Monitoring of tropospheric ozone in the ambient air with passive samplers

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ABSTRACT

Two sampling campaigns in suburban places in the north zone of Santa Clara city, Cuba, have been carried out on a weekly base with the use of Radiello passive diffusion tubes in order to monitor the tropospheric ozone (O_3) levels in 2010. The first campaign was scheduled from February to April (cold season) and the second one in August and October (warm season), both of them at two sampling sites, i.e., Farm and School of Art Instructors. After aqueous extraction, the samples were analyzed by UV–VIS spectrophotometry.

A seasonal trend was observed with the maximum O_3 concentrations in the cold season and the minimum levels in the warm season. Samples collected during the cold season showed the highest O_3 levels. Higher levels were reached at the Farm site with average values of about 58 ± 12 µg/m^3, which exceeded the limit of the Cuban Standard 99:1999. In the warm season, the O_3 concentrations were similar for both sites, but lower than those observed in the cold season. The overall, seasonal average value was found to be 24 µg/m^3. Despite the higher weekly average temperatures in August, the O_3 concentrations during this month showed the lowest values of the whole sampling period, which finding is in agreement with that reported by the Meteorological Institute of Cuba.

Mathematical models, based on the Cochrane-Orcutt algorithm, were fitted to the acquired data set to explain the change in the tropospheric ozone concentrations under various meteorological conditions during the two campaigns. The correlation coefficients for both the cold and the warm seasons demonstrated a strong correlation, i.e., 0.779 and 0.951, respectively. The high correlation of wind speed in the model from the first sampling campaign explains the sharp decrease in O_3 concentrations at the SAI sampling site from the sixth week of sampling.

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1. Introduction

The presence of ozone (O_3) in the troposphere is understood to arise from two basic processes: tropospheric / stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere; and production of ozone from photochemical reactions occurring within the troposphere [1–4]. Ozone is produced in the troposphere as a consequence of interaction of meteorological conditions, sunlight, nitrogen oxides (NOx), O_2 and volatile organic compounds (VOCs) [1,4–6]. The study of this pollutant is interesting from environmental point of view due to its harmful impact on the biosphere, human health, animal population, agriculture productivity and forestry [1,3,7,8]. Therefore, the monitoring of O_3 levels in the ambient air is needed and justified.

Initially, this phenomenon was attributed to highly industrialized countries, but nowadays, it extends to other countries of smaller developments like Cuba. Ozone, under the influence of some meteorological phenomena, such as cold fronts, hurricanes and high pressures systems, can move over long distances. Sharing the same general pattern with several other air pollutants, at most sites, O_3 levels fluctuate seasonally. It is generally higher in winter than summer [2,9].

Meteorology plays an important role in ozone formation and transport. As a result, substantial variations in meteorological conditions can exert such a large impact on ozone concentrations [1]. Anticyclonic pressure systems and low or calm wind conditions promote the accumulation of ozone. Different contributions to the ozone levels may come from the background ozone that originates from stratospheric injection and production far away from local sources, meaning that it involves photooxidation of CH_4 and CO, and regional photochemical production and depletion of O_3 by deposition and loss reactions [10].

The spatial and temporal distribution of O_3 is very different to the other atmospheric pollutants. In particular, considerable impacts can be expected in areas, even hundreds of kilometers leeward to the original precursor emissions, as a result of the transport of an ample range. Generally, the atmospheric O_3 concentrations and the population exposure can be maximized in suburban and rural areas. This has important consequences in the design of monitoring systems [11].

In Cuba, there are two episodic periods of ozone. The first period is from October to March called as the period of high ozone concentrations and the second from April to September, the period of low ozone concentrations [2,9]. The maximum permissible limit of the ozone concentration in air in Cuba is 30 μg/m^3 for a 24 h exposure [12], whereas the World Health organization (WHO) 8 h limit is 120 μg/m^3[11,13,14].

According to the literature, various methods have been reported for the detection of ozone, including spectroscopy and chemiluminescence procedures [15]. Passive sampling has become a widely accepted technology throughout the world for environmental sampling as evidenced by many regulatory guidelines, manuals and protocols published by various environmental standard policy makers worldwide. The contributing organizations include the US Environmental Protection Agency (EPA) US National Institute for Occupational Safety and Health (NIOSH), American Society for Testing and Materials (ASTM), Health and Safety Executive (HSE), Occupational Health and Safety Administration (OSHA), International Organization for Standardization (ISO), Comitée Européen de Normalization (CEN), etc. [16]. Passive samplers are now being considered as the part of an emerging strategy for monitoring a range of priority pollutants [17–19]. The fundamental part of an ecological risk assessment for chemical stressors is the determination of time-weighted average (TWA) concentrations [20]. In this case, only passive sampling techniques can be practically used [16,21]. These techniques are more versatile to study the spatial resolution of pollutants [22–24] and to obtain background data in a specific area [23]. For O_3, error margins of 15% are stated based on comparisons with continuous ozone analyzers [25,26].

