

Diffusivity dependence of ozone depletion over the midnorthern latitudes

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The mixing and reaction properties of advected chemicals (and passive scalars) are determined by the fractal dimension D of the interface between the chemicals. We show that the scaling of the amount m of reacted chemicals with diffusivity κ is $m(0) - m(\kappa) \propto \kappa^{1-D/2}$ in the two-dimensional case. This relation is valid in a range of times and diffusivities where the diffusive length scales of the chemicals are within the range of scales where the chemical interface has a well-defined fractal dimension. We apply the relation to the problems of chlorine deactivation and ozone depletion over the midnorthern latitudes. We determine numerically the fractal dimension of an interface advected by stratospheric winds. This allows us, first, to explain the diffusivity dependence of chlorine deactivation and ozone depletion that was previously observed in numerical simulations (Tan *et al.*, *J. Geophys. Res., [Atmos.]* **103**, 1585 (1998)) and, second, to extrapolate the results of such simulations down to realistically low diffusivities.

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Many situations in physical, chemical, biological, and engineering sciences involve large scale stirring and subsequent reactions of chemicals or biological species. Understanding and modeling these processes continue to be a challenge. One major difficulty is to resolve fine enough scales in order to describe the effects of small molecular diffusivity.

An example of such a process is chlorine deactivation and ozone depletion over the midnorthern latitudes. In a cold arctic winter, polar stratospheric clouds may form. On these clouds, heterogeneous reactions produce chlorine monoxide radicals ClO [1]. The chlorine activated air may subsequently get transported to the midnorthern latitudes [2] where it can catalytically deplete ozone under the influence of light. This then results in increased UV radiation over the densely populated midnorthern latitudes [3]. However chlorine may also become deactivated before it can destroy ozone. One deactivation mechanism involves the reaction between polar air, which is rich in ClO, and midlatitude air, which is relatively rich in nitrogen oxides, e.g. NO₂ [4,5]. The advection involved in the deactivation process ClO + NO₂ → ClONO₂ can effectively be modeled [6] as a two-dimensional advection of the chemicals by the stratospheric wind field \mathbf{v} . This advection process continuously stretches and folds the concentration fields, thereby reducing the length scales of its spatial curled and folded structures. When these structures reach the diffusive length scale $\sqrt{\kappa\sigma^{-1}}$, which is determined by the diffusivity κ and the average strain rate σ , chemicals are mixed at the molecular level and reactions occur. Following [6], the process can quantitatively be understood in terms of the solution of an advection-diffusion-reaction (ADR) equation

$$\frac{\partial}{\partial t} c_i + (\mathbf{v} \cdot \nabla) c_i = \kappa \nabla^2 c_i - \gamma c_1 c_2, \quad (1)$$

where γ is the chemical reaction constant and the c_i , $i=1$ or 2, denote the concentration fields of ClO and NO₂, respectively. Credible estimates for the effective diffusivity κ range from 10⁰ to 10³ m² s⁻¹, corresponding to a diffusion limited size of concentration field curled and folded structures between 1 km and 20 km [6]. The ADR problem (1) can be solved by direct numerical simulation. However, such simulations currently do not resolve the length scales required for realistically low diffusivities, which is unfortunate because the deactivation process is very sensitive to resolving realistically small structures [7,8]. The total production of ClONO₂ has in fact a power law dependence on the diffusivity [6]. State of the art simulations only resolve structures of a few hundred kilometers [6,7], which is between one and two orders of magnitude too coarse. The approach presented here extends the predictions for the rates of chlorine deactivation and ozone depletion to realistically low diffusivities and, furthermore, identifies the key parameter regulating the diffusivity dependence of reactions, namely, the fractal dimension of the interface between different chemicals.

