Environ Sci Pollut Res (2012) 19:295–300
DOI 10.1007/s11356-011-0555-8

SHORT RESEARCH AND DISCUSSION ARTICLE

# On the limits of the air pollution predictability: the case of the surface ozone at Athens, Greece

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Received: 27 March 2011 / Accepted: 16 June 2011 / Published online: 7 July 2011

**Abstract**
*Purpose* The aim of this study is to investigate the potential effects of increased urbanization in the Athens city, Greece on the intrinsic features of the temporal fluctuations of the surface ozone concentration (SOC).
*Methods* The detrended fluctuation analysis was applied to the mean monthly values of SOC derived from ground-based observations collected at the centre of Athens basin during 1901–1940 and 1987–2007.
*Results* Despite the present-day SOC doubling in respect to SOC historic levels, its fluctuations exhibit long-range power-law persistence, with similar features in both time periods. This contributes to an improved understanding of our predictive powers and enables better environmental management and more efficient decision-making processes.
*Conclusions* The extensive photochemistry enhancement observed in the Athens basin from the beginning of the twentieth century until the beginning of the twenty-first century seems not to have affected the long memory of SOC correlations. The strength of this memory stems from its temporal evolution and provides the limits of the air pollution predictability at various time scales.

**Keywords** Air pollution · Historic observations · Detrended fluctuation analysis · Long-range correlations · Surface ozone · Urbanization

Responsible editor: Philippe Garrigues

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## 1 Introduction

For the last three decades, solar ultraviolet radiation reaching the troposphere has been increasing due to stratospheric ozone depletion (Cracknell and Varotsos 1994, 1995; Varotsos et al. 1994, 1995a, 2001a; Varotsos 2002, 2004, 2005; Efstathiou et al. 1998; Kondratyev et al. 1994; Varotsos and Cracknell 1993, 1994). This leads to an indirect amplification of the photochemical ozone production over most continental regions while, in parallel, the anthropogenic emissions of air pollutants (e.g. $NO_x$) in the metropolitan areas are decreasing (Kondratyev and Varotsos 2001; Young 2005; Hocking et al. 2007). The role of the aerosol content to the solar ultraviolet radiation reaching the various atmospheric layers and the earth's surface and development of relevant modelling of regional or global scale (e.g. Kondratyev and Varotsos 1995, 1996a, b; Varotsos et al. 1995b, 2003) are also important. For example, measurements of the distributions of the aerosol characteristics and solar ultraviolet irradiance were conducted by using instrumentation flown on a Falcon aircraft over the entire Greek area from the sea up to the tropopause, showing a 4.3±0.1% $km^{-1}$ increase for altitudes ranging from the ground to 6.2 km (e.g. Katsambas et al. 1997; Alexandris et al. 1999).

Since the late 1980s, there has been an upward trend of low surface ozone concentration (SOC) values, while the peak SOC values have been reduced. In Europe, the summer mean of SOC daily maximum is in the order of 40–60 ppb over continental regions and lower (20–40 ppb) at the boundaries. In general, the highest ozone levels are found in Central and Southern Europe, while during the 1990s, the peak ozone values over several regions in Europe have reduced (Baldasano et al. 2003; WGE 2004; EEA 2007, 2010; Royal Society 2008; Sicard et al. 2009; Denby et al. 2010).

In the Athens basin (Greece), the air quality is often influenced by the sea-breeze effect (Lalas et al. 1983;

Asimakopoulos et al. 1992). Therefore, the chemical budget of the surface ozone content is often determined by the marine alkali halides on which the ozone uptake is strongly dependent from their composition (Ghosh and Varotsos 1999).

It is a truism that most of the atmospheric quantities obey nonlinear laws which usually generate non-stationarities (Chen et al. 2002 and references therein). These non-stationarities often conceal the existing correlations in the examined time series, and therefore, new analytical techniques capable to eliminate non-stationarities in the data should be employed (Hu et al. 2001). The most recent methods used along these lines are wavelet techniques (e.g. Koscielny-Bunde et al. 1998) and detrended fluctuation analysis (DFA), which was introduced by Peng et al. (1994) (e.g. Ausloos and Ivanova 2001; Weber and Talkner 2001; Chen et al. 2002; Collette and Ausloos 2004; Varotsos et al. 2006a, b).

