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Concentration statistics for dispersive media

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ABSTRACT

This report demonstrates the basis for and some applications of an integral method to describe the statistics of concentration fluctuations in dispersive media. The integral approach is derived by using and then extending Lagrange's method for solving the continuity equation. Illustrative applications of the theory deal with diffusion parallel and perpendicular to the mean motion of the host fluid, with consequences of different stochastic loss processes, and with predictions of concentration fluctuations caused by turbulent diffusion and source-strength variations.

1. Introduction

There has been recent interest in concentration fluctuations for trace material in the atmosphere (e.g., see Grandell, 1985). These fluctuations arise from turbulent motions of the air and from stochastic sources and sinks of the trace constituents. Interest in the statistics of concentration fluctuations has arisen, in part, from new air-pollution regulations based on concentration extremes. The purposes here are to demonstrate a theoretical base for an integral description of concentration fluctuations and to present some illustrative applications of the theory.

2. Concentrations in a non-dispersive medium

Let C be the concentration of the trace material of interest, where "trace" means that the material has negligible influence on the dynamics of the host fluid. In this section, diffusion is ignored, and therefore, C is assumed to satisfy the continuity equation

$$\frac{\partial C}{\partial t} + \boldsymbol{v}_E \cdot \nabla C = \dot{G} - \dot{L}, \tag{2.1}$$

in which $\boldsymbol{v}_E(\boldsymbol{r}, t)$ is the (Eulerian) velocity field of the fluid, and $\dot{G}$ and $\dot{L}$ are (deterministic) volumetric gain and loss rates, respectively. For (2.1), C can be either mass density or mass mixing-ratio, and the fluid can be compressible or incompressible: for these different cases, the only difference in (2.1) is a term in $\dot{L}$ linear in C, which will not influence the following analysis (see Appendix A). Baker (1980) has examined the statistics of (2.1), for spatially independent $\boldsymbol{v}_E$ and special cases of $\dot{G}$ and $\dot{L}$, by solving (2.1) using Fourier-transform methods. In what follows, Lagrange's method will be used, and the restriction to spatially independent $\boldsymbol{v}_E$ can be relaxed.

Lagrange's solution to Euler's continuity equation, (2.1), can be obtained either by using Lagrange's method for solving first-order partial differential equations (see Appendix B) or by first transforming (2.1) to Lagrangian coordinates and then solving the resulting ordinary differential equation (see Appendix C). In either case, we use the notation $\boldsymbol{v}_E[\boldsymbol{r}(t), t] = \boldsymbol{v}_L(t)$ for the (Lagrangian) velocity of fluid particle at $\boldsymbol{r}(t)$. For the important special case with the gain rate, $\dot{G}$, independent of C and the loss rate, $\dot{L}$, linear in C (viz., $\dot{L} = l(\boldsymbol{r}, t) C$), then as shown in Appendices B and C, the solution to (2.1) is

$$C(\boldsymbol{r}, t) = C_0[\boldsymbol{r} - \langle \boldsymbol{v}_L \rangle t, 0] \exp\{-\langle l \rangle t\} + \int_0^t d\tau\, \dot{G}[\boldsymbol{r} - \langle \boldsymbol{v}_L \rangle \tau, t - \tau] \exp\{-\langle l \rangle \tau\}, \tag{2.2}$$

in which the (prior) time average of a quantity q is defined via

$$\langle q(t; T) \rangle = \frac{1}{T} \int_{t-T}^{t} dt\, q(\tau), \tag{2.3}$$

i.e., evaluated backward along the "trajectory" that arrives at $\boldsymbol{r}$ at time t.

Two special versions of (2.2) will be used frequently in what follows. First, since any initial concentration, C_0, arises from prior emissions, then (2.2) can be written as

$$C(\boldsymbol{v}, t) = \int_0^{\infty} \mathrm{d}\tau\, \dot{G}[\boldsymbol{r} - \langle \boldsymbol{v}_\mathrm{L} \rangle \tau, t - \tau] \exp\{-\langle l \rangle \tau\}; \tag{2.4}$$

i.e., the sum of the gains at all prior locations and times, suitably decayed by removal en route. Second, for the special case of a single, continuous point source at $\boldsymbol{r}_0$, i.e.,

$$\dot{G}(\boldsymbol{r}, t) = \dot{g}(t)\, \delta(\boldsymbol{r} - \boldsymbol{r}_0), \tag{2.5}$$

in which δ is a Dirac function, then (2.4) yields

$$c(\boldsymbol{r}, t) = \int_0^{\infty} \mathrm{d}\tau\, \dot{g}(t - \tau)\, \mathrm{e}^{-\langle l \rangle \tau} \delta[\boldsymbol{r} - \{\boldsymbol{r}_0 + \langle \boldsymbol{v}_\mathrm{L} \rangle \tau\}], \tag{2.6}$$

where lower-case c has been used to emphasize that (2.6) is the solution for a continuous, point source.

As a simple illustration of these results for a non-dispersive medium, consider the case of a uniform wind field $\boldsymbol{v}_\mathrm{L} = u_0 \hat{\boldsymbol{i}}$, a constant loss rate l_0, and a constant (subscript zero) point source of pollution at $\boldsymbol{r}_0 = (x_0, 0, h)$. Then (2.6) becomes

$$c(\boldsymbol{r}, t) = \int_0^{\infty} \mathrm{d}\tau\, g_0\, \delta[x - x_0 - u_0 \tau] \times \delta(y)\, \delta(z - h)\, \mathrm{e}^{-l_0 \tau}. \tag{2.7}$$

But for any strictly monotonic function of ξ that vanishes at $\xi = \eta$, we have

$$\delta[f(\xi)] = \delta(\xi - \eta) / | f'(\xi = \eta)| \tag{2.8}$$

(which follows easily if δ is interpreted as a probability density function); therefore,

$$\delta[x - x_0 - u_0 \tau] = \frac{1}{u_0}\, \delta\left[\tau - \left\{\frac{x - x_0}{u_0}\right\}\right]. \tag{2.9}$$

Also

$$\int_0^{\infty} \delta(\tau - \tau_0)\, f(\tau)\, \mathrm{d}\tau = f(\tau_0)\, h(\tau_0), \tag{2.10}$$

where $h(\tau_0)$ is the unit (Heaviside) step function. Consequently, (2.7) yields

$$c(\boldsymbol{r}, t) = \frac{g_0}{u_0} \exp\left[-l_0 \left\{\frac{x - x_0}{u_0}\right\}\right] \times h(x - x_0)\, \delta(y)\, \delta(z - h), \tag{2.11}$$

which is transparent. Note that (2.11) does not describe diffusion, a condition to be rectified in the next section.

3. Formulation for stochastic processes

For definiteness, consider the case of a single, continuous point-source (emission rate $\dot{g}(t)$ in, say, moles per unit time). Since linearity has been assumed (e.g., with $\dot{L} = lC$), we can find the solution for an arbitrary spatial distribution of sources via superposition. The (deterministic) result for a single source at $\boldsymbol{r}_0$ [cf. (2.6)], viz.

$$c(\boldsymbol{r}, t) = \int_0^{\infty} \mathrm{d}\tau\, \dot{g}(t - \tau)\, \mathrm{e}^{-\langle l \rangle \tau} \delta[\boldsymbol{r} - \{\boldsymbol{r}_0 + \langle \boldsymbol{v}_\mathrm{L} \rangle \tau\}], \tag{3.1}$$

can be interpreted as the resulting concentration for a single realization of a stochastic process, i.e., with known (deterministic) $\dot{g}$, l, and $\boldsymbol{v}_\mathrm{L}$. Now consider a great number (an "ensemble") of realizations of (3.1), for each of which

$$\underset{\sim}{c}(\boldsymbol{r}, t) = \int_0^{\infty} \mathrm{d}\tau\, \dot{\underset{\sim}{g}}(t - \tau)\, \mathrm{e}^{-\langle \underset{\sim}{l} \rangle \tau} \delta[\boldsymbol{r} - \{\boldsymbol{r}_0 + \langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle \tau\}], \tag{3.2}$$

(in which the tildes identify random-variables). We now seek statistical properties of the random concentration $\underset{\sim}{c}$ (especially its mean and variance) over the ensemble of realizations, with different gain and loss rates and with different trajectories, caused, e.g., by "turbulent diffusion".

