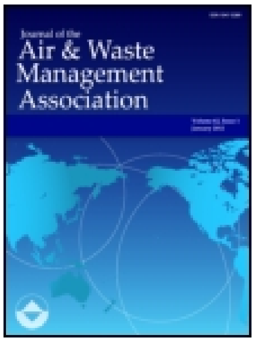

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Ozone Measurements in South Carolina Using Passive Samplers

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ABSTRACT

Passive samplers with two different collection substrates were used to obtain an average ozone concentration for 1 month during the summer of 2002 for each South Carolina county. One sampler contained a filter coated with indigo carmine, whose color fades when exposed to ozone. The fading was measured by reflectance spectroscopy. The other sampler contained filters that were coated with nitrite, which is oxidized to nitrate when exposed to ozone. The nitrate was measured by ion chromatography.

Calibration curves were developed for the two methods by comparing color fading from indigo carmine and nitrate ion concentration from the nitrite filter with ambient ozone concentration measured by a co-located reference continuous UV ozone analyzer. These curves were used to calculate integrated ozone concentrations for samplers distributed across South Carolina.

Using the indigo carmine method, the average ozone concentrations ranged from 21 to 64 ppb (average = 46 ± 7.9 ppb, n = 58) across the 46 counties in the state during one summer month of 2002. Concentrations for the same time period from the nitrite-coated filters ranged from 23 to 62 ppb (average = 41 ± 8.1 ppb, n = 58). Also for the same time period, the 23 continuous UV photometric ozone monitors operated by the South Carolina Department of Health and Environmental Control at sites within 10 miles of some of the passive monitors showed ozone concentrations ranging from 28 to 50 ppb (average = 39 ± 6.3 ppb, n = 22).

IMPLICATIONS

Two passive sampling methods have been calibrated and used to measure simultaneously ambient ozone concentrations in each county in South Carolina. The nitrite-to-nitrate method yielded better results than the fading of indigo carmine. Such easy-to-analyze methods serve as useful screening techniques to find areas of high ozone and to estimate inexpensively background ozone concentrations for setting boundary conditions.

INTRODUCTION

Ground-level ozone (O_3), a secondary pollutant, is formed through photochemical reactions between precursor emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x). With elevated temperatures, sunlight, and levels of NO_x and VOCs present, ozone will form more rapidly than it decomposes, causing it to build up in the atmosphere.

Although NO_x is mainly emitted from transportation and industrial sources, VOCs can also be emitted from chemical manufacturing, paint shops, and other solvent-using sources. Natural sources such as pine trees can produce VOCs as well.

Elevated levels of ground-level ozone are capable of causing adverse health effects. Ozone can affect the ability of the immune system to defend against lung infections. It also causes acute respiratory problems and inflammation of lung tissue, which can lead to the aggravation of asthma in susceptible people. Symptoms related to ozone exposure include cough, shortness of breath, pain at deep inspiration, malaise, headache, and nausea. Although small children and the elderly are at greatest risk, anyone could be potentially affected by ground-level ozone.[1]

As well as being a threat to human health, ground-level ozone also causes harm to the environment. It can interfere with the ability of plants to produce and store food, compromising growth, reproduction, and overall plant health. Ozone also causes damage to natural rubber and synthetic polymers. The strength of textiles, carpets, curtains, and shop canopies is reduced by exposure to ozone.[2]

Annually in South Carolina ~204,000 adults and 77,000 children suffer from asthma. In 2000, 1.2% of all visits to the emergency room were because of asthma and more than 27% of all those hospitalizations were among children. In northern South Carolina (Greenville, Spartanburg, Anderson, Pickens, Cherokee, Oconee, and Abbeville counties) ~52,835 (6.6%) adults suffer annually from asthma. In 2000, there were 1,252 hospitalizations because of asthma in northern South Carolina for all ages. Two thousand seven people under the age of 18 visited the emergency room because of asthma, and 518 people under the age of 18 were hospitalized because of asthma.[3]

In 1971, the U.S. Environmental Protection Agency (EPA) set the National Ambient Air Quality Standard for several air pollutants, including photochemical oxidants. In 1979, the National Ambient Air Quality Standard for ozone was revised and set at 0.12 ppm, measured as a 1-hr average concentration. However, the EPA decided that this ozone standard did not adequately protect human health, so in 1997 the 8-hr standard was established. The new standard, set at 0.08 ppm, is based on a 3-yr average of the annual fourth highest daily maximum 8-hr ozone concentration.[4] South Carolina is currently designated as being in attainment for ozone in all counties. However, under the new 8-hr standard, areas of the state are threatened with possible non-attainment status. Consequences from a non-attainment designation include extensive permitting requirements for industry and possible limitations on the way federal funds may be spent on road projects in non-attainment areas.

The objective of this study was to obtain calibration curves for the two different passive ozone methods—indigo carmine and nitrite ion—by comparison with a reference ambient continuous UV photometric monitor, and then to use these two calibration curves to obtain an average ozone concentration for each passive method for 1 month during the summer of 2002 for each South Carolina county.