It is well known that surface ozone is an important secondary pollutant in the boundary layer. Observational and modelling studies show that the elevated SOC levels in the rural areas of industrialized countries, during summer, are mainly the product of long-range transport of surface ozone precursors and multi-day photochemical production (Lalas et al. 1983; Asimakopoulos et al. 1992; Varotsos et al. 2001b). It should be taken into account that in the third decade of the twentieth century, Athens was already a big town with a population of 700,000 habitants. During that period, a rapid development of industry took place, and many factories were installed west of the port of Piraeus. Therefore, the west wind (blowing in the direction from Piraeus to the National Observatory of Athens (NOA)) transported polluted air to the experimental site NOA. In particular, the emitted precursors at the industrial zone of Piraeus produced ozone photochemically during their journey from Piraeus to NOA.

Recently, Varotsos et al. (2001b) investigated the seasonal variation of the surface ozone mixing ratio at Athens, Greece during the periods 1901–1940 and 1987–1998 and concluded that the nighttime surface ozone mixing ratio remained approximately the same from the beginning until the end of the twentieth century, while the daytime surface ozone mixing ratio has increased by approximately 1.8 times, a fact that may be explained by the enhancement of in situ photochemistry.

In the present study, we are handling the changes of the surface atmosphere by applying the above-mentioned DFA method to the SOC observations, collected at NOA, during the period 1901–1940 and at the Patission monitoring station of the National Service of Air Pollution Monitoring (Fig. 1), during the period 1987–2007. We are focusing on the Athens area because this region has significant air pollution problems due to high population density and considerable emissions of air pollutants, the intense sunshine and the characteristic features of the topography (a basin surrounded by mountains).

## 2 Materials and methods

In the present study, we have used the reevaluated historic record of SOC, which was measured at the NOA, during the period 1901–1940, using De James colorimetric papers. These papers were exposed to surface air during the daytime (0800–2000 hours) and nighttime (2000-0800 hours) and were shielded from the sun and rain. The measurements (correlated to a chromatic scale from 0 to 21)

**Fig. 1** Athens area and locations of the observation stations (NOA, Patission)

depend mainly on the ozone mixing ratio, relative humidity and exposure time. A full description of the reevaluation method is presented by Cartalis and Varotsos (1994). We have also used SOC measurements taken at 30-min intervals at the Patission monitoring station, located close to NOA (at about 3 km from NOA), during the period 1987–2007. The monitoring instruments were operated according to the Monitoring UV photometry technique, with detection limit of 0.1 ppb.

To search efficiently for time scaling, we adopt a data analysis technique which is not debatable due to the non-stationarity of the data (Varotsos et al. 2005). Therefore, to study the temporal correlations of SOC fluctuations, the DFA method is used.

This method of DFA, which stems from random walk theory, allows the detection of intrinsic self-similarity in non-stationary time series (Talkner and Weber 2000). Thus, the benefit of using this method is that it eliminates seasonal trends and non-stationarity effects. According to the DFA method, the time series is first integrated and then it is divided into non-overlapping $N/\tau$ segments of equal length, $\tau$. In each segment, a least squares line is fitted to detrend the integrated time series by subtracting the locally fitted trend. The root-mean-square fluctuations $F_{\mathrm{d}} = \sqrt{\langle F^2(\tau)\rangle}$ of this integrated and detrended time series is calculated over all time scales (segment sizes). In particular, the detrended fluctuation function $F(\tau)$ is calculated as (Kantelhardt et al. 2002):

$$F^2(\tau) = \frac{1}{\tau}\sum_{t=k\tau+1}^{(k+1)\tau}[y(t) - z(t)]^2, \quad k = 0,\ 1,\ 2, \ldots, \left(\frac{N}{\tau} - 1\right) \tag{1}$$

where $z(t)$ is the polynomial of order $l$ least-square fit to the $\tau$ data points contained into a segment.

For scaling dynamics, the segments' mean fluctuation $F^2(\tau)$ is related to the scale of the segments' length by a power law:

$$\left\langle F^2(\tau)\right\rangle \sim \tau^{2\alpha} \tag{2}$$

and the power spectrum function scales with $1/f^{\beta}$, where $\beta = 2\alpha - 1$ (Ausloos and Ivanova 2001).

The value of the exponent $\alpha$ implies the existence or not of long-range correlations. Furthermore, $\alpha$ is a precise measure of the maximum dimension of a multifractal process. When $\alpha \neq 0.5$ in a certain range of $\tau$ values, then long-range correlations in that time interval exist, while $\alpha = 0.5$ corresponds to the classical random walk (white noise). If $0 < \alpha < 0.5$, power-law anticorrelations are present (antipersistence). When $0.5 < \alpha < 1.0$, then persistent long-range power-law correlations prevail, while the case $\alpha = 1$ corresponds to the so-called $1/f$ noise.