If $\dot{\underset{\sim}{g}}$, $\langle \underset{\sim}{l} \rangle$, and $\langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle$ are independent random-variables, then from (3.2) the ensemble- (as opposed to the time-) average of $\underset{\sim}{c}$ is

$$\mathscr{E}\{\underset{\sim}{c}\} = \int_0^{\infty} \mathrm{d}\tau\, \mathscr{E}\{\dot{\underset{\sim}{g}}(t - \tau)\}\, \mathscr{E}\{\mathrm{e}^{-\langle \underset{\sim}{l} \rangle \tau}\} \times \mathscr{E}\{\delta[\boldsymbol{r} - \boldsymbol{r}_0 - \langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle \tau]\}. \tag{3.3}$$

Similarly, for the autocorrelation of $\underset{\sim}{c}$,

$$\mathscr{E}\{\underset{\sim}{c}(\boldsymbol{r}_1, t_1)\underset{\sim}{c}(\boldsymbol{r}_2, t_2)\} = \int_0^{\infty} \mathrm{d}\tau_1 \int_0^{\infty} \mathrm{d}\tau_2\, \mathscr{E}\{\dot{\underset{\sim}{g}}(t_1 - \tau_1) \times \dot{\underset{\sim}{g}}(t_2 - \tau_2)\}\, \mathscr{E}\{\mathrm{e}^{-\langle \underset{\sim}{l} \rangle \tau_1} \mathrm{e}^{-\langle \underset{\sim}{l} \rangle \tau_2}\} \times \mathscr{E}\{\delta(\boldsymbol{r}_1 - \boldsymbol{r}_0 - \langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle \tau_1)\, \delta(\boldsymbol{r}_2 - \boldsymbol{r}_0 - \langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle \tau_2)\}. \tag{3.4}$$

If $\dot{\underset{\sim}{g}}$, $\langle \underset{\sim}{l} \rangle$, and $\langle \underset{\sim}{\boldsymbol{v}}_\mathrm{L} \rangle$ are not independent random-variables (e.g., if $\dot{\underset{\sim}{g}}$ describes particle resuspension and if $\langle \underset{\sim}{l} \rangle$ includes dry deposition, then these would be proportional to the velocity), then in (3.3), for example, correlations between the variables would be needed. In this report, however, only the simpler case of independent random-variables will be considered.

To understand the meaning of the term $\mathscr{E}\{\delta(\boldsymbol{r}-\boldsymbol{r}_0-\langle \underset{\sim}{v}_{\mathrm{L}}\rangle\tau)\}$ in (3.3), and the similar term in (3.4), first simplify notation by letting $\boldsymbol{x}=\boldsymbol{r}-\boldsymbol{r}_0$ and

$$\underset{\sim}{\xi}=\langle \underset{\sim}{v}_{\mathrm{L}}\rangle\tau \equiv \int_{t-\tau}^{t} \underset{\sim}{v}_{\mathrm{L}}(\tau')\,\mathrm{d}\tau' \equiv \underset{\sim}{\xi}(t,\tau). \tag{3.5}$$

Then, using Fourier transforms with parameter $\boldsymbol{k}$, we see

$$\begin{aligned}\mathscr{F}_{\boldsymbol{k}}\mathscr{E}\{\delta(\boldsymbol{x}-\underset{\sim}{\xi})\} &= \mathscr{E}\left\{\int \mathrm{d}\boldsymbol{x}\,\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{x}}\,\delta[\boldsymbol{x}-\underset{\sim}{\xi}(t,\tau)]\right\}\\ &= \mathscr{E}\{\mathrm{e}^{i\boldsymbol{k}\cdot[\boldsymbol{x}=\xi]}\} = \int \mathrm{d}\xi\, f_{\xi}(\underset{\sim}{\xi}=\boldsymbol{x})\,\mathrm{e}^{i\boldsymbol{k}\cdot\xi}\\ &= \mathscr{F}_{\boldsymbol{k}} f_{\xi}(\underset{\sim}{\xi}=\boldsymbol{x}),\end{aligned} \tag{3.6}$$

where the second to last equality follows from the definition of the expected value, in which f_{ξ} is the probability density-function (pdf) for the random variable $\underset{\sim}{\xi}=\langle \underset{\sim}{v}_{\mathrm{L}}\rangle\tau$. In words, the result (3.6) shows that the expected value of this delta function of the random variable $\underset{\sim}{\xi}$ is just the probability that the trace material has traveled from its source at $\boldsymbol{r}_0$ to the sampler at $\boldsymbol{r}$:

$$\mathscr{E}\{\delta[\boldsymbol{r}-(\boldsymbol{r}_0+\underset{\sim}{\xi})]\} = f_{\xi}[\underset{\sim}{\xi}=(\boldsymbol{r}-\boldsymbol{r}_0)], \tag{3.7}$$

which, in hindsight, seems rather obvious.

In a similar manner, by taking a double Fourier transform of (3.4), it is straightforward to show that $\mathscr{E}\{\delta_1\delta_2\}$ is the joint pdf for $\underset{\sim}{\xi}_1$ and $\underset{\sim}{\xi}_2$. Details will be presented in a later section. Further, there appear to be no conceptual difficulties in extending this method to the evaluation of moments of any order. The present method therefore appears able to yield all statistical moments of the exact solution to the convective-diffusion equation (diffusion having been incorporated not with a diffusivity, but via the randomness of the trajectories). The method also explicitly accounts for stochastic gain and removal. In addition, a distributed source can be described simply by changing from $\dot{g}(t)$ to a function such as $g(\boldsymbol{r}_0,t)\,\mathrm{d}\boldsymbol{r}_0$, describing the spatial distribution of sources, and by integrating over all source areas, $\boldsymbol{r}_0$. These results are perhaps not particularly surprising to those who heuristically start from an integral-equation formulation of dispersion (e.g., for a restricted case, see Pasquill and Smith, 1983, p. 141), but it is satisfying to see the general formulation derived directly from the continuity equation. In the next two sections, some applications will be presented.

4. Applications to describe mean concentrations

In this section, to illustrate the theory, the ensemble-mean concentration will be calculated for a few simple cases. In the next section, illustrative calculations of second moments will be given.

4.1. *Plume model with along-wind diffusion and for deterministic gain and loss*

Consider (3.3), with (3.7), for a steady-state source at $(0,0,h)$. To bound the cases of plume reflection versus complete absorption at $z=0$, we write (3.3) as

$$\begin{aligned}\mathscr{E}\{\underset{\sim}{c}(\boldsymbol{r},t)\} = \int_0^{\infty} \mathrm{d}\tau\, g_0\,\mathrm{e}^{-l_0\tau}[f_{\xi}\{x,y,(z-h)\}\\ +\varepsilon f_{\xi}\{x,y,(z+h)\}],\end{aligned} \tag{4.1}$$

with $\varepsilon=1$ for perfect reflection and $\varepsilon=-1$ for perfect absorption at the surface. To proceed, we need the pdf for

$$\underset{\sim}{\xi}(t,\tau) = \int_{t-\tau}^{t} \underset{\sim}{v}_{\mathrm{L}}(\tau')\,\mathrm{d}\tau'. \tag{4.2}$$

A number of assumptions are now introduced. First, assume that the components of $\underset{\sim}{\xi}$ (or at least the first two moments) are independent of the absolute time, dependent only on the time since release, τ. Second, based on the central-limit theorem (or on data in Monin and Yaglom, 1971), assume that the pdf for $\underset{\sim}{\xi}$, f_{ξ}, is Gaussian; therefore, we need only the mean and variance of $\underset{\sim}{\xi}$. Third, assume that the mean-wind is steady along the x-axis, so that

$$\mathscr{E}\{\underset{\sim}{\xi}\} = \mathscr{E}\left\{\int_0^{\tau} \underset{\sim}{v}_{\mathrm{L}}(\tau')\,\mathrm{d}\tau'\right\} = u_0\tau\hat{\boldsymbol{i}}. \tag{4.3}$$

Fourth, assume that the random components of $\underset{\sim}{v}_{\mathrm{L}}$ (about the mean) are independent and possess the same statistics; therefore, using primes to identify these components, we need evaluate only

$$\mathscr{E}\{\underset{\sim}{\xi}'(\tau_1)\underset{\sim}{\xi}'(\tau_2)\} = \int_0^{\tau_1} \mathrm{d}\tau_1' \int_0^{\tau_2} \mathrm{d}\tau_2' \mathscr{E}\{\underset{\sim}{u}_{\mathrm{L}}'(\tau_1')\underset{\sim}{u}_{\mathrm{L}}'(\tau_2')\}. \tag{4.4}$$

Finally, assume

$$\mathscr{E}\{\underset{\sim}{u}_{\mathrm{L}}'(\tau_1')\underset{\sim}{u}_{\mathrm{L}}'(\tau_2')\} = \sigma_u^2 \exp\{-|\tau_1 - \tau_2|/T_{\mathrm{L}}\}, \tag{4.5}$$

where T_{L} is a characteristic (Lagrangian) time-scale for the fluid's "memory" of velocity fluctuations. With (4.5) in (4.4) and evaluating for $\tau_1 = \tau_2 = \tau$, we then obtain

$$\sigma_{\xi}^2(\tau) = 2(\sigma_u T_{\mathrm{L}})^2 \left[\frac{\tau}{T_{\mathrm{L}}} - 1 + \exp\left\{-\frac{\tau}{T_{\mathrm{L}}}\right\}\right]. \tag{4.6}$$

In summary, for the pdf in (4.1), we take

$$f_{\xi}\{x, y, (z \mp h)\} = \frac{1}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \times \exp\left[-\frac{(x-u_0\tau)^2}{2\sigma_x^2} - \frac{y^2}{2\sigma_y^2} - \frac{(z \mp h)^2}{2\sigma_z^2}\right]. \tag{4.7}$$

If (4.7) is used in (4.1), the result is difficult to integrate, except numerically. For $\tau \gg T_{\mathrm{L}}$,

$$\sigma_x^2 \to 2[\sigma_u T_{\mathrm{L}}]^2 \frac{\tau}{T_{\mathrm{L}}} \equiv 2K\tau, \tag{4.8}$$

and this in (4.1) yields

$$\mathscr{E}\{\underset{\sim}{c}\} = \frac{g_0}{4\pi K} \exp\left\{\frac{u_0 x}{2K}\right\} \left[\frac{1}{r_1} \times \exp\left\{-r_1\left(\frac{u_0^2}{4K^2} + \frac{l_0}{K}\right)^{1/2}\right\} + \frac{\varepsilon}{r_2} \exp\left\{-r_2\left(\frac{u_0^2}{4K^2} + \frac{l_0}{K}\right)^{1/2}\right\}\right] \tag{4.9}$$

with

$$r_{1,2}^2 = x^2 + y^2 + (z \mp h)^2. \tag{4.10}$$

The result (4.10) is the same as can be obtained from "K-theory" of diffusion (with constant K), but as shown in Appendix D, the K-theory approach is not without substantial difficulty (accounting for along-wind diffusion).

