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Sampling of air through a tube so as to measure the concentration of tracers it may contain is an old, but even now a common measuring technique used in numerous applications. Unfortunately, the resolution of such measurements is often degraded by dispersion effects which can both attenuate and delay important fluctuations. Such effects increase with tube length. In the case the tracer is a passive scalar, dispersion by differential advection caused by the flow profile, e.g., via Taylor dispersion, and by molecular and turbulent diffusion, has traditionally been suggested as the responsible mechanisms. In the case of a sorbing (“active”) tracer like water vapor, additional dispersion, and delay can be expected to be caused by adsorption and desorption processes (“sorption”) at the tube wall, as attenuation is so strong that it cannot be explained by passive-tracer models. In spite of this expectation, the (old) problem of tube transport of an active tracer has not been properly solved, although attenuation in, e.g., water-vapor fluctuations can cause for instance a 30% underestimation in measurements of evaporation from a ground surface to the atmosphere. A semi-empirical treatment of sorption effects of water vapor has been tried in order to predict attenuation, but it suffered from parametrization problems and did not lead to further work in this direction. Because of its importance, the problem has, however, received much attention during the past ten years. Recent work has mostly focused on empirically correcting for the missing variation in data. It is evident that a fresh look at the effect of sorption processes is called for so as to be able to correct for dispersion effects in active-scalar measurements.

We thus introduce a model for the sorption processes that appear in a tube flow of an active tracer (here water). For a pulse of water vapor, the main assumption is that drops of water begin to grow at the tube wall when the pulse is introduced, a dynamic equilibrium in drop size is reached, and evaporation begins to dominate at the trailing phase of the pulse leading eventually to vanishing of the drops. This phenomenon is expected to explain the attenuation as well as the delay of the pulse in a tube flow. The model was solved for the breakthrough curve (the pulse at the end of the tube) of the tracer, and it was tested using laboratory measurements on pulses of water vapor advected along a tube. A transfer function was derived based on the model, and it was applied to field-measurement data that represented a continuous sampling of air of varying humidity. The drop formation mechanism was tested by imaging a transparent section of the tube.

At a molecular level, a tracer molecule absorbed in a sessile drop undergoes Brownian motion until it is near the surface and receives enough energy from thermal fluctuations to escape. Consequent transfer of evaporated molecules across the stagnant boundary layer at the tube wall back to the flow is also diffusive. The whole process of evaporation back to the flow is thus diffusion limited, and it can be considered as a single diffusion process in which the time spent in the condensed phase is considered as a time delay described by a decreased diffusion coefficient (from that in the boundary layer). We do not know this “effective” diffusion coefficient without solving the whole complicated process. Here this diffusion coefficient is included in parameters used to fit measured data with the model, so its value needs not be known a priori. The essential properties of this effective diffusion process can be captured by one-dimensional (1D) diffusion: Advection with molecular diffusion in the tube (in the x direction) is thus coupled to 1D diffusion away from the tube flow, to which we attach an auxiliary (“effective”) dimension (z) and a length scale (l) as the diffusion process is spatially constrained (to the drop and the boundary layer at the tube wall). Note that similar advection-diffusion problems are rather common in transport in porous media. If the carrier fluid has a tracer concentration \( C_f(x, t) \) (average over tube cross section at x) in a control volume \( \pi R^2 dx \), and the part of the concentration condensed at the tube wall in that volume is \( C_m(x, z, t) \), we have a coupled advection-diffusion equation for the evolution of tracer concentration, given that there is a flow velocity \( v \) in a tube of radius \( R \) and length \( L \), which can be expressed in the form,
The boundary conditions in the case, assuming a

where nucleation of drops can take place. The appropriate

the molecular diffusion coefficient of the tracer in the evaporation process

where like matrix diffusion.20,21 The diffusion part of the above

time after introduction of the pulse, this equation is given

when

that describes the effect

is found as a convolution

with water vapor using a humidity generator (Fig. 1) that

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of the air was measured by the same

in a clean tube. The air flow in the measurements was maintained

by controlling the pressure of the artificial air and the suction

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clean tube. The air flow in the measurements was maintained

by controlling the pressure of the artificial air and the suction

of the flow module. The humidity, temperature, and pressure

of the sampled air were logged at 20 Hz, whereas its flow

was logged at 0.2 Hz.