Passive sampling for tropospheric ozone has become a well developed method for the last decade. On the other hand, some of these methods have not completed all eligible requirements, mainly for not being specific for O_3, but also behaving as passive samplers for other oxidizing pollutants [7]. Various trapping reagents have been used for absorbing O_3, like 1,2-di(4-pyridyl)-ethylene [25,27], potassium iodide [7,25,27,28], nitrite [7,22,25,27,28], indigo/indigo carmine compounds [22,25,27,28], 3-methyl-2-benzothiazolinone acetone azine with 2-phenylphenol [27,28] and p-acetamidophenol [27]. Amongst these reagents, only 1,2-di(4-pyridyl)-ethylene and nitrite give O_3 specific reaction, while the other reagents are hampered by interferences with alternative atmospheric oxidants, like NOx and peroxyacytyl nitrate (PAN) [2,15].

The trapping reagent of 1,2-di(4-pyridyl)-ethylene is generally utilized in Radiello passive samplers. Upon exposure, acid-catalyzed ozonolysis of 4,4'-dipyridylethylene gives 4-pyridylaldehyde (PA). This compound is condensed with 3-methyl-2-benzothiazolinone hydrazone to yield the corresponding yellow coloured azide, which can be determined by means of UV–VIS spectrophotometry [29].

According to the above facts, the aim of this paper is to monitor the levels of tropospheric ozone using Radiello passive samplers on the north zone of Santa Clara city at different sampling locations over various seasons. Moreover, an attempt is made to find correlation between the tropospheric ozone levels and certain meteorological conditions through mathematical models.

2. Experimental

2.1. Climatic characterization

Santa Clara city is located in the center of Cuba in Villa Clara province. As Cuba, this city has also a tropical climate, seasonally humid with maritime influence. There are two climatic periods, the wet period from May to October and dry period from November till April. In this city, the annual daily average temperature is 24 °C. The daily average temperature peaks in the wet period in July at around 26.4 °C and reaches its minimum of 20.9 °C in January. The relative humidity is high; its annual average value is 82%. The prevailing wind direction is eastern. The average wind speed is around 1.4 m/s in wet the period and 2.1 m/s in dry the period.

2.2. Sampling of O_3

Two sampling campaigns were conducted in 2010 in the north zone of Santa Clara city: the first from February 21st to April 25th and the second from August 8th to September 5th and in October from 10th to 31st, corresponding to the cold and warm seasons, respectively. Two outside locations were chosen (Fig. 1), Farm (F) at northeast of the zone, where the clean air arrives at the sampling area and School of Art Instructors (SAI) at southwest, where the air exits this zone, located at coordinates 22º25'04.59"N, 79º59'19.51"W and 22º24' 14.88"N, 79º59' 29.40"W, respectively. The studied zone covers an area of 7.2 km^2. The north zone of Santa Clara is characterized by high population and medium traffic density with vehicles in a bad state of repair (due to the use of obsolete technologies and low fuel quality). The region also contains an industrial area. The sampling sites were located in rural and suburban zones at more than 50 m from a major road, e.g., the city ring.

Sampling of O_3 was carried out by means of radiello® (Fondazione Salvatore Maugeri, Padova, Italy) diffusion tubes. Three diffusion tubes were exposed in each sampling site during 1 week in every campaign. The diffusion cartridges were kept in a fridge at 4 °C before and after sampling till sample processing.

2.3. Analytical procedure for O_3

The radiello® sampler comprises a compound-specific adsorbing cartridge, surrounded by a cylindrical microporous diffusive body mounted on a supporting plate. The adsorbing cartridge is formed by a micropore polyethylene tube filled with silica gel coated with 4,4'-dipyridylethylene and closed at one end by a PTFE cap. For the analysis, the addition of 3-methyl-2-benzothiazolinone hydrazone (MBTH) reacting with PA produces a molecule, called azide that is measured by means of UV–VIS spectrophotometry on a Genesys20 model (Thermo Electron Corporation, Cambridge, UK) spectrophotometer.

Before analysis, the silica gel was placed in a plastic tube for extraction. A volume of 5 ml of MBTH solution was added into the plastic tube containing the silica gel. Then, the plastic tube was hermetically sealed and shaken manually for 1 min. To guarantee a complete reaction, this mixture was left on standing for at least 75 min in the dark at room temperature before spectrophotometric analysis [26]. The absorbance of the extraction solution was measured at 430 nm. The mass of PA in the cartridge was obtained from a linear calibration derived from the spectrophotometric analysis of PA standards [29]. Blank values were determined for cartridges stored in a cooling box during an exposure, when they were transported to the sampling site and returned to the laboratory. The average reading of the blank tubes for each sampling week was subtracted from the reading of the exposed tubes.

2.4. Reagents

All the reagents used were of analytical grade. For dissolution of the chemicals and dilution, Milli-Q water (Millipore, Bedford, MA, US) was used throughout this work. The extraction solution was prepared by dissolution of 5 g of MBTH in 1 L of Milli-Q water, completed with 5 ml of concentrated sulphuric acid 95–98% (m/m). Standard solutions of PA were prepared by appropriate dilution of a 110.3 mg/l stock solution. Accurate weighing of each chemical was performed on a Sartorius BP211D-0CE model (BCBC100) analytical balance (Sartorius AG, Göttingen, Germany). The calibration curves were constructed with