Passive Ozone Samplers

Ozone monitoring traditionally has required large and expensive laboratory instruments. A simpler, inexpensive device was needed to measure indoor and personal exposure. The solution to this dilemma was a passive sampling device, which could easily and reliably monitor ozone in any location without a power supply. These samplers are based on the principle of passive diffusion of a pollutant to an adsorbing collection medium.

Various types of passive samplers have been developed with different types of samplers as well as different collection mediums. Although passive sampling can be an efficient method of measuring ozone, certain aspects may affect the ability of the sampler to produce the desired results. Interference from oxidants such as peroxyacetyl nitrates (PAN), as well as oxides of nitrogen and sulfur, may cause an overestimation of the cumulative ozone concentration. Wind velocity and the associated air turbulence may also contribute to inaccurate ozone measurements. Finally, solar radiation, air temperature, and relative humidity can also have an adverse impact on passive sampling. These interfering factors are usually specific to the sampler design and collection medium used.

Grosjean and Hisham[5] developed a passive sampler consisting of a plastic filter holder, a Teflon membrane filter mounted upstream as the diffusion barrier, and a coated cellulose paper filter downstream. A diffusion gap was created between the two filters. Variations in the diffusion rate of the passive sampler were tested by changing the pore size of the Teflon filter, by changing the Teflon filter to a different plastic grid support, and by using a rectangular badge. An increase in the diffusion rate allows short-term samples to be collected for measuring peak ozone levels, whereas a decrease in the diffusion rate can be used for collecting longer sample runs. The following three different ozone-trapping reagents were examined: indigo carmine, curcumin, and phenoxazine. Indigo carmine and curcumin fade when exposed to ozone, whereas phenoxazine yields a colored product. The color changes or fading, measured by reflectance spectroscopy, are proportional to the product of ozone concentration and the sampling duration. Indigo carmine proved to be the most effective for ozone.

As an alternative to colorant methods, Koutrakis et al.[6] developed a method in which a filter is coated with nitrite ion. In the presence of ozone, nitrite is oxidized to nitrate on the filter. To determine the amount of nitrate present, the filters are extracted with ultra-pure water and analyzed by ion chromatography. The laboratory and field tests present good agreement between the passive method and a reference continuous UV photometric ozone analyzer (coefficient of variance ± 8.7%, $n = 44$). However, face velocity and wind direction with respect to the samplers' placement did affect the collection rate of the samplers. An unpublished report[7] showed negligible interferences for the nitrite method for typical concentrations of PAN, H_2O_2, NO_2, HONO, and SO_2.

Other researchers also developed samplers for passive collection of ozone.[9–12] Based on a review of all of these passive ozone techniques, it was concluded that the methods of Grosjean and Hisham[5] and Koutrakis et al.[6] would provide the most accurate results and still offer ease of sampling and analysis.

MATERIALS AND METHODS

Filter Preparation

Indigo Carmine. To prepare these filters, 400 mL of methanol was measured with a 100-mL graduated cylinder. Indigo carmine, 3.25 g (certified, pH 11.4–13, dye content 94%, Lot No. 04614ks, Catalog No. 13,116-4, Aldrich, St. Louis, MO), was measured on a Sartorius (Edgewood, NY) balance and then dissolved in a dark colored glass bottle with the methanol (400 mL). The bottle was shaken ~100 times, and then the mixed solution was placed in a plastic box large enough to hold the filters under the hood. Whatman 41 cellulose filter paper (24 cm, Catalog No. 1441240, Whatman 41, Whatman, Hillsboro, OR) was placed with the mixed solution for ~3 min or until covered with the dye. The filters were hung in the hood and allowed to dry for 24 hr. Filters were then cut into 3-cm diameter circles and measured by reflectance spectroscopy before outdoor exposure.

Color changes are measured by reflectance spectroscopy with a MacBeth ColorEye 3000 Spectrophotometer (division of Kollmorgen Instruments Corp., Northampton, MA). The spectral response of this instrument closely approximates the Commission Internationale de l'Eclairage colorimetric Standard Observer curves. The color change measured, ΔE, is given by:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \tag{1}$$

where L, a, and b are the standard the Commission Internationale de l'Eclairage coordinates for hue and saturation a and b (which taken together are called chromaticity), and brightness (L). These coordinates distinguish one color from another. Chromaticity is the quality of a color that is the combination of hue and brightness. Hue is the color reflected from, or transmitted through, an object. In common use, hue refers to the name of the color, such as red, orange, or green. Saturation is the strength or purity of a color, or the amount of white light mixed with a hue. An item that is highly saturated has a very intense color. An item that is less intense would be less saturated or have less chromaticity. The brightness of a colored surface depends upon the illuminance and upon its reflectivity.[13] The instrument is calibrated by using a white reflector plate standard, and the light source for all measurements is illuminant D_{65} (daylight, with a color temperature of 6,500 K).

