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Statistical behavior of ozone in urban environment

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ABSTRACT

This paper analyzes the statistical behavior of the ground level ozone concentrations (GLO) observed at a major traffic intersection in Delhi. Five sets of data, i.e. summer (May to July, high solar radiation data), winter (November to January, low solar radiation data), spring (March to April), autumn (September to October), and the entire year have been used to study the seasonal variation in the statistical behavior of GLO. Appropriate statistical distribution form has been identified from alternative candidate distribution models using the goodness-of-fit methods and parameters have been estimated using the method of maximum likelihood. The yearly, winters, spring, and summer datasets were found to follow the log-normal distribution model, while autumn dataset followed Weibull distribution. Analysis shows that ozone concentrations also show similar statistical behavior like other air pollutants and fit mainly to the log-normal distribution as reported for other pollutants in different studies. The seasonality of the datasets shows higher skewness during summers due to longish tail of the distribution mainly on account of higher photo–chemical activity. The probability density functions corresponding to the five datasets were used to compute the probability of exceedence of the National Ambient Air Quality Standards and return period of violation of standards. The distributions have also been used to classify the study region under various air quality descriptor categories. The region is found to violate the air quality compliance criteria 17% of the recorded times in the year. Alternative measures have been discussed to reduce the precursor emissions in order to achieve the air quality goals.
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1. Introduction

Air pollution has emerged as a major problem in the developing countries. It affects not only the human health but also ecology [1], buildings [2] and agricultural productivity [3]. Maintaining the pollution levels below the respective standards for different pollutants is one of the primary goals of an air quality management plan. The regulatory authorities like Central Pollution Control Board of India (CPCB) lay down the compliance criterion of ambient air quality as National Ambient Air Quality Standards (NAAQS). In order to assess the status of air quality, regular monitoring of air pollutants is carried out and large amount of data is collected that is related to these standards. The usual practice followed is the computation of descriptive statistics and construction of time–series plots of these pollutants. The probability density function (pdf) of a pollutant is a useful tool of summarizing the information contained in the entire data set in a concise manner. It depicts the entire range, mean, extremes, probability of occurrences and typical graphical distribution pattern in a typical setting. The probability distribution function also helps in directly relating to the extent of meeting the requirement of NAAQS [4]; it provides a means to compute probability of exceedence of a standard and return period of violation of standard, if any. Several studies have been conducted in the past to understand the statistical behavior of primary pollutants like particulate matter (PM), carbon monoxide (CO) [5–7]. Jia et al. [8] studied the distribution of volatile organic compounds (VOC) exposures. However, limited work has been done in assessing the statistical behavior of ground level ozone (GLO) concentrations in an urban context.

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Ozone can be easily differentiated from the criteria pollutants like PM, NOx, (oxides of nitrogen) and SO_2 (oxides of sulphur). While stratospheric influx is the primary source of ozone, it is also formed through reactions precursor species as a secondary pollutant. Understanding its behavior becomes even more difficult considering the photo-chemistry involved in the reactions of NOx and VOCs. VOCs help in oxidizing primary NO released from various sources to form NO_2. VOCs also help in retaining the existing ozone by competing with it to react with NO. NO_2 is then photolysed to generate atomic oxygen, which combines with oxygen to form O_3 in the troposphere [9]. Ozone is not only linked with effects on human health but also significant impact on crop productivities. There are few studies conducted in past on assessment of GLO in Indian context. Guardani et al. [10] studied the behavior of GLO concentration in urban area. Gilleland et al. [11] described statistical models for monitoring and regulating GLO. Recently, Chelani [12] assessed the statistical persistence of ozone concentrations in an urban setting. Unlike criteria pollutants, the GLO concentration is affected by the photochemistry, which in turn is dependent on the amount of solar radiation. It therefore becomes an interesting research proposition to study the statistical behavior of GLO and change in its behavior, if any, with change in solar radiation and hence with season. As discussed above the GLO concentration is expected to be high during daytime due to the photochemical reactions and thus due to longer sunshine hours during summers, the average concentration is expected to be higher in comparison to the winter's concentration. The annual average concentration, by the same argument is expected to be in between the summer and winter average. The other statistical characteristics are also likely to be affected due to the photochemistry. However, statistical characteristics such as mean and variance provide loose information about the distribution of GLO concentration. The pdf on the other hand provides a more complete and higher order description of pollutant concentration data [13]. The present work thus aims to model the pdf of GLO for five sets of data: (a) summer, (b) winter, (c) spring, (d) autumn, and (e) yearly data, and study the influence of season on the type of pdf, if any.