In Fig. 1, the result (4.9) with $l_0 = 0$ is plotted along with the familiar Gaussian-plume result (in which x-diffusion is ignored),

$$\chi = \frac{\dot{Q}}{2\pi\bar{u}\sigma_y\sigma_z} \exp\left\{-\frac{y^2}{2\sigma_y^2}\right\} \left[\exp\left\{-\frac{(z-h)^2}{2\sigma_z^2}\right\} + \varepsilon \exp\left\{-\frac{(z+h)^2}{2\sigma_z^2}\right\}\right], \tag{4.11}$$

for the corresponding case with $\sigma_y = \sigma_z = 2Kx/\bar{u}$ and for $\varepsilon = 1$ (i.e., no deposition). And, although the desire, here, is more to show applications of the formalism than consequences of the results, the comparison in Fig. 1 reveals the following.

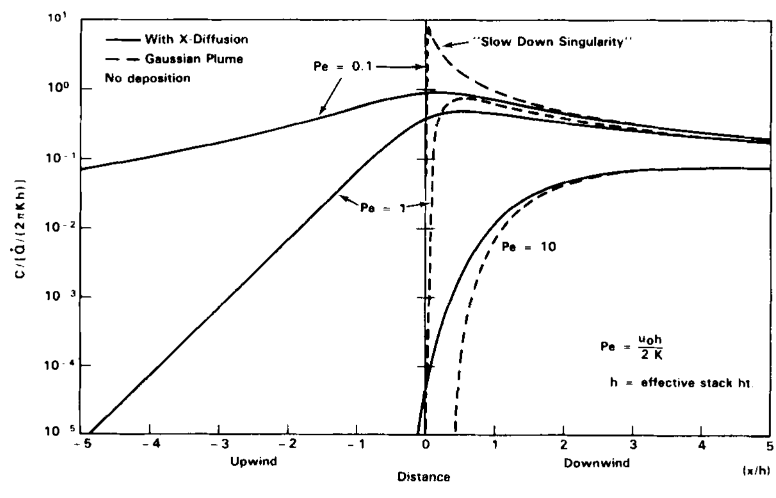

Fig. 1. Plots of eqs. (4.11) and (4.9), with $l_0 = 0$ and $\varepsilon = 1$.

(i) x-diffusion can be ignored beyond a few "stack heights", h, from the source.
(ii) x-diffusion should not be ignored for $x \lesssim h$. Ignoring x-diffusion is the cause of the nonphysical "slow-down singularity" (i.e., $\chi \to \infty$ with $\bar{u} \to 0$), familiar in assessing accident consequences, e.g., for nuclear facilities. Also, ignoring x-diffusion may cause some of the difficulties in deriving σ-values from concentration data.
(iii) x-diffusion should not be ignored in the "acid-rain issue", since the resulting concentration is modeled totally inadequately in the (climatologically averaged) upwind direction, $x < 0$.

For large travel times, such as for the acid-rain issue, it would of course be inappropriate to use the same K or σ values for all directions: horizontal diffusion is then typically very much larger than vertical diffusion. As an illustration, if K_z is ignorable, then (3.3) evaluated with constant gain and removal and with

$$f_{\xi,\eta} = \frac{1}{2\pi\sigma_x\sigma_y}\exp\left\{-\frac{(x-u_0\tau)^2}{2\sigma_x^2} - \frac{y^2}{2\sigma_y^2}\right\}, \qquad (4.12)$$

with $\sigma_x^2 = 2\alpha\tau$ and $\sigma_y^2 = 2\beta\tau$, gives

$$\mathscr{E}\{c(x,y)\} = \frac{g_0}{2\pi\sqrt{\alpha\beta}}\exp\left\{\frac{xu_0}{2\alpha}\right\} \times K_0\left[\left\{\left(\frac{x^2}{\alpha}+\frac{y^2}{\beta}\right)\left(l_0+\frac{u_0^2}{2\alpha}\right)\right\}^{1/2}\right],$$

in which K_0 is the modified Bessel function of second kind. If we also have $\sigma_z^2 = 2\gamma\tau$, then the generalization of (4.9) is

$$\mathscr{E}\{c(r)\} = \frac{g_0}{4\pi}\frac{e^{u_0x/(2\alpha)}}{\sqrt{\alpha\beta\gamma}}\left[\frac{1}{r_1'}\exp\left\{-r_1'\left(l_0+\frac{u_0^2}{4\alpha}\right)^{1/2}\right\} + \frac{\varepsilon}{r_2'}\exp\left\{-r_2'\left(l_0+\frac{u_0^2}{4\alpha}\right)^{1/2}\right\}\right], \qquad (4.13)$$

with

$$(r_{1,2}')^2 = \frac{x^2}{\alpha} + \frac{y^2}{\beta} + \frac{(z \mp h)^2}{\gamma}.$$

4.2. Mean concentration with stochastic loss

For this illustration, we start from (3.3) with (3.7) and with a steady, deterministic source at the origin:

$$\mathscr{E}\{c(r,t)\} = g_0\int_0^\infty d\tau\,\mathscr{E}\{e^{-\langle l\rangle\tau}\}\,f_\xi(\xi = r). \qquad (4.14)$$

We note that, since $\langle l\rangle$ is positive,

$$\mathscr{E}\{e^{-\langle l\rangle\tau}\} = \int_0^\infty d\langle l\rangle\, f_{\langle l\rangle}(\langle l\rangle)\,e^{-\langle l\rangle\tau} \equiv \mathscr{L}_\tau f_{\langle l\rangle}(\langle l\rangle), \qquad (4.15)$$

in which $f_{\langle l\rangle}$ is the pdf for the random loss-rate and $\mathscr{L}_\tau$ is a Laplace transform with parameter τ. Separate subsections are now devoted to cases with and without diffusion.

4.2.1. Negligible diffusion. If diffusion is negligible, i.e., if

$$f_\xi(\xi = r) = \delta(x - u_0\tau)\,\delta(y)\,\delta(z), \qquad (4.16)$$

then (4.14) with (4.15) becomes

$$\mathscr{E}\{c\} = \frac{g_0}{u_0}\mathscr{L}_{x/u_0}\{f_{\langle l\rangle}(\langle l\rangle)\}\,\delta(y)\,\delta(z). \qquad (4.17)$$

As one example of (4.17), suppose $\langle l\rangle$ is deterministic. Then

$$\mathscr{E}\{c\} = \frac{g_0}{u_0}\delta(y)\,\delta(z)\exp\{-xl_0/u_0\}. \qquad (4.18)$$

As a more informative example, suppose $\langle l\rangle$ has a gamma distribution, i.e.,

$$f_{\langle l\rangle}(\langle l\rangle) = \frac{\gamma^{b+1}}{\Gamma(b+1)}\langle l\rangle^b e^{-\gamma\langle l\rangle}h(\langle l\rangle), \qquad (4.19)$$

in which $h(\langle l\rangle)$ is the Heaviside function and the mean value of $\langle l\rangle$ is $(b+1)/\gamma = l_0$, say. Then (4.17) yields

$$\mathscr{E}\{c\} = \frac{g_0}{u_0}\delta(y)\,\delta(z)\left[1 + \frac{l_0x}{(b+1)u_0}\right]^{-(1+b)}. \qquad (4.20)$$

As an example of (4.20), if $b = 1$, then

$$\mathscr{E}\{c\} = \frac{g_0}{u_0}\delta(y)\,\delta(z)\left[\frac{1}{1 + l_0x/(2u_0)}\right]^2, \qquad (4.21)$$

which shows that a distribution of $\langle l\rangle$-values results in a very much slower decrease in the concentration with increasing x (i.e., roughly as $1/x^2$) compared to the exponential decrease of (4.18), appropriate when $\langle l\rangle$ is deterministic.