So as to verify the proposed mechanism, condensation

to be observed independently, and we arrive in an

in dimensionless form, when

is the time after introduction of the pulse, this equation is given

by

where

There are thus three dimensionless variables that characterize

the system: \( \mu = \sqrt{D_f} \), related to molecular diffusion in air

to Taylor dispersion caused by turbulent flow, \( \lambda = 2\phi D_f \sqrt{D}/R \), related to the relative area, where drops can

form, and \( \kappa = \ell/(L\sqrt{D}) \), related to the length scale attached

to the diffusive evaporation process. Here, we have introduced

the dimensionless diffusion coefficients

Equation (2) can best be solved in the form of a series

expansion using Laplace transformation, but this solution is

complicated and it is only given in supplemental material.19

The breakthrough curve, \( C_f(L,t) \), is found as a convolution

of the actual input curve of the tracer and this solution. Moreover, a transfer function (TF) that describes the effect

of sorption processes in frequency space, can be derived for

the model (by analytic continuation of the Laplace transform, see supplemental material19). It is solely parametrized

by \( \mu, \lambda, \) and \( \kappa, \) and describes signal attenuation as a function of dimensionless frequency

\( \omega = \frac{2\pi f}{\lambda^2} \) (f [Hz] is frequency),

\[
\text{TF} = \exp\left[ -\frac{1 + 4\mu^2((\omega + \sqrt{\omega^2 + (\lambda\sqrt{\omega}\tanh(\kappa\sqrt{\omega})}) \sqrt{\omega})}{2\mu^2} \right].
\]  

In the related experiments, a 4.5 m-long tube was filled

with water vapor using a humidity generator (Fig. 1) that

created air of chosen relative humidity (RH). This water

vapor was then released as a pulse into a constant, turbulent

flow of artificial air (17 lpm, 80% N\(_2\), 20% O\(_2\)), and was

transported along a 13.6 m-long tube until it was divided

into a 0.5 m-long sampling tube (7 lpm) and a bypass flow.

From the sampling tube, the flow was directed into an infrared

gas analyzer22 and a flow-rate gauge, where after it was

joined with the bypass flow in a flow module that recorded

the flow rate of the whole setup. All tubes before the infrared

analyzer had a diameter of 8 mm and were made of polytetrafluoroethylene (PTFE). Before the measurements, another

13.6 m-long tube was aged by 20 lpm suction of outdoor air

for two weeks near an urban micrometeorologic measurement

station23,24 so as to provide a realistic reference to a
clean tube. The air flow in the measurements was maintained

by controlling the pressure of the artificial air and the suction

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So as to verify the proposed mechanism, condensation of drops of water at the tube wall was monitored in a transparent section of the tube (in the “main tube” of Fig. 1) using high-speed optical imaging. A 1 mm × 1 mm area (1024 × 1280 pixels) of the (clean and aged) tube wall was videoed at 1 kHz frame rate while a steep change in RH, from 42% to 95%, took place. RH of the air was measured by the same infrared analyzer as before.

High-speed imaging revealed that drops of water were indeed condensed at the tube wall when the RH was increased. In a clean tube these drops were symmetric, had a narrow size distribution, and a uniform spatial distribution at the wall (Fig. 2(a)). In an aged tube, drops had a widely varying size and shape, and a patchy spatial distribution (Fig. 2(b)). Furthermore, condensation of drops in an aged tube started at a lower value of RH, and more water was condensed at the wall (Fig. 2).

The peaks of the breakthrough curves for a clean tube in the laboratory experiment were fairly symmetric for all RHs. A symmetric peak is caused by the symmetric spreading by molecular diffusion and Taylor dispersion of the tracer, while condensation with subsequent evaporation leads to asymmetry of the peak so that there is more weight at later
times. The latter effect was not very prominent in the clean tube, although breakthrough curves were qualitatively similar to those in the aged tube (cf., Fig. 3). Spreading of the pulse by molecular diffusion leads to a pulse that begins to arrive earlier than the “advection time” (τ = 1). Except for the late-time tails, the shapes of the breakthrough curves were mostly explained by Taylor dispersion using a reasonable value for μ, μ = 0.035, by which the early part of the breakthrough curve was explained quite well. Doubling the μ, improved the fit to the late-time behavior, but then agreement with the early-time behavior was lost. It is evident that molecular diffusion and Taylor dispersion do not explain the observed shape of the breakthrough curves for a clean tube and low relative humidities (data not shown). The breakthrough curves for an aged tube were somewhat delayed and had a bit gentler rise of the leading edge (with respect to the μ, μ = 0.035-Taylor-dispersion curve), although these features were only minor for the given RH of 32% (Fig. 3). The main effect of sorption was the strong late-time tailing of the curve, and this was a feature not captured at all by molecular diffusion and Taylor dispersion. Doubling of μ improved also here the fit to tailing, without being satisfactory, however, but then agreement with the leading edge was completely lost (Fig. 3).

The sorption model introduced here described the shape of the breakthrough curve also in the case of an aged tube and high RH (data not shown). The steepness of its leading edge was mainly governed by λ, together with some influence by μ. In a clean tube, λ and κ were found to be tube properties as they did not depend on RH (Fig. 4). Aging of the tube induces chemical heterogeneity as a result of contamination, and then (λ and) λ · κ were found to increase for increasing RH (Fig. 4), and the rise of the leading edge of the breakthrough curve became steeper. The slope of the tail-off was governed by κ that, for an aged tube, decreased for increasing RH (data not shown). Because of this, the shoulder on the late-time side of the main peak began eventually to dominate the behavior around the main peak, exactly as the finite depth of porous matrix affects the behavior of the breakthrough curve in matrix diffusion.