We start with a numerical simulation of the advection of a line interface by winds on the 475-K isentrope (an altitude of approximately 20 km). These winds were measured by the European Centre for Medium-Range Weather Forecast between 9 and 24 January 1992. The interface is initially at 60°N and can be thought of as separating a patch of uniformly distributed ClO over the pole from NO₂-rich air over the midnorthern latitudes. Figure 1 shows the result of the advection process after 15 days; the figure caption contains a description of the simulation employed. During the advection process, the interface develops a geometrically complex structure that, at small enough length scales, is approximately homogeneous and isotropic. We analyze this geometrically complex small-scale interfacial structure in terms of its fractal dimension. The fractal dimension D is well defined if the number $N(\epsilon)$ of boxes of size ϵ needed to

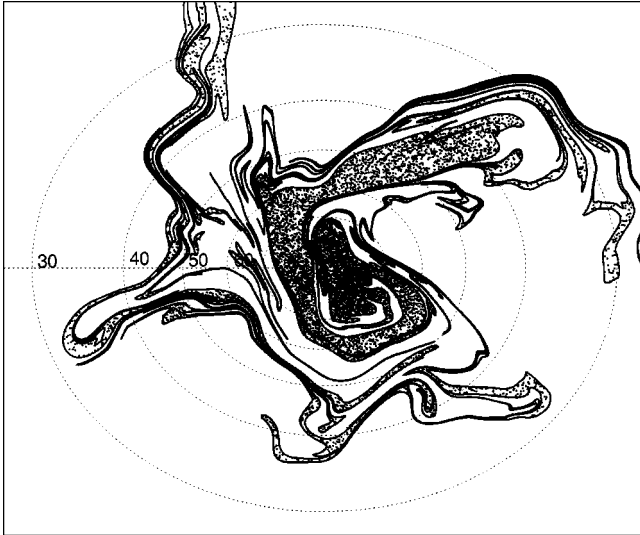


FIG. 1. Interface between ClO and NO₂-rich, stratospheric air after 15 days of advection. Solid line, interface in stereographic projection; dotted lines, latitudes in 10° intervals; dots, passive tracer particles inside the interface. The interface has developed curl and fold structures over a broad range of length scales. The numerical simulation started with an interface aligned with the $\varphi = 60^\circ\text{N}$ latitude. The interface was advected by winds on the 475-K isentrope that are interpolated from a data set provided by the European Centre for Medium-Range Weather Forecasts and recorded beginning on 9 January 1992. The wind dataset has longitudinal and latitudinal resolutions of about 4° and a temporal resolution of 6 h. Between grid points and time slices, the winds were interpolated linearly. The interfacial advection algorithm preserves the continuity of the interfacial line by increasing the number of points making the interface according to interfacial stretching.

cover the interface has a power law dependence $N(\epsilon) \propto \epsilon^{-D}$ [9]. Figure 2(a) shows the box-counting functions $N(\epsilon)$ of the interface in the midnorthern latitudes (30 to 60°N) from day 1 to 15. The figure suggests that the $N(\epsilon)$ have power laws over some range of scales with exponents, i.e., fractal dimensions, that increase with time. Figure 2(b) gives the values and respective scaling ranges of the fractal dimensions, obtained by use of an algorithm [10] that automatically finds the exponent and scaling range that best fits a given $N(\epsilon)$. The results suggest that, for the intents and purposes of most practical applications, fractal dimensions can be defined in a range of scales from (on average) 4×10^{-3} to $1 \times 10^{-1} R_e$ ($R_e = 6370$ km is the Earth's radius) on every day of the simulation. Furthermore, we observe that on the first three days, the interface has dimension $D = 1$, but from day 4 onwards, its fractal dimension increases about linearly in time to reach $D = 1.48$ on day 15. Given the nature of the advecting winds, we are not aware of any mechanism that could produce an interface with a noninteger fractal dimension that changes with time. The spiral generation mechanism of the vortex, which is palpable in the visualizations (Fig. 1), can produce a well-defined noninteger fractal dimension over a significant scaling range (see [11]). However, in isolation, this mechanism leads to a dimension that is constant in time. Nevertheless, the time dependence might be