After the filters are painted, dried, and cut into 30-mm-diameter circles, each filter is assigned a labeled number. Each filter is analyzed after being painted with indigo carmine and before ozone exposure (ΔE_0), then again after exposure (ΔE). The difference between the measurements, $\Delta\Delta E$, was determined by:

$$\Delta\Delta E = \Delta E_0 - \Delta E \tag{2}$$

Nitrite Ion

The nitrite method used 15-mm-diameter glass fiber filters coated with nitrite ion (obtained from Harvard University School of Public Health, Cambridge, MA), which in the presence of ozone (O_3) is oxidized to nitrate ion. The solution to coat the collecting filters included sodium and potassium salts of nitrite and carbonate in a solution of glycerol, methanol, and water, as described by Koutrakis et al.[6]

After exposure the filters were extracted by using the following procedure. Ultra-pure water, in aliquots of 2 mL, was placed in a clean cup along with the two filters. The cups were then placed on a shaker table for 3 hr at 150 rpm. After shaking, ~1-mL aliquots of each sample were placed in labeled ion chromatography (IC) glass vials. The samples were then placed in the refrigerator until analyzed. A Dionex ion chromatography system (DX-100 Ion Chromatograph, Dionex Corp., Sunnyvale, CA) with an IonPac® column (IonPac® AG4A 4 mm [10–32] P/N 37042) was used for analysis of the anion, NO_3^-. Carbonate/bicarbonate eluent was used for the IC (233 mg/L Na_2CO_3 and 235 mg/L $NaHCO_3$).

Two replicates of each of the five standards chosen were prepared from UltraGrade Nitrate Ion Chromatography Solution (UltraScientific, North Kingstown, RI, 1,000 μg/L nitrate in water, Lot No. IG-0382) and run on the IC. The results from the standards were used to create a calibration curve, which was necessary to convert the sample peak area to a concentration of NO_3^- in the samples. A new calibration curve was constructed each time the IC was run.

Passive Sampler Preparation

Passive ozone samplers were used for the collection of data. The samplers produced by 3M for assessing occupational exposure to volatile organic compounds were modified to use filter substrates, as shown in Figure 1. Parts of the sampler include the following: front cap, diffusion membrane or barrier, spacer, collection filter, and badge body.

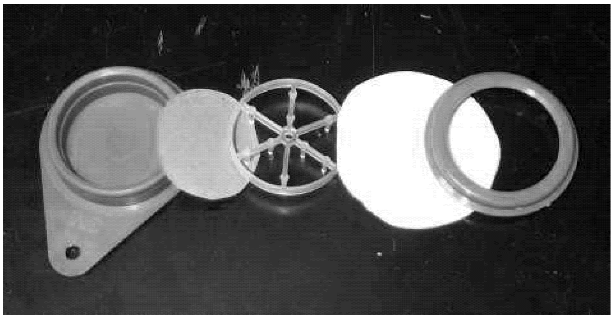

Figure 1. Diagram of a passive badge sampler with the following parts, right to left: (1) front cap; (2) diffusion membrane or barrier; (3) spacer; (4) collection filter (one indigo carmine or two nitrite filters); and (5) badge body.

The polymer badge body is 3.3 cm in diameter and 1 cm deep. The spacer sets the diffusion distance at 10 mm and holds the collection filter in place. The diffusion barrier, comprised of two filters, attaches to the badge body with the front cap by friction fit. Two filters were used for the diffusion barrier. A quartz filter (Gelman Sciences Pallflex membrane filter Tissuequartz 2500QAO-UP) and a track-etched polycarbonate membrane filter (Whatman Nuclepore, Ann Arbor, MI, 47 mm pore size 3 μm). Two nitrite-coated filters were placed in the sampler to provide maximum capacity for O_3. The two filters were extracted together. A single filter painted with indigo carmine was used per sampler.

Experimental Design

Sampling Sites and Events. One of the main objectives of this project was to determine the average ozone concentration for 1 month in each of 46 counties in South Carolina. To accomplish this, high school students were asked to help obtain the ozone data. Lead high school science teachers in every county were sent a letter requesting addresses for two motivated students to whom a passive sampler would be sent. South Carolina Department of Health and Environmental Control (SCDHEC) district health directors were also contacted about placing the samplers at their county health departments. The participants were asked to hang the sampler outside for 30 days from June 24, 2002 to July 24, 2002. At the end of the time period, the samplers were returned for analysis.

The following instructions were sent to the participants:

- The sampler was to be placed outside where it would remain dry.
- The chosen location was not to be exposed to direct sunlight, rain, or other weather conditions that could damage the sampler.
- The instructions suggested that an ideal location would be to hang the sampler under the eaves of a roof on the outside of a building (on a balcony or porch, for example). It was important that air was able to reach the sampler on all sides.
- The sampler was not to be attached directly to a wall or placed near the ground. The sampler should have hung at least 0.5 m (~1.65 ft) from the nearest wall and 1.5 m (~5 ft) or more above ground level.
- The desired method of hanging the filter was horizontally, with the filter facing downwards. The sampler was sent to participants with the strings attached.