This result has already been emphasized by Rodhe (1980) for the case of precipitation scavenging and follows quite generally from Jensen's lemma for a convex removal-function. A convex function of l, $\chi(l)$, is one whose chord lies above or on the graph of χ. Jensen's inequality (see any advanced statistical text) states that if χ

is a convex function of l (e.g., here, $\chi(l) = e^{-\tau l}$), then

$$\mathscr{E}\{\chi(\underset{\sim}{l})\} \geqslant \chi[\mathscr{E}\{\underset{\sim}{l}\}]. \tag{4.22}$$

Applied in the present case, (4.22) states that the ensemble average of the concentration is usually larger than estimates derived using the average removal-rate.

The reasonableness of this result can be seen from an alternative definition of a convex function: its graph is above its tangent. Consequently, for any point λ where the slope is evaluated,

$$\chi(l) \geqslant \chi(\lambda) + \chi'(\lambda)[l - \lambda]. \tag{4.23}$$

Therefore, if λ is taken to be $\mathscr{E}\{\underset{\sim}{l}\}$, then (4.23) yields

$$\mathscr{E}\{\chi(\underset{\sim}{l})\} \geqslant \chi[\mathscr{E}\{\underset{\sim}{l}\}] + 0. \tag{4.24}$$

For some dependencies of the concentration on the removal rate, use of the mean removal-rate may be an adequate approximation; however, for a convex functional-dependence on l, use of the mean removal-rate not only ignores the stochastic nature of the removal process, but does so with a consistent bias toward more rapid removal.

4.2.2. Diffusion plus stochastic loss. As an illustration of how this formalism can be used to model precipitation scavenging, suppose that, in addition to a deterministic loss-rate l_0 (e.g., caused by chemical conversion), there is a Poisson-distributed stochastic loss: with average frequency λ_p (the average frequency with which the trace material encounters relatively short-duration precipitation bands), there are random pulses (at times $\underset{\sim}{t}_i$) of removal with random integrated removals $\underset{\sim}{\varepsilon}_i$; i.e.,

$$\underset{\sim}{l}(\tau) = l_0 + \underset{\sim}{\varepsilon}_i \delta(\tau - \underset{\sim}{t}_i). \tag{4.25}$$

Then

$$\int_0^\tau \underset{\sim}{l}(\tau')\,d\tau' = l_0 \tau + \sum_{i=1}^{\underset{\sim}{n}(\tau)} \underset{\sim}{\varepsilon}_i, \tag{4.26}$$

where $\underset{\sim}{n}(\tau)$ is the (random) number of "storms" (or rain cells) encountered during the time interval $(0, \tau)$, considered to be long compared to the duration (typically $\sim 10^3$ s) of an individual rain cell. If (4.26) is used in (4.14) and if y- and z-diffusion are ignored, then (4.14) becomes

$$\mathscr{E}\{\underset{\sim}{c}\} = g_0 \int_0^\infty d\tau\, e^{-l_0\tau} \mathscr{E}\left\{\exp\left[-\sum_{i=1}^{\underset{\sim}{n}(\tau)} \underset{\sim}{\varepsilon}_i\right]\right\} \frac{1}{\sqrt{2\pi}\sigma_x} \times \exp\left\{-\frac{(x - u_0\tau)^2}{2\sigma_x^2}\right\} \delta(y)\,\delta(z). \tag{4.27}$$

Before trying to evaluate (4.27), look at the random variable that appears in (4.27):

$$\underset{\sim}{\Pi} = \exp[-\underset{\sim}{\Sigma}], \quad \text{with } \underset{\sim}{\Sigma} = \sum_{i=1}^{\underset{\sim}{n}(\tau)} \underset{\sim}{\varepsilon}_i,$$

which is known as a compound Poisson-process. As is derived in many statistical texts (e.g., Ross, 1983), the "moment-generating function" of $\underset{\sim}{\Sigma}$ is

$$\Phi_\tau(s) = \mathscr{E}\{\exp[s\underset{\sim}{\Sigma}]\}$$

$$= \sum_{n=0}^\infty \mathscr{E}\{\exp[s\underset{\sim}{\Sigma}]/\underset{\sim}{n} = n\}\ \text{prob}\{\underset{\sim}{n} = n\}$$

$$= \sum_{n=0}^\infty \mathscr{E}\{\exp[s(\underset{\sim}{\varepsilon}_1 + \underset{\sim}{\varepsilon}_2 + \cdots + \underset{\sim}{\varepsilon}_n)]/\underset{\sim}{n} = n\} \times e^{-\lambda_p\tau}(\lambda_p\tau)^n/n! \tag{4.28}$$

$$= \sum_{n=0}^\infty [\mathscr{E}\{\exp(s\underset{\sim}{\varepsilon}_1)\}]^n e^{-\lambda_p\tau}(\lambda_p\tau)^n/n! \tag{4.29}$$

$$= \sum_n [\phi_{\underset{\sim}{\varepsilon}}]^n e^{-\lambda_p\tau}(\lambda_p\tau)^n/n! \tag{4.30}$$

$$= \exp\{\lambda_p\tau[\phi_{\underset{\sim}{\varepsilon}}(s) - 1]\}, \tag{4.31}$$

where (4.28) follows from the definition of a Poisson process, (4.29) follows from the assumption that the statistical distribution is the same for all $\underset{\sim}{\varepsilon}_i$, and in (4.30), $\phi_{\underset{\sim}{\varepsilon}}$ is the moment generating function of $\underset{\sim}{\varepsilon}$:

$$\phi_{\underset{\sim}{\varepsilon}}(s) = \mathscr{E}\{\exp(s\underset{\sim}{\varepsilon})\} \equiv \int_{-\infty}^{+\infty} e^{s\varepsilon} f_{\underset{\sim}{\varepsilon}}(\varepsilon)\,d\varepsilon. \tag{4.32}$$

For example, if the random fraction, $\underset{\sim}{\varepsilon}$, is uniformly distributed in (0, 1), then

$$\phi_{\underset{\sim}{\varepsilon}}(s) = \int_0^1 e^{s\varepsilon}\,d\varepsilon = \frac{1}{s}[e^s - 1]. \tag{4.33}$$

Now, returning to (4.27), we see that the expected value in the integrand is the moment generating function Φ_τ, with $s = -1$.

Eq. (4.27) can now be evaluated for different distributions of $\underline{\varepsilon}_i$ (and, in fact, for more general loss-rates). As perhaps the simplest example, if $\sigma_x = 2K\tau$ and if $\underline{\varepsilon}$ is uniformly distributed in (0, 1) [i.e., use (4.33) with $s = 1$], then the resulting integral is known (e.g., Erdélyi, 1954):

$$\frac{\mathscr{E}\{\underline{c}\}}{\delta(y)\,\delta(z)} = \begin{cases} \dfrac{g_0}{u_0}\dfrac{1}{(1+\delta)^{1/2}} \times \exp\left\{-\dfrac{u_0 x}{2K}[(1+\delta)^{1/2}-1]\right\}, & x > 0 \\[2ex] \dfrac{g_0}{u_0}\dfrac{1}{(1+\delta)^{1/2}} \times \exp\left\{+\dfrac{u_0 x}{2K}[(1+\delta)^{1/2}+1]\right\}, & x < 0 \end{cases} \tag{4.34}$$

where

$$\delta = \frac{4K}{u_0^2}\left[l_0 + \frac{\lambda_p}{e}\right], \tag{4.35}$$

which is essentially the inverse of the Péclét number (the ratio of transport to diffusive "speeds").

It is informative to examine (4.34) in some detail. For $x > 0$ and δ small,

$$\exp\left\{-\frac{u_0 x}{2K}[(1+\delta)^{1/2}-1]\right\} \simeq \exp\left\{-\frac{x}{u_0}\left(l_0 + \frac{\lambda_p}{e}\right)\right\}, \tag{4.36}$$

showing that the concentration is reduced at the rate $(l_0 + \lambda_p/e)$, which is slightly slower than the average removal rate [for $\mathscr{E}\{\underline{\varepsilon}\} = 1/2$] of $l_0 + \lambda_p/2$, where, again, λ_p is the average frequency of precipitation events. This result is therefore consistent with Jensen's inequality, (4.22). For $x > 0$ and δ large (large diffusion compared to transport or, e.g., frequent precipitation events), then (4.34) gives an e-fold length of essentially $(eK/\lambda_p)^{1/2}$, which can be substantially larger (viz., slower removal) than the value of u_0/Λ, frequently used in Gaussian plume models modified to account for precipitation scavenging, with Λ an average scavenging rate. Fig. 2 summarizes this case of stochastic scavenging, but with only x-diffusion. For a more general case (stack of height h, image source, diffusivities α, β, γ in the x, y, and z directions), then the result can be found as for (4.13).