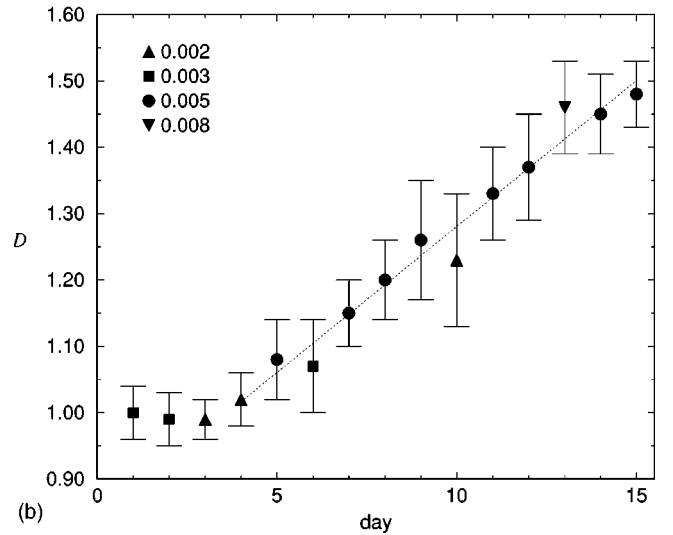
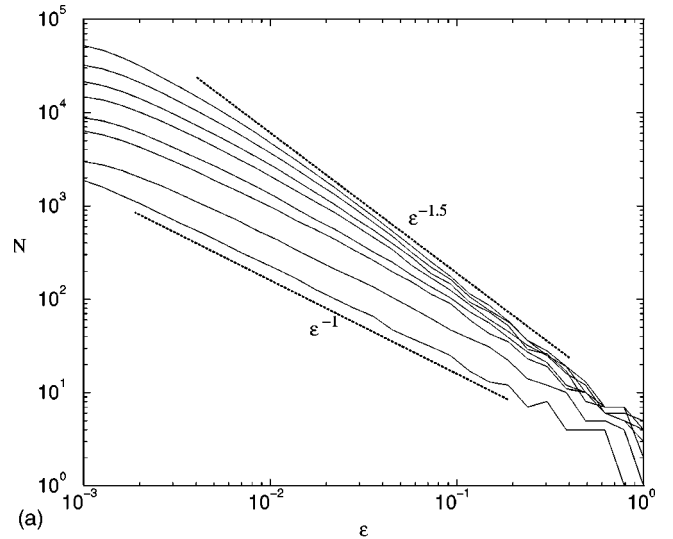


FIG. 2. Fractal dimensions of interfaces on different days. (a) Logarithmic plot of the box-counting function $N(\epsilon)$, obtained by covering the interface (on a sphere) with boxes of size ϵ , given in fractions of the Earth's radius $R_e = 6370$ km. The box-counting functions are depicted for all odd days 1,3,5, . . . ,15; lower curves correspond to earlier days. Power laws corresponding to fractal dimensions 1 and 1.5 are given by dotted lines. (b) Time evolution of the fractal dimension D of the advected interface. Fractal dimensions are obtained by use of a systematic algorithm [10] that automatically finds the exponent and scaling range that best fits a measured $N(\epsilon)$. Best fit ranges begin at the maximal scale $1 \times 10^{-1} R_e$ and end at minimal scales, detected by the algorithm, as indicated by the symbols, ranging from 2×10^{-3} to $8 \times 10^{-3} R_e$ (with an average of $4 \times 10^{-3} R_e$). Each error bar corresponds to the standard deviation of all possible exponents in a best fit range. Dotted line, linear interpolation of dimension between days 4 and 15.

accountable to the transience of this mechanism before the chaotic nature of the flow eventually erases the spirals (see [12]). Asymptotically for long enough times, we should expect the dimension to saturate to the space-filling value of 2. In summary, our box-counting results show that the interface has a nontrivial multiple-scale structure that can be suffi-

ciently well approximated by a fractal dimension in an intermediate range of scales, and that this fractal dimension varies with time. This conclusion is important for understanding the diffusive properties of mixing and reaction processes on these intermediate scales, as we show below.