RESULTS AND DISCUSSION

Nitrite Method Calibration Curve

Calibration data were collected over 4 weeks in May and June 2002. The passive samplers were exposed for times ranging from 1 week to 1 month. At the same time, ambient ozone concentrations as measured by an automatic ozone analyzer were recorded and averaged over the corresponding exposure interval of each passive sampler. Figure 2 shows the calibration data for the passive nitrite method versus continuous monitor, with 30 data points. The graph shows the nitrate as measured by ion chromatography against the average continuous ozone concentration in parts per billion multiplied by the exposure time in hours. These results indicate that the best fit is a linear one between the nitrate concentration and the ppb ozone*hr, with a correlation coefficient value (R^2) of 0.8311. The least squares fit was used to derive eq 3:

$$ozone\,[ppb] = \frac{nitrate\,[ppm] - 2.1771}{0.0025} \times \frac{1}{hr\ exposed} \quad (3)$$

Indigo Carmine Calibration Curve

Figure 3 shows the calibration data from the indigo carmine experiments, which were carried out by using the

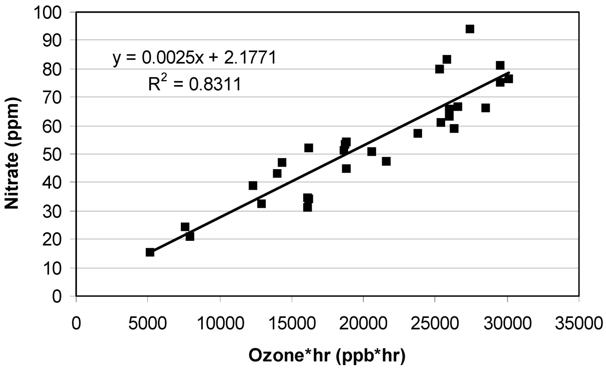

Figure 2. Calibration curve of the nitrite method.

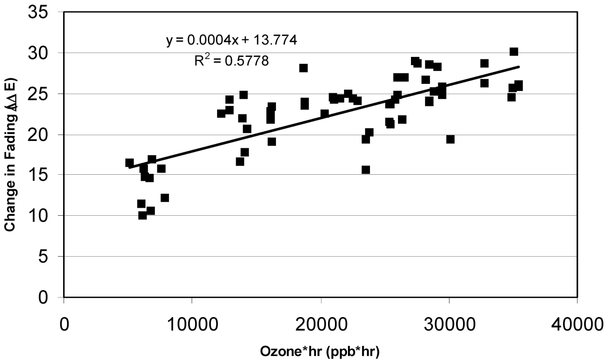

Figure 3. Calibration curve of the indigo carmine method.

same method as the nitrite samples. There are 55 data points shown on the graph, collected over the same period of time and at the same location as the nitrite samples. The graph shows the fading as measured by reflectance spectroscopy (in units of ΔΔE) versus the average continuous ozone concentration in parts per billion multiplied by the filter exposure time in hours.

The linear correlation for indigo carmine method is not as strong as for the nitrite method, with the R^2 value of 0.5778. This is consistent with a study from Zhou and Smith[10] that reported that the correlation of the indigo carmine was weaker than that of the other trapping reagents tested in their study, among which was the nitrite method. Although Grosjean and Hisham[5] reported that color change increased linearly with ozone dose for indigo carmine, their experiments were conducted in an artificial test atmosphere without exposure to possible interferences from ambient air. However, in their research, when indigo carmine was exposed to ambient levels of PAN and NO_2 equal to those of ozone, a positive interference of 16% and 15%, respectively, was found.[5]

Table 1. Average ozone concentrations for counties in South Carolina.

