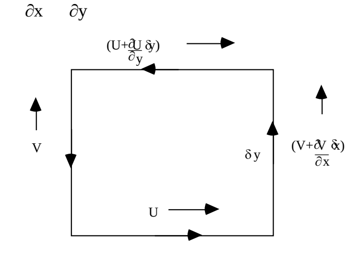
$$\varsigma = \frac{\lim}{A \to 0}\frac{\oint \vec{V}\bullet dl}{A}$$

or

$$\varsigma\delta x\delta y = U\delta x + (V + \frac{\partial V}{\partial x}\delta x)\delta y - (U + \frac{\partial U}{\partial y}\delta y)\delta x - V\delta y$$

or

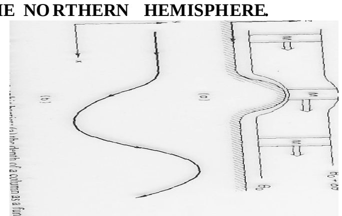
$$\varsigma = \frac{\partial V}{\partial x} - \frac{\partial U}{\partial y}$$



THE FINAL PART OF THE DEFINITION OF POTENTIAL VORTICITY IS THE VERTICAL GRADIENT OF θ. THIS AS A MEASURE OF THE DEPTH OF THE FLUID.

EXAMPLE:

CONSIDER A UNIFORM (NO GRADIENTS IN THE HORIZONTAL DIRECTIONS) WESTERLY FLOW OF AIR, OVER A CHAIN OF MOUNTAINS IN THE NORTHERN HEMISPHERE.



SINCE THE AIR FLOW IS ASSUMED TO BE UNIFORM INITIALLY IT HAS NO RELATIVE VORTICITY. PV WILL BE POSITIVE DUE TO THE CORIOLIS TERM.

THE θ SURFACE AT THE BASE OF THE FLOW MUST RISE AS THE AIR MOVES OVER THE MOUNTAINS SO THE DEPTH OF THE FLUID IS DECREASED, AND THE GRADIENT OF θ WITH PRESSURE IS INCREASED. THUS THE CHANGE IN THE TERM IN PV INVOLVING θ WILL BE IN THE SENSE TO INCREASE PV.

TO CONSERVE PV, THE RELATIVE VORTICITY OF THE FLUID MUST BECOME NEGATIVE SO THAT IT CAN REMOVE SOME OF THE PV DUE TO THE CORIOLIS TERM.

FOR THE RELATIVE VORTICITY TO BECOME NEGATIVE THE AIR MUST TURN TOWARD THE SOUTH.

AS THE AIR LEAVES THE MOUNTAINS THE GRADIENT OF θ WILL DECREASE AS THE DEPTH OF THE AIR PARCEL INCREASES. THEN THE AIR WILL SWING BACK TOWARD THE NORTH.

HENCE CONSERVATION OF PV REQUIRES AN OSCILLATORY MOTION BE INDUCED AS AIR FLOWS OVER A MOUNTAIN RANGE. SUCH OSCILLATIONS ARE SEEN ON DAILY WEATHER MAPS WHERE AIR FLOWS OVER EXTENDED MOUNTAIN RANGES, SUCH AS THE ROCKIES.

A Perez et al

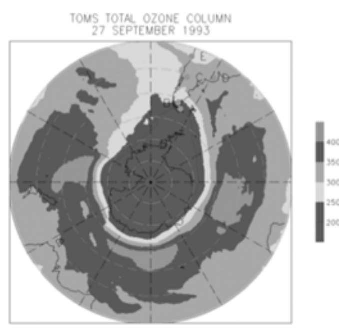


Figure 5. Total ozone map (TOMS) corresponding to 27 September (day 270) 1993.

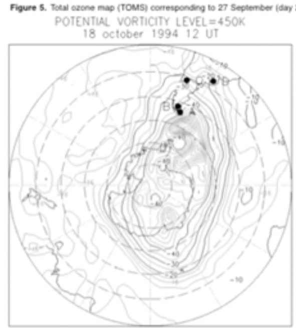


Figure 6. Potential vorticity map at the 450 K level corresponding to 18 October 1994. Rio Grande (A) and Punta Arenas (B) ground stations are well inside the potential vorticity −30 contour.