We now derive our central result that the fractal dimension D determines the power law between the mass m of ClO and the diffusivity κ

$$m(0) - m(\kappa) \propto \kappa^{1-D/2}. \quad (2)$$

Results by Toroczka *et al.* [13] can be shown to give a similar relation for active particles in open flows. The power law (2) is valid when the chemical fields have some physical and chemical properties (a) to (e): (a) The chemicals are initially on/off scalar fields, i.e., in any small region of the atmosphere, the chemical concentration is either approximately constant (on) or effectively zero (off); (b) the chemical diffusivities are sufficiently small, i.e., in the range of times t under consideration, the diffusive spreading of the chemicals (which is at most $\sqrt{\kappa t}$ for long times) is small in comparison with the overall length scale of the problem; (c) the (effective) diffusivities of all chemicals are equal; (d) the chemical reactions are so fast that they are limited by the advection-diffusion process rather than by the speed of their reaction; (e) the advected chemicals are statistically isotropic, homogeneous, and have a well-defined fractal dimension. For realistic [6] parameters and initial conditions of the chemical fields, it can be shown that the process of ozone depletion fulfills assumptions (a) to (d) and our simulation suggests that (e) is also fulfilled. The following derivation of Eq. (2) comprises of two steps. First, we show that the nonlinear ADR problem (1) can be related to a linear advection-diffusion (AD) problem. Second, we explain that the fractal dimension determines the diffusivity dependence of the AD problem.

The ADR equation (1) can be linearized using assumptions (c) and (d). Subtracting the equation for the chemical concentration field c_1 from the equation for c_2 , we find a linear AD equation for $f := c_1 - c_2$,

$$\left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) - \kappa \nabla^2 \right] f = 0. \quad (3)$$

Eliminating the concentration field c_2 in Eq. (1) with f , we find for c_1

$$\left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) - \kappa \nabla^2 \right] c_1 = -\gamma [c_1(c_1 - f)]. \quad (4)$$

For a fast chemical reaction, see assumption (d), Eq. (4) is dominated by its right hand side. In those times and places where the right hand side is nonzero, a large reaction constant drives the solution very quickly towards a solution where the right-hand side vanishes,

$$c_1(\mathbf{x}, t) = f(\mathbf{x}, t) H[f(\mathbf{x}, t)], \quad (5)$$

where H is the Heaviside function that is 1 for positive argument and 0 otherwise, makes the right hand side of Eq. (4)

TABLE I. Diffusivity dependence of chlorine (ClO) deactivation over the midnorthern latitudes. Chlorine deactivation is measured by the mass m of ClONO₂ produced from ClO. The production of ClONO₂ has a power law dependence $m \propto \kappa^\beta$ on the diffusivity κ . With Eq. (2), the fractal dimensions D and errors ΔD from Fig. 2(b), we predict exponents in agreement with numerically measured exponents on those days where the interface is fractal, i.e., $D \geq 1$.

Day	$(1 - D/2) \pm \Delta D/2$	Exponent ^a β
3	$(D = 1)$	0.60
7	0.43 ± 0.03	0.45
11	0.34 ± 0.04	0.30

^aFrom [6].

vanish and, therefore, approximates well the solution of Eq. (4). We now express the masses $m_1 = \int d^2x c_1$ and $m_2 = \int d^2x c_2$ of chemicals c_1 and c_2 in terms of f . For chemical fields c_1 and c_2 that are initially on/off fields, see assumption (a), $f \equiv c_1 - c_2$ has initially one of the three values $+f_0$, 0 , and $-f_0$ at any point in space, where f_0 is the ‘‘on’’ value of c_1 and c_2 . f maintains this plus-zero-minus structure to a good approximation during the advection-diffusion process (3) because the region where diffusion acts is small, see assumption (b). Note that we approximate f by 0 in the small region where diffusion has mixed $+f_0$ with $-f_0$. The variance $E = \int d^2x f^2$ of f is then given by f_0^2 multiplied by the sum of two areas, the areas where c_1 or c_2 are nonzero, respectively. Comparing this with the masses of c_1 and c_2 , which are given by f_0 multiplied by the area where, respectively, c_1 or c_2 is nonzero, we obtain $E = f_0(m_1 + m_2)$. This relation together with $m_1 - m_2 = \text{const}$, which follows from the reaction equation of the chemicals, yields for the mass of c_1 ,

$$m_1 = \frac{E}{2f_0} + \text{const}. \quad (6)$$

We have, therefore, related the mass of the nonlinear ADR problem to the variance of the solution of the linear problem AD problem.