Dates Exposed	City	County Location	Ozone (ppb) from Nitrite	Ozone (ppb) from Indigo Carmine	Dates Exposed	City	County Location	Ozone (ppb) from Nitrite	Ozone (ppb) from Indigo Carmine
6/24–8/09	Calhoun Falls	Abbeville	40	23	6/24–7/24	Greenwood	Greenwood	45	51
6/24–7/24	Aiken	Aiken	35	51	6/25–7/26	Greenwood	Greenwood	47	43
6/25–7/26	Aiken	Aiken	39	47	6/24–7/24	Varnville	Hampton	26	43
7/12–8/09	Allendale	Allendale	34	62	6/24–7/24	Little River	Horry	35	47
6/24–7/24	Powdersville	Anderson	58	45	6/24–7/24	Ridgeland	Jasper	25	41
7/14–8/14	Bamberg	Bamberg	33	46	6/24–7/24	Camden	Kershaw	23	NA
6/24–7/24	Denmark	Bamberg	53	55	6/24–7/24	Lancaster	Lancaster	47	49
7/11–8/14	Barnwell	Barnwell	39	44	6/25–7/25	Laurens	Laurens	43	39
6/24–7/24	Beaufort	Beaufort	47	52	6/24–7/24	Bishopville	Lee	36	45
6/24–7/24	Goose Creek	Berkeley	30	NA	6/24–7/24	Lexington	Lexington	45	55
7/19–8/19	St. Matthews	Calhoun	32	52	6/24–7/24	Mullins	Marion	37	51
6/24–7/24	Charleston	Charleston	62	53	6/24–7/24	Bennettsville	Marlboro	42	54
6/24–7/24	Gaffney	Cherokee	55	37	6/28–7/24	McCormick	McCormick	42	64
6/24–7/24	Chester	Chester	45	41	6/24–7/25	Newberry	Newberry	36	52
6/24–7/24	Chesterfield	Chesterfield	44	52	6/24–7/26	Newberry	Newberry	44	55
6/24–7/24	Manning	Clarendon	36	35	6/25–7/25	Walhalla	Oconee	32	50
6/24–7/24	Walterboro	Colleton	44	45	6/27–7/29	Bowman	Orangeburg	31	50
6/24–7/24	Hartsville	Darlington	30	46	6/24–7/25	Orangeburg	Orangeburg	NA	39
6/24–7/24	Dillon	Dillon	35	49	6/23–7/26	Easley	Pickens	38	37
6/25–7/29	Summerville	Dorchester	40	46	6/24–7/24	Columbia	Richland	35	29
6/24–7/24	Edgefield	Edgefield	43	48	6/21–7/22	Columbia	Richland	53	44
6/24–7/24	Johnston	Edgefield	36	49	6/25–7/25	Blythewood	Richland	45	48
6/24–7/24	Winnsboro	Fairfield	42	40	6/25–7/25	Columbia	Richland	45	52
6/25–7/25	Florence	Florence	41	53	6/28–7/24	Saluda	Saluda	51	55
7/2–8/10	Traveler's Rest	Greenville	40	38	6/25–7/25	Roebuck	Spartanburg	35	40
6/24–7/24	Greenville	Greenville	39	52	6/24–7/24	Sumter	Sumter	41	21
7/4–8/11	Taylors	Greenville	51	42	7/2–8/2	Sumter	Sumter	41	41
7/2–8/2	Traveler's Rest	Greenville	55	45	6/24–7/24	Union	Union	52	52
6/25–7/24	Greenwood	Greenwood	NA	45	6/26–7/24	Kingstree	Williamsburg	40	49
6/24–7/24	Ninety Six	Greenwood	49	51	6/24–7/24	Clover	York	47	43

The least squares fit was used to derive eq 4:

$$ozone\,[ppb] = \frac{\Delta\Delta E - 13.774}{0.0004} \times \frac{1}{hr\ exposed} \qquad (4)$$

South Carolina Ozone Concentrations

Equations 3 and 4 were used to obtain the average ozone concentrations for the samplers sent out to participants in the different counties. Of the 69 packages sent out, 60 packages were returned and then analyzed. Because the samplers were sent out to volunteers who assisted in data collection, it was difficult to control sampler exposure time. Some samplers were exposed from June 24 to July 24, 2002, as instructed. However, 28 of the 60 samplers returned had exposure times a little different than the specified time period. Table 1 shows the resulting average ozone concentrations from the nitrite and fading technique for each county in South Carolina.

Data were collected in every South Carolina county except Georgetown. Some counties had several sampling sites, whereas some counties only had one sampling site. Nitrite method data was not available for Berkeley and Kershaw Counties, and Orangeburg and Greenwood Counties did not have indigo carmine method data. Generally, during our experiments the average ozone concentrations were relatively low, and below the level of concern (85 ppb).

Using the nitrite method, Charleston County had the highest average ozone concentration at 62 ppb, whereas Kershaw County had the lowest value at 23 ppb. The average value for the whole state was 41 ppb ($\sigma = 8.1$, $n = 58$). For the indigo carmine method, McCormick County had the highest concentration at 64 ppb, whereas Sumter County had the lowest concentration at 21 ppb. The average value for the whole state was 46 ppb ($\sigma = 7.9$, $n = 58$). Figures 4 and 5 show the distribution in South Carolina of ozone concentrations using the nitrite and indigo carmine methods, respectively.

Figure 4 shows a cluster of concentrations within the 30–39.9 ppb range along the Midlands (Richland, Sumter, Lee, Clarendon, Orangeburg, Williamsburg, etc.) and again in the North (Oconee, Pickens, Greenville, Spartanburg). The only concentration within the 60–69.9 ppb range is located in Charleston County. Generally, the coastal counties have good atmospheric mixing because of the sea breeze, which keeps the ozone concentrations