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Holton et al.: STRATOSPHERE-TROPOSPHERE EXCHANGE 33, 4 / REVIEWS OF GEOPHYSICS

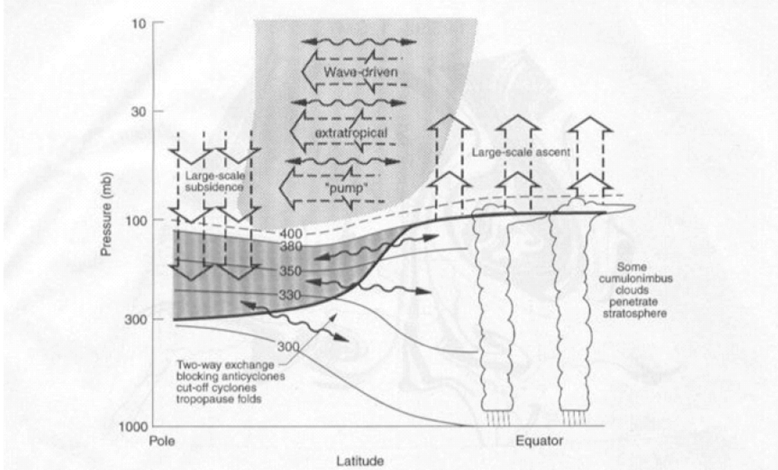

Figure 3. Dynamical aspects of stratosphere-troposphere exchange. The tropopause is shown by the thick line. Thin lines are isentropic or constant potential temperature surfaces labeled in kelvins. The heavily shaded region is the ''lowermost stratosphere,'' where isentropic surfaces span the tropopause and isentropic exchange by tropopause folding occurs. The region above the 380-K surface is the ''overworld,'' in which isentropes lie entirely in the stratosphere. Light shading in the overworld denotes wave-induced forcing (the extratropical ''pump''). The wavy double-headed arrows denote meridional transport by eddy motions, which include tropical upper tropospheric troughs and their cutoff cyclones, as well as their midlatitude counterparts including folds [see *Hoskins et al.*, 1985, Figure 2a]. Not all eddy transports are shown, and the wavy arrows are not meant to imply any two-way symmetry. The broad arrows show transport by the global-scale circulation, which is driven by the extratropical pump (see section 3). This global-scale circulation is the primary contribution to exchange across isentropic surfaces (e.g., the 400-K surface) that are entirely in the overworld.

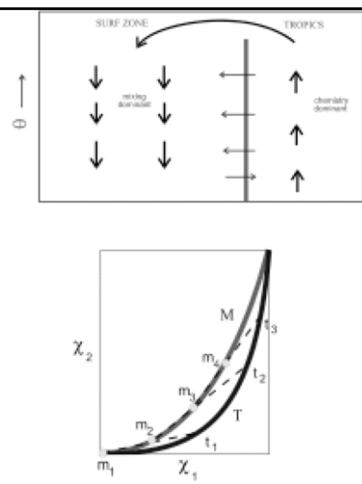

Figure 5. Schematic showing the deveopment of tracer-tracer relationships in the stratospheric "surf zone". Upper figure shows a schematic latitude/potential temperature cross section, with upwelling in the tropics and downwelling in the surf zone. Lower figure shows the relationship between the mixing ratios of two tracers in the tropics (curve "T") and in the surf zone (curve "S"). See text for discussion and for explanation of other symbols. (After Plumb, 2002.)

Tracer/tracer plots are useful

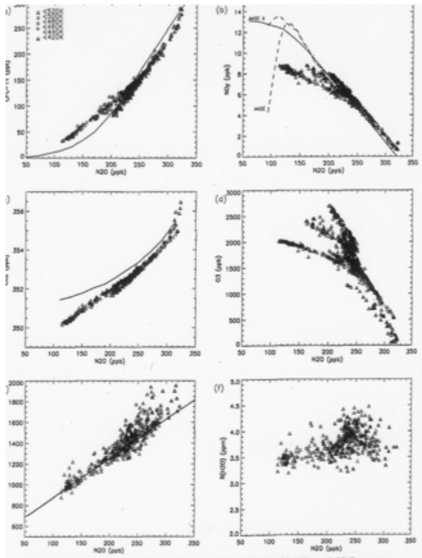

Plate 1. Scatterplot of (a) CFC-11, (b) NO_y, (c) CO_2, (d) O_3, (e) CH_4, and (f) R_{H2O}, versus N_2O for data from the April-May 1993 flights of SPADE. The different colors correspond to the different θ of the measurements (see legend in Plate 1a). The curves corresponds to fits to the other ER-2 data: Plate 1a to AASE II, Plate 1b to AASE II (solid) and AASE I (dashed curves: upper curve is for $\theta = 470 \pm 10$K, lower curve is for $\theta = 450 \pm 10$K), Plate 1c to the February 18, 1994 ASHOE/MAESA flight, and Plate 1e to AASE II data.