This paper attempts to analyze the statistical behavior of the GLO concentrations in an urban setting. For this purpose 8-h average data for the year 2010 has been taken. The data have been further divided in four data sets – summer (May to July, high solar radiation data), spring (March to April), autumn (September to October), and winter (November to January, low solar radiation data) to study seasonal variation in the statistical behavior of GLO. Appropriate pdfs identified for the entire year and the four seasons have been used to compute the exceedence probability of NAAQS violations.

2. Materials and methods

2.1. Study location and data

CPCB runs an automated air quality monitoring station near a major traffic intersection in the central region of the capital city of Delhi. The traffic intersection has a very high vehicular density. 8-h ambient ozone concentration data have been collected from the CPCB for the year 2010. The ozone concentrations are measured using online ozone analyzer (model O342M, Environment SA, France) which works on UV absorption technology. The lower detection limit is 0.4 ppb. The instantaneous ozone concentration data are averaged for 1-h/8-h reporting. The entire data set has been analyzed to model the statistical form of GLO. In addition, summer (May to July), spring (March to April), autumn (September to October), and winter (November to January) months data have been extracted to study variation in the distribution form with change in solar radiation. Z-scores method [14] is used to scrutinize the outliers. The outliers with z-score values more than 3 were scrutinized and removed from the dataset. Further analysis is carried out based on the dataset without outliers.

2.2. Methodology

Exploratory analysis has been carried out for the five data sets. For this purpose, the descriptive statistics has been computed; box-and-whisker plot with frequency histogram constructed to preliminarily assess the distribution form. This is followed by the modeling of the distribution form of the GLO data using the MINITAB version 14.1 software. It may be noted that "there is no a priori reason to expect that atmospheric distribution should adhere to a specific distribution" [15]. However, most of the distributions that have been found to fit the air quality are special cases of the four-parameter generalized gamma distribution, which include the one- and two-parameter exponential distributions; the one-, two- and three-parameter Weibull and standard gamma distributions; and lognormal distribution [16]. Thus, the challenge is to determine the best distribution model that fits the data set under study amongst the alternative potential candidate models. This involves modeling the distributions of air pollutant concentration, GLO in the present study. The modeling broadly includes two steps: (a) identification of appropriate distribution form from alternative candidate models; and (b) estimation of parameters of the identified model. The model identification has been carried out by Chi-square, Kolmogorov–Smirnov and Anderson-Darling goodness-of-fit tests. However, the final model selection is based on the Anderson-Darling test as it gives more weight to the tails, which is more relevant in the air pollution context. Moreover, it is more sensitive test as it makes use of the specific distribution in calculating critical values [17]. In all, fourteen distribution forms most commonly used in air pollution studies have been fitted to identify the best-fit distribution. The parameter estimation is done by method of moments, method of least squares (MLS) and method of maximum likelihood (MLE). Mage and Ott [18] based on several Monte Carlo simulations found that MLE provides the best estimates. Thus, MLE was preferred as the method for estimating model parameters in the present study. The details of the above mentioned model identification and parameter estimation techniques have been provided in detail in Ref. [17]. Using the best-fit distribution models, the compliance of the ozone standards at the major traffic intersection location is assessed for different seasons of 2010. The observed concentrations of ozone are also compared with the NOx concentrations to analyze the effect of titration chemistry in which primary NO emissions from sources like vehicles react with ozone to destruct it. This is a primary cause for lower ozone concentrations in the city centres in comparison to the surrounding regions.

3. Results and discussion

The 8-h ozone concentrations at the major traffic intersection monitoring station during the year 2010 are shown in Fig. 1. It shows clear violation of 8-h standard (100 μg m^{-3}) many times during the year. The annual average ozone concentration at major traffic intersection is 61 μg m^{-3} with a standard deviation of 50. Seasonal variation in the ozone is clearly evident from the graph. The GLO concentration is observed to be high during the summer months due to higher photochemical activity. The winter months show lower concentration values. Ali et al. [19] shows the regression analyses of surface ozone with maximum temperature in Delhi, which also stated that ozone was mainly produced by photochemistry. The average diurnal variation across different days

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