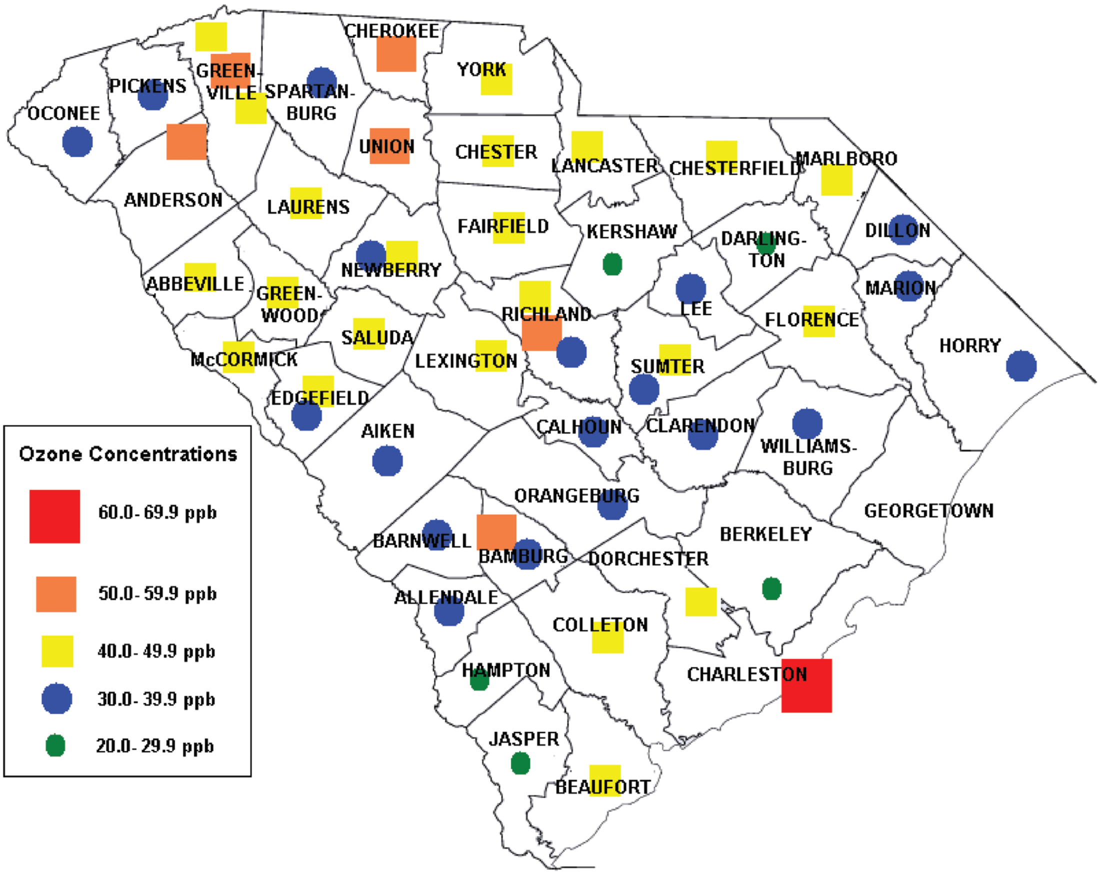

Figure 4. Average ozone concentrations from samplers containing nitrite-impregnated filters.

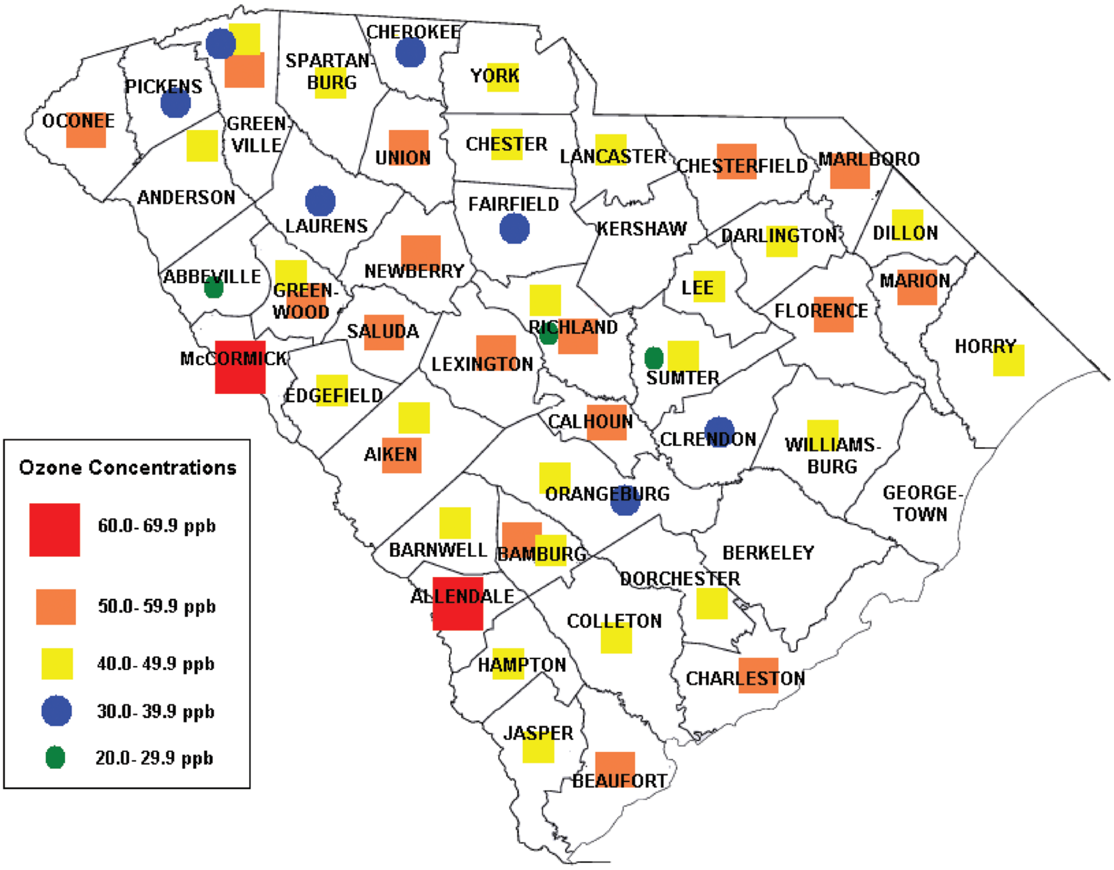

Figure 5. Average ozone concentrations from samplers containing indigo carmine-painted filters.

lower relative to other areas. The location of the sampler in a heavily urban area in Charleston could have contributed to this high ozone value.

