

0. CHEMICAL TRACER MODELS: AN INTRODUCTION

Concentrations of chemicals in the atmosphere are affected by four general types of processes: transport, chemistry, emissions, and deposition. 3-D numerical models that simulate these processes to describe the variability in space and time of chemicals in the atmosphere, using meteorological information as input, are called *chemical transport models* (CTMs). They do so by solving the *continuity equations* for mass conservation of the chemicals in the atmosphere. In this segment of the course we derive and discuss the continuity equation in its various forms (chapter 1) and then present equations and algorithms to describe the contributing processes including transport (chapter 2), chemistry (chapter 3), aerosol microphysics (chapter 4), and wet and dry deposition (chapter 5).

CTMs give a mathematical representation of our current knowledge of the processes determining atmospheric composition, and as such they have a very wide range of applications in atmospheric chemistry research. They are commonly used to interpret atmospheric observations in terms of our understanding of underlying processes. They provide source-receptor relationships to understand how concentrations at a given location are sensitive to emissions upwind. They enable construction of global and regional budgets of atmospheric chemicals, allowing future projections for different scenarios. They define prior knowledge for retrievals of satellite observations of atmospheric composition, and give a consistency check between observations of different chemicals from different platforms. They can be applied to formally constrain surface fluxes using atmospheric concentration measurements (*inverse modeling*), or to integrate a large ensemble of observations together for optimal description of atmospheric composition (*chemical data assimilation*). Inverse modeling and chemical data assimilation are covered in a separate segment of this course.

CTMs by definition do not simulate atmospheric dynamics – they use meteorological information as input. They should therefore be distinguished from *general circulation models* (GCMs) that simulate atmospheric dynamics on a global scale, or finer-resolution dynamical models such as *regional climate models* (RCMs) that do so on a regional scale. GCMs and RCMs simulate climate dynamics through solution to the equations for conservation of momentum, energy, and water. They may also include continuity equations for chemicals other than water, either to describe their interactions with climate (ozone, aerosols...) or to serve as tracers. GCMs and other dynamical models may be *free-running* in which case they simulate the climate in a statistical sense but not the weather for a particular year; this is used in simulations of climate change or when one needs a first-principles representation of climate dynamics. Alternatively, they can be constrained to simulate a particular meteorological year through numerical assimilation of weather observations; the resulting *assimilated meteorological data* provide a global continuous 3-D representation of weather that is true to observations but also internally consistent with our physical understanding. CTMs generally use assimilated meteorological data to simulate chemical observations for a particular year. They may use GCM meteorological data to simulate atmospheric composition for past or future climates, or when it is considered important to avoid data shocks from the numerical assimilation.

1. THE CONTINUITY EQUATION

1.1. Forms of the continuity equation

The continuity equation describes the mass conservation for a chemical, and we are interested here in chemicals in the atmosphere. A standard measure of concentration is the *number density* n (molecules cm^{-3}). Consider a Cartesian coordinate system for the atmosphere with an elemental volume $dv = dx dy dz$ centered at location \mathbf{x} (x, y, z). The chemical is transported with a flux vector \mathbf{F} (F_x, F_y, F_z) in units of molecules $\text{cm}^{-2} \text{s}^{-1}$, where F_x is the transport in the x -direction. Consider an inert chemical transported in the x -direction. For the elemental volume as pictured below, the flux across the wall at $x-dx/2$ is $F_x(x-dx/2)$, and the associated change in mass in the volume per unit time is $F_x(x-dx/2)dA = F_x(x-dx/2)dydz$. The associated change in number density is obtained by dividing this change in mass per unit time by the volume of the element, $F_x(x-dx/2)dydz/(dx dy dz) = F_x(x-dx/2)/dx$. In the same way, the change in the number density associated with the flux across the wall at $x+dx/2$ is $-F_x(x+dx/2)/dx$. The total change in number density in the elemental volume is obtained by summing these two effects:

$$\frac{\partial n}{\partial t} = \frac{F_x(x - \frac{dx}{2}) - F_x(x + \frac{dx}{2})}{dx} = -\frac{\partial F_x}{\partial x} \quad (1.1)$$

We extend this result to transport in three dimensions:

$$\frac{\partial n}{\partial t} = -\frac{\partial F_x}{\partial x} - \frac{\partial F_y}{\partial y} - \frac{\partial F_z}{\partial z} = -\nabla \cdot \mathbf{F} \quad (1.2)$$

where $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ is the *gradient vector*, $\nabla \cdot$ is the *divergence operator*, and $\nabla \cdot \mathbf{F}$ is the *flux divergence* measuring what flows out minus what flows in.

