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Short communication

The net decay time of anomalies in concentrations of atmospheric pollutants

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HIGHLIGHTS

- We examine the time for an anomaly in air pollution concentration to decay.
- Lag correlation statistics are used to determine decay times of air pollutants.
- Decay times are longest (>1 d) in the cold season, at night, in rural areas.
- Decay times are shortest (~1 h) in the warm season, in the daytime.

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ABSTRACT

This paper introduces a new parameter to characterize the random component in temporal variability of atmospheric pollutants and proposes a simple statistical technique for its evaluation. That parameter is the net decay time (or the time scale) of the local anomalies in concentrations of atmospheric pollutants, rather than the traditionally used chemical lifetimes of total amounts of the species. Using widely available data of hourly multi-year surface trace gas pollutant concentrations we demonstrate a simplified way to estimate the net decay time with an exponential approximation of lag-correlation functions. We assessed the decay times of fluctuations in observations of eight atmospheric pollutants (SO_2, NO, NO_2, NO_y, O_3, CO, NH_3, and HNO_3) at two urban sites and one cleaner rural site in the Eastern US. The time scales of temporal fluctuations (net decay times) vary from about one hour to slightly more than one day. These scales are generally much shorter in urban environments than in remote regions. We also compared day- and night-time observations in warm and cold seasons. At night in the cold season, time scales of fluctuations in atmospheric pollutants are usually the longest. Such estimates should be useful to air quality prediction, public health, and satellite remote sensing research communities.

1. Introduction

Long-term monitoring of atmospheric pollutants at many locations in the USA provides data now widely available for scientific analysis. Bloomer et al., (2010) used a climatological approach to study the main components in the temporal variation of time dependent expected value in surface concentrations of atmospheric ozone in the eastern USA. They demonstrated the significance of diurnal and seasonal cycles in the variation of mean values and in their long term trends that should be monitored to aid air pollution control, air quality prediction (e.g., air health index forecast), and climate change projection activities. The same is true for other atmospheric pollutants.

In this paper we statistically assess what we call the “random” component in variations of observed concentrations of atmospheric pollutants, and estimate the parameter called the “net decay time”. Originally employed to explain how high frequency weather variability can be converted into low frequency fluctuations in climate (Hasselmann, 1976) this concept helps understand the nature of predictability. This parameter has also been used to

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study the scales of temporal variability of soil moisture with evaporation and precipitation (Manabe and Delworth, 1990) in an investigation of the red noise response of soil moisture to white noise forcing by precipitation.

In application to atmospheric pollutants, we assume that a statistical model of temporal variability of their random fluctuations corresponds to a first-order Markov process in which the autocorrelation function is exponential with decay time as the parameter. When the time dependent expected value is subtracted from the observed concentrations of air pollutants, we obtain fluctuations or anomalies from the expected values that are random and due to variations in factors such as local emissions (e.g., traffic patterns) and meteorology (e.g., cloud cover, precipitation). Computed anomalies of atmospheric pollutant concentrations can be used to estimate parameters of their statistical distributions and their expected life times, which vary for different chemicals at different locations. These estimates together with estimates of time dependent expected value are needed to make reasonable decisions about the required level of accuracy and temporal resolution of satellite monitoring atmospheric pollutants. Health officials may be also interested to have information about the expected lifetime of observed local anomalies of different pollutants. The same information may be needed for the assimilation of observed data in atmospheric chemical models used for weather/air quality prediction.

The main goal of this paper is to show that the parameters of statistical distribution of local fluctuations of atmospheric pollutants and their decay times can be easily estimated from widely available observational data. These decay times depend on the chemical lifetime of air pollutants and also on the intensity of atmospheric dispersion processes. They are the "lifetimes" of observed local anomalies in concentrations of air pollutants, not the "lifetimes" or "residence time" of the chemicals in the atmosphere. This paper introduces a new parameter to characterize local temporal variability of atmospheric pollutants, the net decay time of anomalies in concentrations of atmospheric pollutants, which can be used as measure of mean lifetime of anomalies.