There was also a further late-time tail in the breakthrough curves for aged as well as clean tubes, not explained by condensation and subsequent evaporation of water at the tube wall. This tail was caused by (capillary) condensation of water in corners and narrow passages in valves, where evaporation was slowed by stronger adhesion to solid material. Modeling of this effect was not attempted.

Field measurements of turbulent fluctuations of water vapor were also used to verify the performance of the model in frequency space. These data were measured with the eddy-covariance technique, the standard means to measure turbulent vertical fluxes. Outdoor air was sampled at 31 m above the ground, and continuously drawn through a 41 m-long tube to a similar infrared gas analyzer as in the laboratory measurements. The flow rate and logging frequency were also kept the same, but the tube material was stainless steel, and a PTFE membrane filter was used in front of the analyzer. In this study, 30 min power spectra from July 2007 and 2011 in addition to RH measurements of ambient air were used. The water-vapor power spectra were used in combination with power spectra of the air-temperature fluctuations to determine the TF of the measurement system. Temperature fluctuations could be assumed to be unattenuated because measurements were done using a sonic anemometer up in the tower. Scalar similarity between temperature and water-vapor transport was assumed, and the TF was determined as the ratio of the water-vapor power spectrum to that of temperature. More information on the measurements can be found elsewhere.
The TFs of the field measurements show that turbulent water-vapor fluctuations were strongly attenuated in the tube, and more so for an aged tube (Fig. 5). Tube attenuation is often considered as a first-order recursive filter, analogous to a resistor-inductor circuit, which causes a Lorentzian TF.\textsuperscript{3,20} The Lorentzian form of TF worked quite well for passive tracers and for a new clean tube, but it was not complex enough to describe sorption processes in an aged tube (Fig. 5). In contrast with this, the TF of the proposed model (Eq. \textsuperscript{4}) gave excellent fits ($\lambda$ and $\kappa$ as fitting parameters) to the observed data, it described in particular the “slump” in the interval $10^{-2} - 10^{-1}$ Hz in the TF of 2011. This kind of “slump” is only observed for a certain range of $\lambda$ and $\kappa$ values of the model, and it is related to the shoulder on the late-time side of the peak in the pulse of Fig. 3. Such a “slump” has been observed before in field measurements, but it has been ignored\textsuperscript{4} and has thus lead to incorrect data correction. The applicability of the sorption model to the TF of field measurement adds to the confidence of the validity of the model.

The fitting variables, $\lambda$ and $\kappa$, depend in principle on the momentary concentration of the water vapor, but then Eq. (2) would be badly nonlinear and would not allow for an analytical solution. For simplicity, we have thus assumed that this dependence can be replaced by that on concentration average, i.e., $\lambda = \lambda(C_{ave})$ and $\kappa = \kappa(C_{ave})$ with a suitably long averaging time ($C_{ave} = \langle C \rangle$). For clean tubes, this assumption works beautifully as $\lambda$ and $\kappa$ were observed not to depend on the average concentration (e.g., at homogeneously hydrophobic tube walls $\phi$ is not expected to depend on RH), at least not for very high values of RH). In aged tubes, parts of the tube wall are covered by hydrophilic contaminants, and $\phi$ can be expected to increase with increasing RH as indeed it was observed to do. Even in this case, the model was found to work well in laboratory as well as field measurements when $\lambda$ and $\kappa$ were used as fitting parameters. Their present values cannot, however, be applied in other situations. On the other hand, their values can be determined by one measurement (breakthrough curve or TF), and they can then be used until the situation changes appreciably, and their validity can easily be checked by a new fit.

In conclusion, a sorption model for active tracers was introduced, and tested by laboratory and field measurements. The model assumes that an active tracer is transported by a carrier fluid in a tube, it is first (partly) condensed at the tube wall and then evaporated back to the flow, which causes a delay and attenuation in the measured concentration signal. Evaporation of drops was treated as a diffusion-type process. The formation of “drops” of water was verified by high-speed imaging. The behavior of the breakthrough curve of water vapor was well explained by the model, and the model captured in particular the late-time tail in a clean as well as aged tube and for varying humidity, which the traditional Taylor dispersion failed to explain. The three dimensionless variables, which control the behavior of the system, were independent of RH in a clean tube, and behaved in a consistent fashion when RH varied in an aged tube. Furthermore, a TF based on the sorption model explained field measurements: A “slump” in a certain frequency range of TF was captured by the proposed physically based model, while a traditional (Lorentzian) TF failed to describe it. The TF introduced here is applicable to field measurements hampered by signal attenuation.

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