Let us now consider the general case where the chemical is not inert, meaning that it can be produced or consumed locally within the atmosphere. Within our elemental volume dv , we may then have to account for a local production rate P (molecules $\text{cm}^{-3} \text{s}^{-1}$) and a local loss rate L (molecules $\text{cm}^{-3} \text{s}^{-1}$) as additional terms in the continuity equation. P could represent emissions or chemical production, while L could represent chemical loss or precipitation scavenging. We then have:

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{F} + P - L \quad (1.3)$$

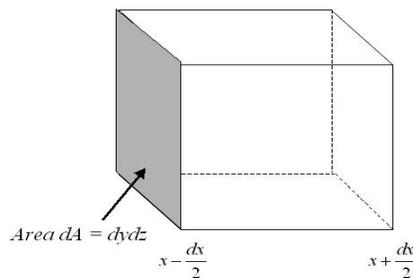


Figure 1. Elemental volume for derivation of the continuity equation

Here $\partial n / \partial t$ is the *accumulation* term representing the local temporal trend in the number density, $-\nabla \cdot \mathbf{F}$ is the previously discussed *transport* term, P is the local *source* term, and L is the local *sink* term representing the local loss rate (molecules $\text{cm}^{-3} \text{s}^{-1}$). $\partial n / \partial t$ is called an *Eulerian derivative* as it describes the evolution in time at a fixed point in space, and (1.3) is called an *Eulerian form* of the continuity equation. “Eulerian” means in a fixed frame of reference. We will derive later an alternate *Lagrangian form* of the continuity equation in a moving frame of reference. Also, because the first term on the right-hand side is a flux divergence, (1.3) is called a *flux form* of the continuity equation. We will derive later an *advective form*.

Let us express the mass flux \mathbf{F} in equation (1.3) in a more physically useful way. This mass flux includes contributions from wind-driven transport (which we call *advection*) and molecular diffusion:

$$\mathbf{F} = \mathbf{F}_{\text{adv}} + \mathbf{F}_{\text{diff}} \quad (1.4)$$

The advective flux \mathbf{F}_{adv} is given by $n\mathbf{U}$ where \mathbf{U} is the local wind velocity. The molecular diffusion flux \mathbf{F}_{diff} is given by Fick’s law:

$$\mathbf{F}_{\text{diff}} = -D\nabla n \quad (1.5)$$

where D ($\text{cm}^2 \text{s}^{-1}$) is the molecular diffusion coefficient. The continuity equation can then be written as:

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n\mathbf{U}) + D\nabla^2 n + P - L \quad (1.6)$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator.

In the troposphere and stratosphere, we can show that molecular diffusion is negligibly slow compared to advection for transport scales larger than ~ 1 cm. The time Δt required to travel a distance Δx by molecular diffusion is given by Einstein’s equation:

$$\Delta t = \frac{(\Delta x)^2}{2D} \quad (1.7)$$

The molecular diffusion coefficient of air is $0.2 \text{ cm}^2 \text{ s}^{-1}$ at sea level and varies inversely with pressure. Traveling a distance $\Delta x = 10 \text{ m}$ at sea level thus requires about a month. In comparison, winds are typically of the order of $1\text{-}10 \text{ m s}^{-1}$ in the horizontal and $0.1\text{-}1 \text{ cm s}^{-1}$ in the vertical; the associated transport is orders of magnitude faster than molecular diffusion. This ceases to hold in the upper atmosphere at $\sim 100 \text{ km}$ altitude, where the pressure is $\sim 10^6$ times lower than at the surface; at that altitude, molecular diffusion becomes important in the vertical direction and results in gravitational separation of the atmosphere.