## 3 Results and discussion

In the present study, the DFA method is applied to the deseasonalized and detrended mean monthly SOC values (during daytime and nighttime, separately), for the periods 1901–1940 and 1987–2007, in order to search for the existence of long-range correlations. The deseasonalization was implemented by applying a commonly used method subtracting the 40-year (21 years) average of the SOC monthly mean values from those in each year (deviations from the normal) at NOA (Patission station). It should be mentioned here that similar results were obtained from the application of DFA (i.e. SOC fluctuations exhibit persistent long-range power-law correlations) when the deseasonalization was achieved by using the classical Wiener method (filtering out the principal intra-annual, annual and inter-annual components). The detrending was accomplished by applying polynomial best fit to the whole SOC time series. It has recently been recognized (Hu et al. 2001) that the existence of long-term trends in a time series may influence the results of the correlation analysis. Therefore, the effects of SOC trends have to be distinguished from SOC intrinsic fluctuations.

Figure 2a shows the DFA function in log-log plot and the best fit equation with the corresponding correlation coefficient, $y = 0.77x + 0.04$ and $R^2 = 0.97$, for the deseasonalized and detrended SOC mean monthly values (in micrograms per cubic meter), at NOA, during 1901–1940, for daytime (0800–2000 hours). The slope $a$ corresponds to the DFA exponent mentioned in Section 2. Figure 2b illustrates the DFA function in log-log plot and the best fit equation with the corresponding correlation coefficient, $y = 0.73x + 0.11$ and $R^2 = 0.97$, for the deseasonalized and detrended SOC mean monthly values, at Patission station, during 1987–2007, for daytime (0800–2000 hours).

In the following, Fig. 3a, b presents the results obtained from the application of the DFA method to the deseasonalized and detrended SOC mean monthly values (in micrograms per cubic meter) for nighttime (2000–0800 hours), at NOA, during 1901–1940, and at Patission station, during 1987–2007, respectively. The corresponding best fit equations to the DFA functions in log-log plots are $y = 0.76x + 0.08$ ($R^2 = 0.97$) and $y = 0.75x + 0.01$ ($R^2 = 0.96$), respectively.

Since the DFA exponents for daytime (nighttime) are $a = 0.77 > 0.5$ ($a = 0.76 > 0.5$) at NOA and $a = 0.73 > 0.5$ ($a = 0.75 > 0.5$) at Patission station (Figs. 2a, b and 3a, b), we conclude that SOC fluctuations exhibit persistent long-range power-law correlations during the periods 1901–1940 and 1987–2007 and for all time lags between 4 months–10 years ($0.6 < \log\tau < 2.07$) and 4 months–5 years ($0.6 < \log\tau < 1.8$), respectively.

Given that long-range dependence and long memory are synonymous notions, this finding is equivalent to saying

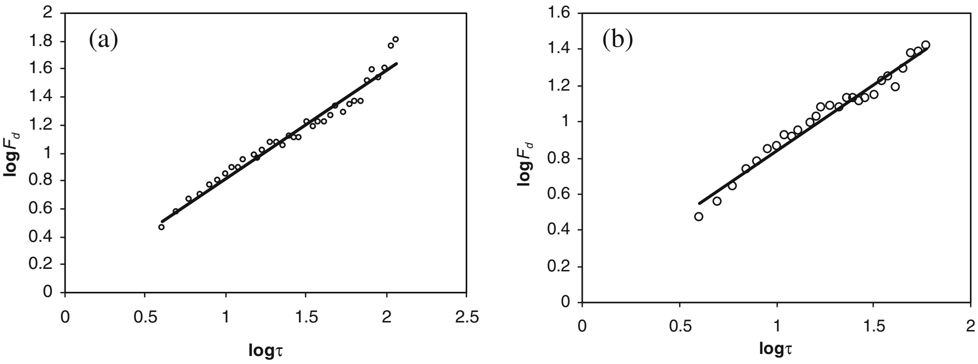

**Fig. 2** **a** The DFA function in log-log plot and the best fit equation with the corresponding correlation coefficient, $y=0.77x+0.04$ and $R^2=0.97$, for the deseasonalized and detrended SOC mean monthly values (in micrograms per cubic meter), at NOA, during 1901–1940, for daytime (0800–2000 hours), **b** the DFA function in log-log plot and the best fit equation with the corresponding correlation coefficient, $y=0.73x+0.11$ and $R^2=0.97$, for the deseasonalized and detrended SOC mean monthly values, at Patission station, during 1987–2007, for daytime (0800–2000 hours)

that the detrended SOC anomalies exhibit long memory (i.e. that enables predictability) and are thus associated with fractal behaviour. In other words, the fluctuations of the detrended SOC anomalies in small time intervals are closely related to the fluctuations in longer time intervals in a power-law fashion (when the time intervals vary from about 4 months to about 10 years). The larger is slope *a*, the better is the predictability (i.e. the larger the value of *a*, the stronger the correlation in the time series).