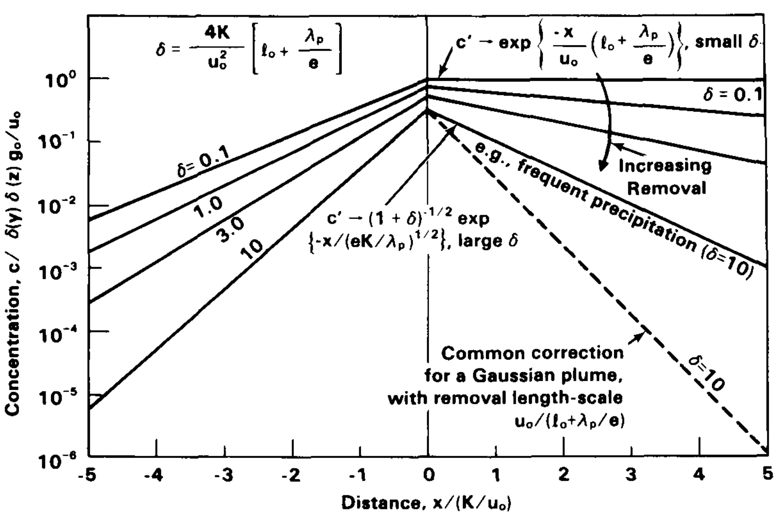

Fig. 2. Plots of eq. (4.34) showing the dependence of the mean concentration on downwind distance for different levels of stochastic scavenging and compared with the frequently used Gaussian plume model incorrectly "corrected" for precipitation scavenging.

5. Applications to describe concentration fluctuations

We now turn to second-order moments, rather than just the first-order moments considered in the previous section, but since calculations of second- (and higher-) order moments become quite involved, only two examples will be presented. In the first, we seek an estimate of the magnitude of concentration fluctuations arising from diffusion, alone, without a mean wind. In the second example, we add a mean wind and a stochastic gain term. A third example, attempting to explain Junge's empirical result relating concentration fluctuations to pollutant residence time in the atmosphere, was abandoned when it was found that Junge's result depends on a peculiar definition of concentration fluctuations (Slinn, 1988).

5.1. Random walk from a continuous point-source

A familiar analogy for the random-walk problem is in terms of a single, inebriated pedestrian. For the present problem, imagine a continuous stream of drunkards leaving a saloon, the drunkards take random steps along a sidewalk (the y-axis), some fall into the street, and the problem is to find the mean concentration of drunkards still on the sidewalk, plus a measure of the fluctuations in the concentration, at any point.

Mathematically, we start with (3.3), which for a constant loss rate, l_0, a constant gain rate, g_0, and the origin of the y-axis at the saloon door, becomes

$$\mathscr{E}\{\underset{\sim}{c}\} = g_0 \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-l_0 \tau} \mathscr{E}\{\delta[y - \underset{\sim}{\eta}(\tau)]\}, \tag{5.1}$$

with $\underset{\sim}{\eta} = \langle \underset{\sim}{v}_L \rangle \tau$. Now use

$$\mathscr{E}\{\delta[y-\underset{\sim}{\eta}]\} = f_\eta[\underset{\sim}{\eta} = y] = \frac{1}{\sqrt{2\pi}\sigma_y(\tau)} \exp\left\{-\frac{y^2}{2\sigma_y^2}\right\}, \tag{5.2}$$

with $\sigma_y^2 = 2\beta\tau$. The resulting integral is available in Laplace-transform tables; the result is

$$\mathscr{E}\{\underset{\sim}{c}\} = \frac{g_0}{2\sqrt{l_0 \beta}} \exp\left\{-\left[\frac{l_0 y^2}{\beta}\right]^{1/2}\right\}. \tag{5.3}$$

As two asides, note that there is no steady-state solution unless there is loss, and note that if σ_y^2 = constant, then the solution would have been

$$\mathscr{E}\{\underset{\sim}{c}\} = \frac{g_0}{l_0} \frac{1}{\sqrt{2\pi}\sigma_y} \exp\left\{-\frac{y^2}{2\sigma_y^2}\right\}.$$

To obtain a measure of the concentration fluctuations, we evaluate [cf., (3.4)]

$$\mathscr{E}\{\underset{\sim}{c}(y_1,t_1)\underset{\sim}{c}(y_2,t_2)\} = g_0^2 \int_0^\infty \mathrm{d}\tau_1\, \mathrm{e}^{-l_0\tau_1} \int_0^\infty \mathrm{d}\tau_2\, \mathrm{e}^{-l_0\tau_2} \times \mathscr{E}\{\delta[y_1 - \underset{\sim}{\eta}(\tau_1)]\delta[y_2 - \underset{\sim}{\eta}(\tau_2)]\}, \tag{5.4}$$

with

$$\mathscr{E}\{\delta[y_1 - \underset{\sim}{\eta}_1]\delta[y_2 - \underset{\sim}{\eta}_2]\} = f_{\eta_1,\eta_2}(\underset{\sim}{\eta}_1 = y_1, \underset{\sim}{\eta}_2 = y_2) = \frac{1}{2\pi\sigma_1\sigma_2\sqrt{1-r^2}} \exp\left\{-\frac{1}{2(1-r^2)} \times \left[\frac{y_1^2}{\sigma_1^2} - \frac{2ry_1y_2}{\sigma_1\sigma_2} + \frac{y_2^2}{\sigma_2^2}\right]\right\}, \tag{5.5}$$

in which $\sigma_1^2 = 2\beta\tau_1$, $\sigma_2^2 = 2\beta\tau_2$, and, for a Wiener–Levy process (integral of white noise, consistent with taking the large-time approximation for σ), the correlation coefficient is given by (e.g., see Papoulis, 1965)

$$r^2 = \begin{cases} \tau_1/\tau_2, & \tau_1 \leqslant \tau_2 \\ \tau_2/\tau_1, & \tau_2 \leqslant \tau_1 \end{cases}. \tag{5.6}$$

It is possible to perform the integrations in (5.4), but a simpler method is to work with a double Fourier transform of (5.4) and use the characteristic function for the joint normal:

$$\Phi(k_1, k_2) = \exp\{-\tfrac{1}{2}[\sigma_1^2 k_1^2 + 2r\sigma_1\sigma_2 k_1 k_2 + \sigma_2^2 k_2^2]\}.$$

By either route, the result (evaluated at the same y and t) is

$$\mathscr{E}\{\underset{\sim}{c}^2(y,t)\} = \frac{g_0^2}{2\sqrt{2 l_0 \beta}} \exp\left\{-\left[\frac{2 l_0 y^2}{\beta}\right]^{1/2}\right\}. \tag{5.7}$$

Consequently, the square of the normalized standard deviation (or "coefficient of deviation"), one measure of the concentration fluctuations, is

$$f_c^2 = \frac{\sigma_c^2}{\mathscr{E}^2\{\underset{\sim}{c}\}} = \frac{[\mathscr{E}\{\underset{\sim}{c}^2\} - \mathscr{E}^2\{\underset{\sim}{c}\}]}{[\mathscr{E}\{\underset{\sim}{c}\}]^2} = -1 + \sqrt{2}\exp\left\{(\sqrt{2}-1)\sqrt{\frac{2 l_0 y^2}{\beta}}\right\}. \tag{5.8}$$

For the case of more practical interest (corresponding to (4.13), with three dimensions, diffusivities α, β, and γ, and with both a mean wind and loss), algebra leads to

$$\mathscr{E}\{\underset{\sim}{c}(\mathbf{r},t)\underset{\sim}{c}(\mathbf{r},t)\} = \frac{g_0^2}{(4\pi)^3}\frac{e^{xu_0/2\alpha}}{\alpha\beta\gamma} \times\left[\int_0^\infty d\tau_1\left\{\exp\left(-l_0+\frac{u_0^2}{4\alpha}\right)\tau_1\right\}\right. \times\int_0^{\tau_1}\frac{d\tau_2 e^{-l_0\tau_2}}{[\tau_2(\tau_1-\tau_2)]^{3/2}}\exp\left\{-\frac{1}{4\tau_2}r'^2\right\}+\int_0^\infty\frac{d\tau_1}{\tau_1^{3/2}} \times\exp\left\{-l_0\tau_1-\frac{r'^2}{4\tau_1}\right\}\int_{\tau_1}^\infty\frac{d\tau_2}{[\tau_2-\tau_1]^{3/2}} \left.\times\exp\left\{-\left(l_0+\frac{u_0^2}{4\alpha}\right)\tau_2\right\}\right],$$

with $(r')^2 = x^2/\alpha + y^2/\beta + (z \mp h)^2/\gamma$. Unfortunately, though, these integrals do not converge. The root problem is the incorrect use of $\sigma^2 \sim \tau$ for small time. However, a more reasonable time dependence of σ (e.g., 4.6) leads to analytically intractable integrals. Consequently, there appears to be no alternative but to proceed numerically, a task left for future studies. In the meantime, the plots of (5.8) in Fig. 3, inconsistently comparing (5.8) with data collected during cases when the fluids (air and water) had mean motion, nevertheless suggest that the theory does contain the major feature demonstrated by the data: an increase in the coefficient of deviation with increasing distance from the plume centerline.