We focus our attention here on the lower atmosphere, where molecular diffusion can be safely neglected. We can therefore express the continuity equation as

$$\frac{\partial n}{\partial t} = -\nabla \cdot (n\mathbf{U}) + P - L \quad (1.8)$$

which is amenable to solution for n if \mathbf{U} , P , and L are known. A general problem is satisfactory knowledge of \mathbf{U} , considering the chaotic behavior of atmospheric motions. This problem will be discussed in chapter 2. Another frequent complication is the coupling to other species that may arise in the P and L terms because of chemical reactions. Consider a system of p chemically interacting species. The continuity equation for species i is

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{U}) + P_i(\mathbf{n}) - L_i(\mathbf{n}) \quad (1.9)$$

where \mathbf{n} is the vector of number densities n_j ($j = 1, \dots, p$). We thus have a system of p coupled PDEs to solve. This problem will be discussed in chapter 3.

Expressing the continuity equation in terms of the number density provides the simplest physical picture when working in a fixed frame of reference. We can, alternatively express the equation in terms of the *mixing ratio* C of the chemical (mol mol^{-1}), defined as the number of moles of the chemical per mole of air. Mixing ratio means the same thing as mole fraction, and the latter would be better terminology, but the mixing ratio terminology is entrenched. The mixing ratio is related to the number density by $n = Cn_a$, where n_a is the number density of air. We replace into (1.8):

$$\frac{\partial(Cn_a)}{\partial t} = -\nabla \cdot (Cn_a \mathbf{U}) + P - L \quad (1.10)$$

and expand:

$$C \frac{\partial n_a}{\partial t} + n_a \frac{\partial C}{\partial t} = -C \nabla \cdot (n_a \mathbf{U}) - n_a \mathbf{U} \cdot \nabla C + P - L \quad (1.11)$$

Let us now consider the continuity equation for air itself. For air we can neglect P and L as very small, and the corresponding continuity equation is

$$\frac{\partial n_a}{\partial t} = -\nabla \cdot (n_a \mathbf{U}) \quad (1.12)$$

Replacing into equation (1.7) we get a different form of the continuity equation in terms of the mixing ratio:

$$\frac{\partial C}{\partial t} = -\mathbf{U} \cdot \nabla C + P' - L' \quad (1.13)$$

where $P' = P/n_a$ and $L' = L/n_a$ are the production and loss rates in mixing ratio units. Notice that in this latter form the wind velocity is outside of the gradient operator. The physical explanation is that simple compression of air ($\nabla \mathbf{U} \neq \mathbf{0}$) modifies the number density but not the mixing ratio. Equation (1.13) is called the *Eulerian advective form* of the continuity equation. One can simplify equation (1.13) further by introducing the total derivative, which describes the change with time of a variable within a moving volume element:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{dx}{dt} \frac{\partial}{\partial x} + \frac{dy}{dt} \frac{\partial}{\partial y} + \frac{dz}{dt} \frac{\partial}{\partial z} = \frac{\partial}{\partial t} + \mathbf{U} \cdot \nabla \quad (1.14)$$

We can thus write the continuity equation as

$$\frac{dC}{dt} = P' - L' \quad (1.15)$$

which describes the change with time in the mixing ratio of a gas in a moving volume element solely in terms of its local production and loss terms. This is the *Lagrangian* form of the continuity equation, as opposed to the Eulerian form describing the change with time in a fixed frame of reference. The total derivative in equation (1.14) is also called the *Lagrangian derivative* or *Lagrangian operator*. The Lagrangian form is applied to the mixing ratio, not the number density, because the number density within a moving air parcel would vary as the pressure or temperature changes. The simplicity of the Lagrangian form as expressed in (1.15) is appealing, and is the foundation for the simple *parcel models* that follow the evolution of a parcel isolated from the rest of the atmosphere. The problems of the Lagrangian form are that (1) it does not provide for the mixing between volume elements, (2) one still needs to describe the trajectory of the volume elements in an Eulerian framework in order to obtain a useful geographical representation of the concentration field. Almost all 3-D CTMs presently used in research applications are based on the Eulerian form, but most also incorporate Lagrangian ideas as will be discussed later.