To search for the source of the fractality in SOC found above, we have employed the shuffling procedure (i.e. the SOC values are put into random order). The shuffling procedure preserves the distribution of the SOC variations but destroys any temporal correlations. In this way, the SOC dataset becomes a Markov process but with exactly the same SOC fluctuation distributions. With the application of the DFA method to each SOC time series, all the shuffled SOC series were found to be characterized by exponents $a\approx0.5$ indicating uncorrelated behaviour. In other words, shuffling quickly destroyed the memory effects. The latter suggest that the fractality in SOC stems from the SOC temporal evolution and not from the distribution of its variations.

It is worthwhile noting that the above-mentioned SOC persistence at the beginning of the twentieth century seems to have similar features to the corresponding SOC persistence of the period 1987–2007 (for both daytime and nighttime). This leads to the result that the enhancement of the in situ photochemistry in the Athens basin seems not to have affected the long-term memory of SOC correlations from the beginning of the twentieth century until the beginning of the twenty-first century (i.e. the predictability level is almost the same).

In parallel, the long memory in the fluctuations of the detrended daytime SOC anomalies, during both periods, may be considered similar to the corresponding long memory of the nighttime SOC fluctuations. Given that the SOC variability is closely associated with that of surface temperature, the long-term memory in SOC should be stemmed from the long-term memory in the surface temperature variability. In this context, Kiraly et al. (2006) have showed that long-range temporal power-law correlations extending up to several years have been detected in surface temperature data from the Global Daily Climatology Network. Preliminary results from our analysis

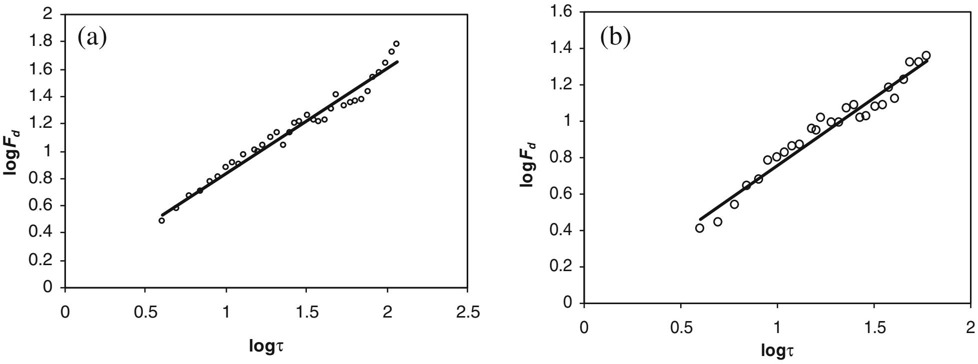

**Fig. 3** As in Fig. 2, but for the nighttime (2000–0800) SOC values **a** at NOA station, during 1901–1940, with, $y=0.76x+0.08$ and $R^2=0.97$, and **b** at Patission station, during 1987–2007, with, $y=0.75x+0.01$ and $R^2=0.96$

of the historical surface temperature in Athens revealed persistent long-range power-law correlations which resemble those of the wind speed and sun radiation. These results along with similar ones obtained from the analysis of the historical data from other sites will be presented in a forthcoming paper.

## 4 Conclusions

The present study focuses on the relative predictive power of the surface air pollution that can be expected at different time scales and whether it vanishes altogether at certain ranges. To this end, the DFA method is applied to the deseasonalized and detrended SOC mean monthly values (during daytime and nighttime) for the periods 1901–1940 and 1987–2007. That application revealed persistent long-range power-law correlations (for all time lags between 4 months and 10 years) and exhibited long memory associated with fractal structure that enables predictability. It is suggested that the long memory effect in SOC stems from its temporal evolution and not from the distribution of its variations.

Moreover, SOC persistence at the beginning of the twentieth century showed similar features to the corresponding SOC persistence at the beginning of the twenty-first century, a fact which means that the industrialisation and the enhancement of in situ photochemistry in the Athens basin did not affect the SOC fractal behaviour. Finally, very little difference was observed between daytime and nighttime SOC fluctuations for both periods. The results obtained could contribute to the development of more reliable simulating models for the surface air-pollutants fluctuations and the time scale variations in their predictability (Varotsos et al. 2005; Broday 2010).

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