Samplers containing the indigo filters, in general, had higher concentrations than those containing the nitrite-coated filters (this may be because of small positive interferences to the indigo method from other pollutant gases, as mentioned above). The values were scattered across the state with no apparent trends. For ranges of 20–29.9, 30–39.9, 40–49.9, 50–59.9, and 60–60.9 ppb, there were 3, 7, 27, 19, and 2 samples, respectively. For the nitrite-coated filters, for ranges of 20–29.9, 30–39.9, 40–49.9, 50–59.9, and 60–60.9 ppb, there were 5, 22, 24, 6, and 1 sample, respectively.

Ozone concentrations from 22 SCDHEC automated ozone analyzers located in counties across South Carolina were averaged for the time period of June 24 to July 24, 2002, and are shown in Figure 6. Generally higher concentrations were found Upstate, but the highest value was observed at the Sandhill monitor in Richland County. The lowest values were found along the coastal region, as expected. The ozone concentrations ranged from 28 ppb in Williamsburg County to 51 ppb in Richland County. The average value was 39 ppb ($\sigma = 6.3$, $n = 22$).

The data from the two methods evaluated in this project were compared with the data from ozone monitors operated by SCDHEC located in the same county that were at a distance of less than 10 miles from the passive sampler location. Even though 21 passive samplers were in the same county as a monitor operated by SCDHEC, in 11 instances the distance between the two was too large to be suitable for comparison. The ozone concentrations from the SCDHEC monitors were averaged for the same time periods that the passive samplers were exposed.

Figures 7 and 8 show a comparison of the ozone concentration as measured by the nitrite and indigo passive samplers, respectively, and the continuous monitors operated by SCDHEC. The counties in Figures 7 and 8 are arranged in order of increasing distance from the continuous monitors, with co-located samplers at Anderson County and a distance of ~10 miles between the passive sampler and the SCDHEC monitor at Oconee. The error bars on the ozone concentration as estimated by our experiments represent the residual of the experimental data as shown in the calibration curves (Figures 2 and 3). These were found to be 6 and 25.5 ppb for the nitrate and indigo carmine methods, respectively. The larger error bar on the ozone concentrations estimated with the indigo