1.2. Analogies to the continuity equation

Let us reflect on the generality of the continuity equation as expressed by the above forms. It is nothing more than a conservation equation for a quantity that varies in space and time. Such conservation equations are found in all fields of science, and they all have similar forms. Consider for example the Schrödinger equation of quantum mechanics describing the evolution of the state function Ψ for a single particle of mass m and potential energy V :

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \quad (1.16)$$

Closer to our interests here, consider the Navier-Stokes equation of fluid dynamics describing the evolution of the velocity field \mathbf{U} :

$$\frac{\partial \mathbf{U}}{\partial t} = -\mathbf{U} \cdot \nabla \mathbf{U} + \nu \nabla^2 \mathbf{U} - \frac{\nabla P}{\rho} + \mathbf{g} \quad (1.17)$$

where ν is the kinematic viscosity, ρ is the air density, ∇P is the pressure gradient, and \mathbf{g} is the acceleration of gravity. The first term on the right-hand-side is the advection term for \mathbf{U} ; similarly to the mixing ratio, \mathbf{U} is not modified by the compression of air and therefore we have \mathbf{U} outside of the gradient operator. The second term is analogous to the diffusion term in the continuity equation, while the last two terms (pressure-gradient and gravity) are local accelerations affecting \mathbf{U} and are thus analogous to the P and L terms of the continuity equation.

1.3. Discretization of the continuity equation

The continuity equation in its Eulerian form is a first-order partial differential equation (PDE) in space and time. Given an initial concentration field and spatial boundary conditions, one can integrate it to predict the evolution of the concentration field. In a global model, suitable horizontal boundary conditions are of the periodic type where the period is the Earth's circumference. Vertical boundary conditions are generally of the flux type, e.g., zero flux at the top of the atmosphere and specified emissions or uptake rates (or rate constants) at the Earth's surface. The solution must in general be numerical and involve discretization in space and time, as described below.

1.3.1. Discretization in space

Discretization in space involves representation of the 3-D continuous domain with a finite number m of *gridpoints*, and making assumptions about the structure of the concentration field between gridpoints. The continuity equation is then solved at each gridpoint, after finite differencing of the transport term, resulting for each species in a system of m coupled first-order ordinary differential equations (ODEs) in time. The finite differencing of the transport term is described in chapter 2. Sometimes this spatial

discretization is expressed as a 3-D assemblage of *gridboxes* instead of gridpoints, with assumptions made about the structure of the concentration field within each gridbox. The two approaches are strictly equivalent, and in what follows we will refer to either depending on which gives the best physical picture. With current computing resources, models can include of the order of 10^6 gridpoints. In a global model this implies a horizontal resolution of the order of 100 km and a vertical resolution of the order of 1 km.

Almost all global CTMs use a *latitude-longitude* horizontal grid in which gridpoints are evenly spaced in latitude and longitude. In the vertical direction, one has to deal with topography. Many models use a *sigma* terrain-following coordinate:

$$\sigma = \frac{p - p_T}{p_S - p_T} \quad (1.18)$$

where p is pressure, p_T is the pressure at model top, and p_S is the local surface pressure. Sigma values range from 1 at the surface to 0 at model top, and vertical levels in the model are then specified by their sigma values. More recent models tend to use an *eta* coordinate system that smoothly transitions from the sigma coordinate near the surface to a pressure coordinate in the stratosphere. In the eta coordinate system, the pressure at vertical level k is given by

$$p_k = \alpha_k(p_S - p_T) + \beta_k \quad (1.19)$$

with specified values of α_k and β_k that define the vertical resolution of the model. At the surface, $\beta_k = 0$ resulting in a pure sigma coordinate; while at high altitudes, $\alpha_k = 0$ resulting in a pure isobaric coordinate.