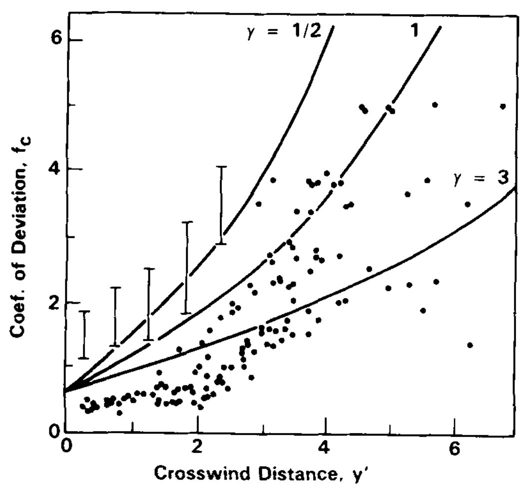

Fig. 3. Plots of eq. (5.8), with normalized "crosswind" distance $y' = (\gamma l_0/\beta)^{1/2}y$. Data for concentration fluctuations for plumes in the atmosphere (I) from Ramsdell and Hinds (1971) and in a lake (●) from Murthy and Casandy (1971).

5.2. *Along-wind diffusion plus stochastic gain*

The complexities of the integrals encountered in the previous subsection, in the evaluation of second moments, force retreat to another relatively simple case (one-dimensional along-wind diffusion plus a stochastic gain-term), which nevertheless is of practical interest. For this case, the mean value is the same as in (4.34) (derived using $\sigma_x^2 = 2K\tau$, for $\tau \gg T_L$), with $\lambda_p = 0$, leaving a deterministic loss rate l_0. For the second moment, cf. (3.4), we assume a stochastic gain term, with

$$\mathscr{E}\{\dot{g}(t_1-\tau_1)\dot{g}(t_2-\tau_2)\} = \sigma_g^2\exp\{-\gamma|\tau_1-\tau_2|\}, \tag{5.9}$$

and a jointly normal pdf for $\underset{\sim}{\xi}_1$ and $\underset{\sim}{\xi}_2$, similar to (5.5), but with mean values $u_0\tau$. Thus, the double Fourier transform of the pdf is

$$\Phi_{\xi_1,\xi_2}(k_1,k_2) = \exp\{iu_0[k_1\tau_1+k_2\tau_2]\} \times\exp\{-\tfrac{1}{2}[\sigma_{x_1}^2k_1^2+2r\sigma_{x_1}\sigma_{x_2}k_1k_2+\sigma_{x_2}^2k_2^2]\}, \tag{5.10}$$

with σ_x as before and the correlation coefficient, r, as in (5.6).

The evaluation of (3.4), even for this case of only x-diffusion, is rather tedious: using Fourier transforms, there are eight poles (within the contour integration) at which residues must be found. For $x \geq 0$, $x_1 = x_2 = x$, and $t_1 = t_2$, the result is

$$\frac{\mathscr{E}\{\underset{\sim}{c}^2\}}{(g_0/u_0)^2} = \frac{2}{[(1+\varepsilon)(1+2\varepsilon)]^{1/2}} \times\exp\{-x'[(1+2\varepsilon)^{1/2}-1]\} \times\left[1+\left(\frac{\sigma_g}{g_0}\right)^2\left\{\frac{1+\varepsilon}{1+\varepsilon+\varepsilon'}\right\}^{1/2}\right], \tag{5.11}$$

in which

$$\varepsilon = \frac{4l_0K}{u_0^2} = 4\left(\frac{\sigma_u}{u_0}\right)^2\frac{T_L}{T_r}, \quad \varepsilon' = \frac{4\gamma K}{u_0^2}, \quad x' = \frac{u_0x}{2K}, \tag{5.12}$$

where $T_r = l_0^{-1}$ is a measure of the material's residence time in the atmosphere. In contrast, (4.34) yields for the square of the mean [for $x > 0$ and in the notation of (5.11)]

$$\frac{\mathscr{E}^2\{\underset{\sim}{c}\}}{(g_0/u_0)^2} = \frac{1}{(1+\varepsilon)} \exp\{-2x'[(1+\varepsilon)^{1/2} - 1]\}. \tag{5.13}$$

There are several interesting features of these results.

(*A*) *For $\sigma_g = 0$ (see Fig. 4)*

(*A.1.*) *No loss*

Even without loss (viz., $l_0 = 0 = \varepsilon$), there is a steady-state solution (if there is a ventilating wind):

$$\langle c\rangle^2 \equiv \mathscr{E}^2\{\underset{\sim}{c}\}/[g_0/u_0]^2 = 1, \tag{5.14a}$$

$$\langle c^2\rangle \equiv \mathscr{E}\{\underset{\sim}{c}^2\}/[g_0/u_0]^2 = 2, \tag{5.14b}$$

$$f = \sigma/\langle c\rangle = [\langle c^2\rangle - \langle c\rangle^2]^{1/2}/\langle c\rangle = 1. \tag{5.14c}$$

The result (5.14c) predicts that, for all $x > 0$, there are large fluctuations when there is no loss term: the standard deviation is equal to the mean value.

(*A.2.*) *Large loss*

If $\varepsilon \to \infty$, both the first and second moments decrease exponentially with increasing distance,

$$\langle \underset{\sim}{c}\rangle^2 \to \varepsilon^{-1} \exp\{-2\sqrt{\varepsilon}x'\} \tag{5.15a}$$

$$\langle \underset{\sim}{c}^2\rangle \to \sqrt{2}\varepsilon^{-1} \exp\{-\sqrt{2\varepsilon}x'\}, \tag{5.15b}$$

but the coefficient of deviation, f, increases with x:

$$1 + f_c^2 = \langle \underset{\sim}{c}^2\rangle/\langle \underset{\sim}{c}\rangle^2 \to \sqrt{2}\exp\{2 - \sqrt{2})\sqrt{\varepsilon}x'\}, \tag{5.15c}$$

in essence because the mean concentration falls more rapidly with x than does $\langle \underset{\sim}{c}^2\rangle$. Because of this sensitivity of f^2 on $\langle c\rangle$, which is not easy to obtain accurately (either experimentally or theoretically), it is hoped that future experimental studies would report not only f^2 (e.g., Deardorff and Willis, 1984), but also $\langle \underset{\sim}{c}^2\rangle$.

(*A.3.*) *No wind*

With $u_0 \to 0$, it can be seen that (5.11), with $\sigma_g = 0$, reduces to (5.7).

(*B*) *$\sigma_g \neq 0$*

For variations in the source strength and for ε and ε' small, then

$$f_c \to \left[\frac{\sigma_g}{g_0}\right]^2 = f_g^2, \tag{5.16}$$

essentially independent of x. As a practical application of (5.16), suppose that this theory were describing modeling uncertainties (rather than natural variabilities) and that σ_g was a measure of uncertainties in specifying source strengths. Then (5.16) gives, for example, that if $(\sigma_g/g_0) = 50\%$,

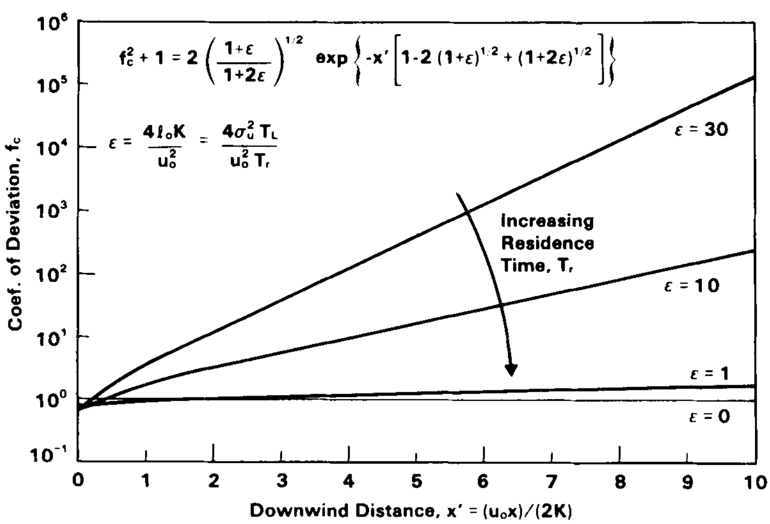

Fig. 4. Plots of the coefficient of deviation, derived from eqs. (5.11) and (5.13), as a function of downwind distance, for different residence times, T_r, and for $\sigma_g = 0$.

then with little loss from a well-mixed layer, with no cross-wind variations, and with major fluctuations caused by x-diffusion, $f_c = (0.5)^2 = 0.25$. More realistically, if emissions were known to within 10%, then this first measure of the uncertainty in the calculated concentration gives $f_c \sim 1\%$, which certainly is negligible compared with other uncertainties, e.g., in the "acid-rain issue".