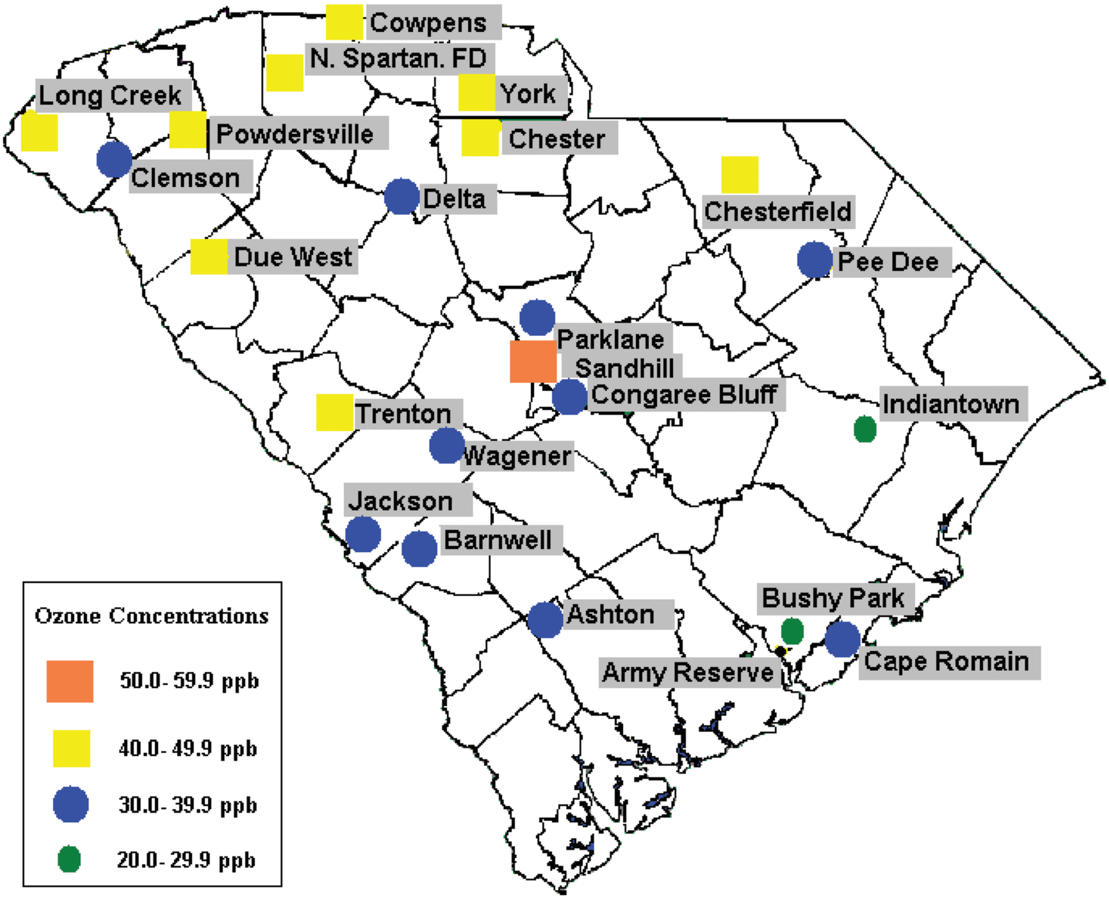

Figure 6. Ozone concentrations in South Carolina as determined from automatic ozone analyzers operated by SCDHEC.

carmine method than the nitrate method is a result of the greater scatter of data on the calibration curve (Figure 3). It is seen that there is good agreement, in general, between the results from passive sampling and SCDHEC ozone monitors.

Both methods may be used to assess ambient ozone concentrations. The nitrite method has yielded better results than the indigo carmine method ($R^2 = 0.83$ versus $R^2 = 0.58$, respectively). On the other hand, the implementation of the indigo carmine method is simpler because it does not require knowledge of an IC, depending instead on the use of a spectrophotometer, which is more straightforward to operate.

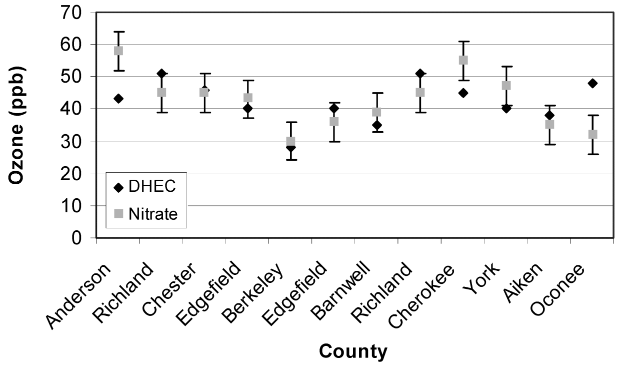

Figure 7. Comparison of ozone data as measured by the nitrite method and the SCDHEC ozone monitor within 10 miles of the sampler. Error bars on the ozone concentration as estimated by the nitrate method represent the residual error calculated from the calibration line shown in Figure 2 (6 ppb).

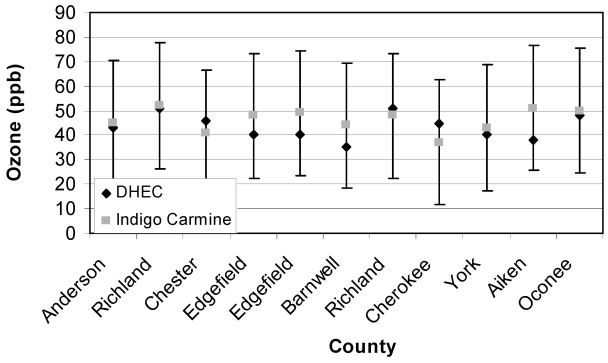

Figure 8. Comparison of ozone data as measured by the indigo carmine method and the SCDHEC ozone monitor within 10 miles of the sampler. Error bars on the ozone concentration as with the indigo carmine method represent the residual error calculated from the calibration line shown in Figure 3 (25.5 ppb).

CONCLUSIONS

Passive samplers using two types of coated filters as collection substrates were evaluated for measuring ambient ozone concentrations. One filter was coated with indigo carmine and the other filter was coated with a nitrite salt. Calibration curves were developed for the two methods by comparing fading of the indigo carmine and nitrate ion concentration from the nitrite filters with ambient ozone concentration as determined by a reference continuous UV photometric ozone analyzer. These curves were used to calculate the average ozone concentrations for samplers distributed across South Carolina. The passive sampler measurements were in good agreement with measurements made by continuous instruments at locations within ~10 miles of the sampling sites.

Passive sampling is not generally suitable for short-term measurements, but can be appropriate for determining long-term effects, such as human exposure evaluations and assessment of ozone dose to determine the long-term effects on the environment. The new EPA 8-hr standard for ozone of 0.08 ppm, together with its averaging method (the 3-yr average of the fourth highest annual 8-hr ozone concentration) may be seen as placing more importance on long-term average ozone concentrations, as opposed to the previous 1-hr maximum ozone concentration of 0.12 ppm.

Passive sampling is useful because measurements at many sampling locations can be carried out simultaneously at low cost. Results from such measurements can be used to estimate the spatial distribution of ozone, and identify those areas with potentially high ozone concentrations where more intensive sampling with continuous analyzers would be warranted.

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