GCMs often describe horizontal fields of meteorological variables in terms of sums of sinusoidal waves rather than in gridded space, in order to take advantage of the general wave structure of these variables. In these *spectral models* there is no horizontal grid, and the resolution is determined by the highest *wavenumber* resolved, where wavenumber 1 has as period the circumference of the Earth, wavenumber 2 has half that period, and so on. This spectral approach is almost never used in CTMs because chemicals have a discrete structure driven by local sources and sinks that is not conveniently represented by sinusoidal waves. When data from a spectral GCM are used to drive a CTM, the meteorological variables are first mapped from spectral space onto a latitude-longitude gridded space in which the chemicals are then transported.

1.3.2. Operator splitting

The discretization in space leaves us with a system of m coupled ODEs describing the temporal change in concentration at every gridpoint. In a coupled chemical system we have $m \times p$ coupled ODEs. We can simplify the problem by recognizing that the transport term $-\nabla \cdot (n\mathbf{U})$ involves coupling only between neighboring grid points and does not involve coupling between chemical species, while the chemical term $(P-L)$ does not involve coupling with other gridpoints. Separation of these two terms can be written in differential form as

$$\frac{\partial n}{\partial t} = \left[\frac{\partial n}{\partial t} \right]_{transport} + \left[\frac{\partial n}{\partial t} \right]_{chemistry} \quad (1.20)$$

with

$$\left[\frac{\partial n}{\partial t} \right]_{transport} = -\nabla \bullet (n\mathbf{U}) \quad (1.21)$$

$$\left[\frac{\partial n}{\partial t} \right]_{chemistry} = P - L \quad (1.22)$$

We can then decouple these two terms in finite difference form over time steps Δt by defining a *transport operator* \mathbf{T} and a *chemical operator* \mathbf{C} such that

$$n(t_o + \Delta t) = \mathbf{C} \bullet \mathbf{T}(n(t_o)) \quad (1.23)$$

where \mathbf{T} and \mathbf{C} solve (1.21) and (1.22) separately over Δt . \mathbf{T} is applied to $n(t_o)$ to yield an intermediate result n' :

$$n' = \mathbf{T}(n(t_o)) \quad (1.24)$$

and \mathbf{C} is then applied to n' over Δt to yield $n(t_o + \Delta t)$.

The separation of the transport and chemical operators in equation (1.23) is called *operator splitting*, and it simplifies the problem considerably by reducing its dimensionality. The underlying assumption is that coupling between transport and chemistry can be neglected over Δt . The assumption is safe when Δt is small relative to the time scale over which the chemicals are changing, but such a constraint can be unnecessarily tight when dealing with highly reactive gases. For example, if a gas has a lifetime against chemical loss that is very short relative to the time scale $\Delta x/u$ for transport across gridboxes, then its concentration is set by the local chemical environment and transport can be neglected; there is no need to worry about it in operator splitting. Global CTMs typically use 15-60 minute time steps for operator splitting. A good way to test whether this is acceptable is to compare two model simulations where the order of the operators has been swapped. The difference measures the error associated with operator splitting. If it is considered too large, then one should reduce Δt and repeat the test.

One generally splits the transport operator \mathbf{T} further into components in the 3 directions (\mathbf{T}_x , \mathbf{T}_y , \mathbf{T}_z) to simplify numerics, enable larger time steps, and facilitate parallelization of the code. Each of \mathbf{T}_x , \mathbf{T}_y , and \mathbf{T}_z solves 1-D forms of (1.21). Winds are generally much stronger in the east-west direction (conventionally x) than in the north-south direction (y) and they are weakest in the vertical direction (z). A popular arrangement of operators is as follows:

$$n(t_o + \Delta t) = \mathbf{T}_x \bullet \mathbf{T}_y \bullet \mathbf{T}_x \bullet \mathbf{T}_z \bullet \mathbf{T}_x \bullet \mathbf{T}_y \bullet \mathbf{T}_x n(t_o) \quad (1.25)$$

so that the transport operator in the east-west direction is applied over $\Delta t/4$, that in the north-south direction is applied over $\Delta t/2$, and that in the vertical direction is applied over Δt .