6. Conclusions

The following conclusions can be made:

- An integral formulation for concentration fluctuations can be derived directly from the continuity equation, using Lagrange's method.
- To describe diffusion by this method, use was made of the result that the expected value of a delta function of $(\boldsymbol{x} - \underset{\sim}{\boldsymbol{\xi}})$, with $\underset{\sim}{\boldsymbol{\xi}}$ a random variable, is the pdf for $\underset{\sim}{\boldsymbol{\xi}}$, evaluated at $\boldsymbol{x}$.
- Gaussian plume models ignore along-wind diffusion, which many times is ill advised.
- When there is randomness in pollution removal, less pollution is removed, downwind of a point source, than would be expected if Jensen's inequality were not appreciated.
- In the examples investigated, the concentration fluctuations (e.g., as measured by the standard deviation) generally did not decrease so rapidly with distance as did the mean concentrations.
- Uncertainties in modeling the source strengths in the acid-rain issue are not expected to have such a significant influence on overall uncertainties as those derived from randomness and uncertainties in transport, diffusion, and removal processes.

It is clear that many additional applications of the theory presented here could be investigated.

7. Acknowledgements

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8. List of frequently used symbols

Subscripts

E = Eulerian
L = Lagrangian
0 = constant value

Special notation

$\underset{\sim}{\xi}$ = identifies ξ as a random variable
$\langle \underset{\sim}{\xi} \rangle$ = time average of ξ, except as defined in eqs. (5.14) and (5.15)
$\bar{\underset{\sim}{\xi}}$ = average of ξ over some other variable (e.g., x)

Symbols and functions

c = concentration for a continuous, point source
C = concentration (mass density, ML^{-3}, or mass mixing-ratio, MM^{-1})
$\delta[\ ]$ = Dirac delta function
$\mathscr{E}\{\underset{\sim}{\boldsymbol{\xi}}\}$ = expected value (ensemble average) of $\underset{\sim}{\boldsymbol{\xi}}$
$f_{\underset{\sim}{\xi}}(\underset{\sim}{\boldsymbol{\xi}} = \boldsymbol{r})$ = probability density function for the random variable $\underset{\sim}{\boldsymbol{\xi}}$ evaluated at $\underset{\sim}{\boldsymbol{\xi}} = \boldsymbol{r}$
$\mathscr{F}_k[\ ]$ = Fourier transform (with wave number k)
g = gain (or production) rate (MT^{-1})
$\dot{G}$ = volumetric gain rate ($ML^{-3}T^{-1}$)
$h[\ ]$ = Heaviside step function
l = first-order loss rate (T^{-1})
$\dot{L}$ = volumetric loss rate ($ML^{-3}T^{-1}$)
$\mathscr{L}_p[\ ]$ = Laplace transform (with parameter p)

9. Appendix A

The purpose of this appendix is to justify the statement in the text that C in eq. (2.1) can be either mass density or mass-mixing ratio and that the fluid can be compressible or incompressible. Toward that goal, let χ be the mass density of the trace species of interest. Let $\dot{P}$ and $\dot{R}$ respectively be the rate at which the substance is produced and removed per unit volume. Then in the continuum approximation (or treat χ as an unnormalized statistical density-function), χ satisfies the continuity equation

$$\frac{\partial \chi}{\partial t} = -\nabla \cdot \overrightarrow{\text{flux}} + \dot{P} - \dot{R}. \quad (A.1)$$

If the host medium does not disperse the substance (assumed for eq. 2.1) and if, relative to the fluid velocity $\boldsymbol{v}_f$, the substance has a "slip velocity" $\boldsymbol{v}_s$ (e.g., caused by gravity or diffusiophoresis), then the flux in (A.1) is given by

$$\overrightarrow{\text{flux}} = \boldsymbol{v}\chi \equiv [\boldsymbol{v}_f + \boldsymbol{v}_s]\chi. \quad (A.2)$$

With (A.2), (A.1) becomes

$$\frac{\partial \chi}{\partial t} + \boldsymbol{v} \cdot \nabla \chi = \dot{P} - [\dot{R} + \chi \nabla \cdot \boldsymbol{v}]. \quad (A.3)$$

The reader is asked to notice that $\chi \nabla \cdot \boldsymbol{v}$ in (A.3) is an effective removal (or production) of χ, linear in χ, and therefore, as stated in the text, this additional removal-term does not influence the analysis.

Now introduce the mixing ratio $M = \chi/\rho$, where ρ is the mass density of the host medium. If there are no volumetric sources and sinks of this host fluid, then its continuity equation is

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \boldsymbol{v}_f). \quad (A.4)$$

If (A.4) is used in (A.3), then it becomes

$$\rho\left[\frac{\partial M}{\partial t} + \boldsymbol{v} \cdot \nabla M\right] = \dot{P} - [\dot{R} + M \nabla \cdot (\rho \boldsymbol{v}_s)]. \quad (A.5)$$

For the case that $\boldsymbol{v}_s = 0$, then (A.5) becomes the same as (2.1) in the text, which completes the justification that C can be either mass density or mass-mixing ratio and that the fluid can be compressible or incompressible, if the gain and loss terms are defined suitably.

10. Appendix B

The purpose of this appendix is to use Lagrange's method to obtain the solution to Euler's continuity equation (2.1). To simplify notation, consider the one-dimensional version of (2.1):

$$\frac{\partial C}{\partial t} + u_E \frac{\partial C}{\partial x} = \dot{G} - \dot{L}. \quad (B.1)$$

Lagrange's result (see many textbooks on first-order partial differential equations) is that the general solution to (B.1) is

$$f_4 = F(f_1), \quad (B.2)$$

where F is an arbitrary function (later to be determined from initial conditions) and where $f_1(x, t, C) = \alpha$ and $f_4(x, t, C) = \beta$ (with α and β constants) are solutions of the "characteristic equations"

$$\frac{dt}{1} = \frac{dx}{u_E(x, t)} = \frac{dC}{\dot{G} - \dot{L}}. \quad (B.3)$$

The first equality in (B.3) gives $f_1(x, t) = \alpha$, which describes the trajectory of each fluid element (and similarly for three dimensions); the second equality in (B.3) gives f_4.

Consider, then, the first equality in (B.3):

$$\frac{dx}{dt} = u_E(x, t). \quad (B.4)$$

On the right-hand side of (B.4), $x = x(t)$, and therefore $u_E[x(t), t]$ is the Eulerian velocity evaluated at time t as a "marked fluid-particle" passes point $x(t)$. Using alternative notation, let

$$u_E[x(t), t] = u_L(t), \quad (B.5)$$

where $u_L(t)$ is the (Lagrangian) velocity experienced by the particle. Then (B.4) has the solution

$$x(t) = x(0) + \int_0^t u_L(\tau)\, d\tau \quad (B.6)$$

or

$$\left[x(t) - \int_0^t u_L(\tau)\, d\tau\right] = x(0) \equiv \alpha = f_1(x, t), \quad (B.7)$$

and similarly for other dimensions.

Solving the second equality in (B.3) requires specifications of $\dot{G}$ and $\dot{L}$. For the important case with $\dot{G}$ independent from C and $\dot{L}$ linear in C, viz., $\dot{L} = l(\boldsymbol{r}, t)\, C$, then the solution is easily found to be

$$f_4(x, t, C) = \beta = C(x, t) \exp\left\{\int_0^t l[x(t'), t']\, dt'\right\} - \int_0^t dt'\, \dot{G}[x(t'), t'] \exp\left\{\int_0^{t'} l[x(t''), t'']\, dt''\right\}. \quad (B.8)$$

Consequently, Lagrange's solution, (B.2), to Euler's continuity equation is

$$C\exp\left\{\int_0^t l\,\mathrm{d}t'\right\} - \int_0^t \mathrm{d}t'\,\dot{G}\exp\left\{\int_0^{t'} l\,\mathrm{d}t''\right\} = F\left[x - \int_0^t u_{\mathrm{L}}(\tau)\,\mathrm{d}\tau\right], \tag{B.9}$$

in which F is an arbitrary function, but which can be defined by the initial conditions. Thus, for $t = 0$, (B.9) gives

$$F[x] = C(x, 0) \equiv C_0(x), \tag{B.10}$$

and therefore, with (B.10) in (B.9), for three dimensions, and for time measured positive when backward from current values, the result is as given in (2.2) in the text.

11. Appendix C

The purpose of this appendix is to demonstrate how (2.2) can be obtained by transforming (2.1) to Lagrangian coordinates and then solving the resulting ordinary differential equation. In the next paragraph it will be shown that, in Lagrangian coordinates (i.e., in a non-inertial coordinate-system that, at each point, moves with the (Lagrangian) velocity $\boldsymbol{v}_{\mathrm{L}}(t) = \boldsymbol{v}_{\mathrm{E}}(\boldsymbol{r}, t)$ of the fluid at that point), Euler's continuity equation, (2.1), becomes

$$\frac{\partial C}{\partial t}(\boldsymbol{\xi}, t) = G(\boldsymbol{\xi}, t) - L(\boldsymbol{\xi}, t) \tag{C.1}$$

in which $\boldsymbol{\xi}$ is a parameter defining each "fluid particle" (e.g., its location at $t = t_0$). For L linear in C (viz., $L = lC$), the solution to (C.1) is obviously

$$C(\boldsymbol{\xi}, t) = \left[A(\boldsymbol{\xi}) + \int_{t_0}^t \mathrm{d}t'\,G(\boldsymbol{\xi}, t') \times \exp\left\{\int_{t_0}^{t'} \mathrm{d}t''\,l(\boldsymbol{\xi}, t'')\right\}\right] \exp\left\{-\int_{t_0}^t \mathrm{d}t'\,l(\boldsymbol{\xi}, t')\right\}, \tag{C.2}$$

where $A(\boldsymbol{\xi})$ is an arbitrary function of $\boldsymbol{\xi}$. If $\boldsymbol{\xi}$ gives the location of all fluid particles at $t = t_0$, and if $C(\boldsymbol{\xi}, 0) = C_0(\boldsymbol{\xi})$, then from (C.2), $A(\boldsymbol{\xi}) = C_0$, and (C.2) can be seen to be the same as (2.2) in the text.