Now we show how the variance of f depends on the geometry of the advected field. For a statistically homogeneous and isotropic two-dimensional on/off field with fractal dimension D , see assumption (e), the spectrum $\Gamma(k)$, which is the variance per wave number k , is a power law $\Gamma(k) \propto k^{D-3}$ [14]. Molecular diffusion only eliminates structures smaller than the diffusive length scale and does not affect larger structures. For flows with large-scale advection, the diffusive length scale is proportional to $\sqrt{\kappa}$ and hence the diffusivity dependence of the variance scales like $E(0) - E(\kappa) \propto \int_{\kappa^{-0.5}}^{\infty} dk \Gamma(k)$. Using Eq. (6), this yields Eq. (2).

We have verified that Eq. (2) together with the fractal dimensions from Fig. 2(b) reproduce the numerically measured exponents [6] for the diffusivity dependence of ClONO₂ production, i.e., chlorine deactivation, see Table I. We also predict the diffusivity dependence of the rate of ozone depletion. Assuming that the ozone never depletes

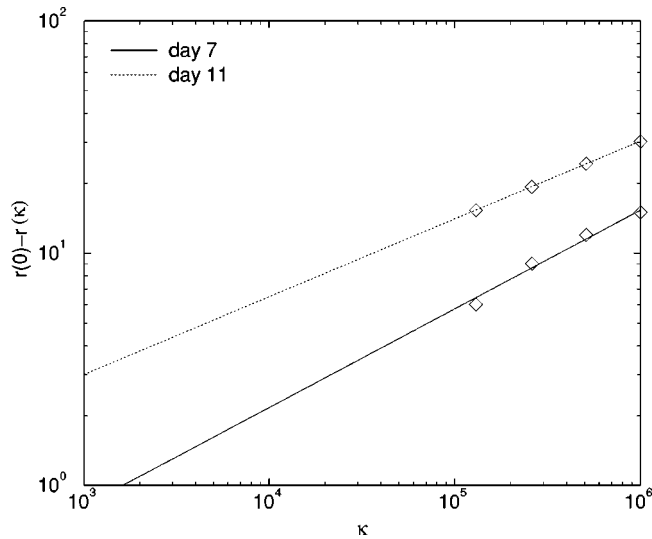


FIG. 3. Effective diffusivity κ dependence of the rate of ozone depletion $r(\kappa)$ for selected days. The scaling of $r(0)-r(\kappa)$ is calculated from Eq. (2) and the fractal dimensions from Fig. 2(b). \diamond represent results that were obtained by a numerical solution of Eq. (1) [6]. We observe that for increasing time, the diffusivity dependence becomes shallower due to the increased dimension of the chemical interface. The multiplicative constant of the power law is chosen to fit the results for an initial ClO concentration of 2 ppbv and an initial NO_2 concentration of 0.6 ppbv.

completely, the Molina cycle [15] leads to the rate of ozone depletion being proportional to the square of ClO concentration. Because of the on/off property, we can conclude that the squared concentration of ClO is proportional to the mass of

ClO. The rate of ozone depletion over the midnorthern latitudes is, therefore, given by Eq. (2), with mass m replaced by the rate of ozone depletion $r = \partial/\partial t c_{\text{O}_3}$, where c_{O_3} is the ozone concentration. The diffusivity dependencies are valid for diffusivities between $\kappa = 2 \times 10^3 \text{ m}^2 \text{ s}^{-1}$ and $\kappa = 1 \times 10^6 \text{ m}^2 \text{ s}^{-1}$ because these diffusivities correspond to the length scales between $4 \times 10^{-3} R_e$ and $1 \times 10^{-1} R_e$, respectively, where we observe a fractal dimension of the interface. This means that we can extend previous results down to realistic diffusivities, as shown in Fig. 3. Numerically, our method requires a few orders of magnitude less computational time than solving the ADR Eq. (1) for very low diffusivities. Therefore Eq. (2) predicts the diffusivity scaling of ClO at diffusivities that are at present inaccessible by direct numerical simulations of ADR processes.

In conclusion, we have explained the diffusivity dependence of the mass of advected chemicals in terms of the fractal dimension of the interface between different chemicals. Using a measurement of these fractal dimensions, derived from numerical advection by a real stratospheric wind field, we predict the ozone depletion for realistically low diffusivities. The method is more widely applicable. If an experimentally or numerically obtained snapshot of a field is given, it is possible to predict its diffusivity dependent mixing and reaction properties.

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