2. Observations

We analyze hourly air quality observations for 2008–2013 of eight minor gaseous pollutants: SO_2, O_3, CO, NO, NO_2, HNO_3, NO_y and NH_3 at three research stations. One of these stations, Addison, NY, is located in Pinnacle State Park, PSP (42.091° N, 77.210°W, 505 m a.s.l.), which is a remote, forested area, far from industrial pollution sources (Schwab et al., 2009). Two other stations are located in the industrial, polluted urban regions in Atlanta, GA, JST (33.778°N, 84.417°W, 285 m a.s.l.) and N. Birmingham, AL, BHM (33.553°N, 86.815°W, 200 m a.s.l.) (Blanchard et al., 2013; Hidy et al., 2014). The observations are reported as time series of simple arithmetic hourly means of concentrations expressed as volume mixing ratios.

Hourly information on emissions of SO_2 and NO_x from power plants for 2008–2013, was obtained from US EPA Air Markets Program Data (http://ampd.epa.gov/ampd/), for every state containing a station. Data were integrated for each of these states and expressed in emissions per km^2 of the state's area. The EPA reported mass of emitted NO_x, is computed with the assumption that NO is completely converted into NO_2.

3. Method

Following climatological tradition, we assume that the concentrations each of the atmospheric pollutants, $f(t)$, can be expressed as the sum of two components: a time dependent expected value, $F(t)$, and the random fluctuation, $f'(t)=f(t)-F(t)$, where t is time, $F(t)=E[f(t)]$, operator E means expected value, and $E[f'(t)]=0$. Time series of fluctuations (or anomalies) can be studied as periodical, random processes. Variances and lag-correlation functions of such processes are also subject to seasonal and diurnal cycles. For some of pollutants at some locations, random fluctuations are the main component of the temporal variations.

For the computation of random fluctuations, the time dependent expected value must first be estimated and subtracted. In the general case, for arbitrary times of observation in time series, the expected value $F(t)$ can be approximated as a superposition of the first few annual and diurnal Fourier harmonics (Vinnikov et al., 2004). For regular hourly observations of atmospheric trace gases, a simpler approach has been applied. Seasonal variations in the expected value for each of 24 individual hours of a day ($h = 0, 1, 2, 3, \ldots, 23$) have been approximated by four harmonics of an annual period:

$$F(t) = F(d,h) = a_0(h) + \sum_{k=1}^{4}\left[a_k(h)\sin\left(\frac{2\pi kd}{365.25}\right) + b_k(h)\cos\left(\frac{2\pi kd}{365.25}\right)\right], \quad (1)$$

where d is day number from arbitrary chosen date, and the length of a year is assumed to be equal to 365.25 days, to treat our calendar leap year problem. The unknown coefficients of approximation $a_k(h)$ and $b_k(h)$ are estimated using the ordinary least squares technique. Details of this approach are described and tested in (Vinnikov et al., 2002).

To be able to use statistical methods developed for random stationary processes, we have made the following steps. We plotted observed hourly time series to assess their homogeneity visually. For each of the variables, we limited our analysis to relatively short time intervals (3–5 years). During selected intervals, long-term trends were relatively small compared to other components of temporal variability and can be ignored. We then estimated and subtracted the time dependent expected value to obtain the time series of temporal fluctuations as described above. The selected, quasi-homogeneous time intervals are referenced as the time domain "All". We then divided this domain into the four equal subdomains: "N/C", "N/W", "D/C", "D/W", where "C" means cold season (months from October to March), "W" means warm season (months from April to September), "N"- means nighttime (hours from 7 p.m. to 6 a.m.), and "D"– means daytime (hours from 7 a.m. to 6 p.m. LST). Note, that "time of observation" in these data is the time of the beginning of hourly interval. For each of these domains at each station, we estimated mean values, standard deviations and lag-correlation functions for each of the pollutants.

Figs. 1–3 display the plots of lag-correlations from which estimates of T, the decay time are derived. In each plot, the dependent variable is the natural logarithm of the normalized empirical lag-correlation function $r(\tau)=R(\tau)/R(0)$, where $R(\tau) = E[f'(t)f'(t+\tau)]$. The independent variable is the time lag, τ, for each of observed species, and the inverse of the slope gives the decay time, T. We plot data for three stations for the entire time domain, "All", and the four temporal sub-domains.

The estimate of $r(\tau)$ in these plots is computed as single correlation coefficient for all pairs of observations with lag τ inside the domain or sub-domain. Because we expect that $r(\tau)$ is an exponential function, we plotted natural logarithms of estimated correlation coefficients $\ln(r(\tau))$ versus time lag τ, and these should display linear dependence. Note, that empirically estimated $R(\tau=0)=s^2$ is the variance of the observed hourly averages, which is smaller than σ^2, an unknown variance of instant values of variables.