For some readers, the demonstration in the previous paragraph may be sufficient. Thus, for readers familiar with the use of Lagrangian coordinates in fluid mechanics, (C.1) may seem quite obvious. For other readers, however, it may be useful if additional details were provided. The next few paragraphs present a derivation of (C.1) and then some details about different choices for $\boldsymbol{\xi}$.

To obtain the continuity equation (C.1) from first principles, consider the fluid "particle" in the volume element $\Delta\boldsymbol{\xi} \equiv \Delta\xi_1\,\Delta\xi_2\,\Delta\xi_3 = \Delta V_0$ about $\boldsymbol{\xi}$ at some arbitrary time t_0. From a simple geometric argument (for a non-dispersive fluid), it can be seen that at time t, the same fluid element occupies the volume element

$$\Delta\boldsymbol{x} = \Delta x_1\,\Delta x_2\,\Delta x_3 \equiv \Delta V = J\left(\frac{x_1, x_2, x_3}{\xi_1, \xi_2, \xi_3}\right)\Delta V_0, \tag{C.3}$$

where J is the Jacobian of the transformation $\boldsymbol{x} = f(\boldsymbol{\xi})$, which also depends on the velocity field and the elapsed time. Meanwhile, the amount of host fluid contained in this identified volume is conserved; hence,

$$\rho\,\Delta V = \rho J\,\Delta V_0 = \rho_0\,\Delta V_0. \tag{C.4}$$

Consequently, for the host fluid, mass conservation requires $J = \rho_0/\rho$, which is the host fluid's continuity equation in these moving (Lagrangian) coordinates.

Meanwhile, for some constituent carried with this non-diffusing host fluid, then during each $\mathrm{d}t$, there is a net gain of the material (concentration, χ, say in moles/m^3)

$$\mathrm{d}\chi\,\Delta V = [\mathscr{P} - \mathscr{R}]\,\mathrm{d}t\,\Delta V \equiv [\mathscr{P} - \mathscr{R}]\,\mathrm{d}t\,J\,\Delta V_0. \tag{C.5}$$

Consequently, an inventory of the constituent's mass, for the time interval t_0 to t, gives

$$\chi\,\Delta V \equiv \chi J\,\Delta V_0 = \chi\,\Delta V_0 + \int_{t_0}^t \mathrm{d}t'\,J[\mathscr{P} - \mathscr{R}]\,\Delta V_0. \tag{C.6}$$

In terms of mixing ratios ($M = \chi/\rho$) and using $J = \rho_0/\rho$, (C.6) becomes

$$M = M_0 + \int_{t_0}^t \mathrm{d}t'\,\frac{1}{\rho}\,[\mathscr{P} - \mathscr{R}]. \tag{C.7}$$

This result is seen to be the same as (C.1) by examining the differential form of (C.7):

$$\frac{\partial M}{\partial t} = \frac{1}{\rho}[\mathscr{P} - \mathscr{R}], \tag{C.8}$$

and use $C = M$, $G = \mathscr{P}/\rho$, and $L = \mathscr{R}/\rho = l_0 \chi/\rho = l_0 M$.

The final goal for this appendix is to demonstrate some details associated with the choice to "tag" fluid particles with their location at the current time rather than at some earlier time. To assist in this demonstration, label the current time by T and let the current location of a fluid particle be $x(T) \equiv X(T)$. Measure earlier time with the positive variable τ:

$$\tau = T - t. \tag{C.9}$$

The motion of a fluid particle is given by

$$\frac{\mathrm{d}\boldsymbol{x}(t)}{\mathrm{d}t} = \boldsymbol{v}_{\mathrm{L}}(t) \rightarrow -\frac{\mathrm{d}\boldsymbol{x}(T-\tau)}{\mathrm{d}\tau} = \boldsymbol{v}_{\mathrm{L}}(T-\tau). \tag{C.10}$$

Therefore,

$$\boldsymbol{x}(T-\tau) = \boldsymbol{x}(\tau = 0) - \int_0^\tau \boldsymbol{v}_{\mathrm{L}}(T-\tau')\,\mathrm{d}\tau', \tag{C.11}$$

with $\boldsymbol{x}(\tau = 0) \equiv \boldsymbol{X}(T)$. Thus, the current location of the fluid particle is

$$\boldsymbol{X}(T) = \boldsymbol{x}(\tau) + \int_0^\tau \boldsymbol{v}_{\mathrm{L}}(T-\tau')\,\mathrm{d}\tau'. \tag{C.12}$$

With use of this "backward time-variable", τ, and with use of the current location, $\boldsymbol{X}$, rather than an earlier location, $\boldsymbol{\xi}$, to identify fluid particles, then (C.1) becomes

$$-\frac{\partial C}{\partial \tau}\bigg|_X = G(\boldsymbol{X}, T-\tau) - l(\boldsymbol{X}, T-\tau)\,C(\boldsymbol{X}, T-\tau), \tag{C.13}$$

whose solution is

$$C(\boldsymbol{X}, T-\tau) = \left[A - \int_0^\tau \mathrm{d}\tau'\, G(\boldsymbol{X}, T-\tau') \times \exp\left\{-\int_0^{\tau'} l\,\mathrm{d}\tau''\right\}\right] \times \exp\left\{\int_0^\tau l(\boldsymbol{X}, T-\tau')\,\mathrm{d}\tau'\right\}. \tag{C.14}$$

By setting $\tau = 0$ in (C.14), the integration constant A is seen to be $C(\boldsymbol{X}, T)$; i.e., the concentration at the current time, which is what is sought. Finally, to complete the solution, we return to Eulerian variables via

$$C_{\mathrm{L}}(\boldsymbol{X}, T-\tau) \rightarrow C_{\mathrm{E}}[\boldsymbol{x}(T-\tau), T-\tau], \tag{C.15}$$

with

$$\boldsymbol{x}(T-\tau) = \boldsymbol{X}(T) - \int_0^\tau \boldsymbol{v}_{\mathrm{L}}(T-\tau')\,\mathrm{d}\tau', \tag{C.16}$$

and return to the notation in the text, wherein the current position and time are labelled by $\boldsymbol{r}$ and t. Thereby, (2.2) is obtained.

12. Appendix D

The purpose of this appendix is to sketch how (4.9) in the text can be obtained via K theory. Toward this end, consider the simpler problem in unbounded space

$$\bar{u}\frac{\partial c}{\partial x} = K\nabla^2 c + \dot{Q}\,\delta(\boldsymbol{r}). \tag{D.1}$$

A Fourier transform of (D.1), with parameters (ξ, η, ζ), gives

$$\hat{c} = \frac{\dot{Q}/K}{\left[\xi^2 + \frac{iu}{K}\xi + \eta^2 + \zeta^2\right]}, \tag{D.2}$$

and therefore,

$$c(\boldsymbol{r}) = \frac{\mathrm{e}^{\bar{u}x/(2K)}}{(2\pi)^3}\int_{-\infty}^{+\infty}\mathrm{d}\xi'\int_{-\infty}^{+\infty}\mathrm{d}\eta\int_{-\infty}^{+\infty}\mathrm{d}\zeta \times \frac{\dot{Q}/K\,\mathrm{e}^{i(\xi' x + \eta y + \zeta z)}}{\left[(\xi')^2 + \eta^2 + \zeta^2 + \frac{u^2}{4K^2}\right]}. \tag{D.3}$$

The integrals in (D.3) can be performed by transforming to spherical coordinates (k, θ, ϕ); after integrating over ϕ and θ, the remaining integral is

$$c(\boldsymbol{r}) = \frac{\dot{Q}}{2\pi^2 Kr}\exp\left\{\frac{\bar{u}x}{2K}\right\}\int_0^\infty \mathrm{d}k\,\frac{k}{k^2 + \alpha^2}\sin kr, \tag{D.4}$$

which is a known integral. The result for this simple case is therefore

$$c(\boldsymbol{r}) = \frac{\dot{Q}}{4\pi Kr}\exp\left\{\frac{\bar{u}x}{2K}\right\}\exp\left\{-\frac{\bar{u}r}{2K}\right\}, \tag{D.5}$$

which is essentially the same as (4.9) in the text.

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