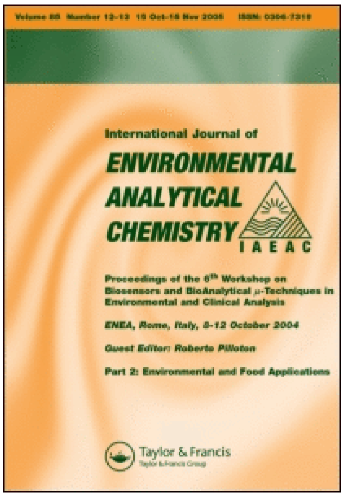

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PASSIVE SAMPLING OF ATMOSPHERIC PHOTOCHEMICAL OXIDANTS

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A simple, cost-effective passive sampler is described that is suitable for measuring parts per billion (ppb) levels of photochemical oxidants (ozone + nitrogen dioxide + peroxyacetyl nitrate + peroxypropionyl nitrate) in ambient air. The passive sampler makes use of oxidant-fugitive colorants, and color changes are proportional to the oxidant dose, i.e. the product of oxidant concentration and sampling duration. Field tests have been carried out at a southern California mountain forest location with co-located passive samplers and continuous measurements of O_3, NO_2, PAN and PPN. Consistency with laboratory tests of the color change with oxidants studied singly (O_3, NO_2, PAN) or as a mixture is discussed. Interferences from formaldehyde and sulfur dioxide are negligible. Four colorants have been tested and yield detection limits ranging from 8 to 54 ppb. day (1–8 ppb. week, and so on).

KEY WORDS: Passive sampler, photochemical pollutants, atmospheric measurement methods, ozone, nitrogen dioxide, peroxyacyl nitrates

INTRODUCTION

We have recently described a simple, cost-effective passive sampler for atmospheric ozone[1,2]. This passive sampler involves diffusion sampling of ozone onto a filter coated with an ozone-fugitive colorant, indigo carmine. Color differences before and after sampling are measured by reflectance spectroscopy, and the color change (fading) varies in proportion to the dose of ozone (dose = product of ozone concentration and sampling duration). Laboratory tests have shown that color changes are proportional to the ozone concentration at constant sampling duration and are also proportional to sampling duration at constant ozone concentration[1]. Field tests of the ozone passive sampler have shown excellent agreement between results obtained in the field and those obtained in the laboratory[2] and have led to the implementation of a passive sampler-based monitoring network of ozone concentration at some fifty California mountain forest sites where ozone damage to forests has been documented[3]. Using the same passive sampler configuration, but replacing the ozone-fugitive colorant by other filter coatings, passive samplers have also been developed that are suitable for measuring parts per billion levels of formaldehyde[4] and sulfur dioxide[5] in ambient air.

In this article, we describe the results of experimental tests that focus on passive sampling of photochemical oxidants. In polluted air, ozone is virtually always accompanied by other oxidants including nitrogen dioxide (NO_2) and peroxyacyl nitrates ($RC(O)OONO_2$) of which the most abundant members are peroxyacetyl nitrate (PAN, $R = CH_3$) and peroxypropionyl nitrate (PPN, $R = C_2H_5$). Because photochemical oxidants often exhibit similar properties (e.g. ozone, PAN and PPN are all phytotoxic and have adverse effects on human health), it is clearly useful to obtain time-integrated data regarding ambient levels of photochemical oxidants so that population exposure, dose to forests and agricultural crops, impact on ecosystems (e.g. wilderness areas), damage to objects of art and other cultural property, etc., can be assessed in the context of air pollution control strategies. Accordingly, we examine in this article the feasibility of several oxidant-fugitive colorants for passive sampling of photochemical oxidants. These colorants have been previously included in exploratory laboratory tests with focus on their fugitiveness towards ozone, and have been shown to yield color changes upon exposure to O_3, NO_2 and PAN in purified air[1,2]. Field tests were carried out at a forested southern California's mountain location bordering the Los Angeles urban area. This location experiences high levels of photochemical oxidants[6,7] and suffers from oxidant damage[6]. The field tests involved side-by-side measurements with passive samplers and with continuous analyzers for monitoring of ambient levels of O_3, NO_2, PAN and PPN. In this way the colorants tested as passive samplers for oxidants could be assessed with respect to their response to one or more of the oxidants present in photochemically-polluted air.

EXPERIMENTAL METHODS

Field measurements

Measurements of photochemical oxidants were carried out during the summer and fall 1990 at Tanbark Flat (USDA Forest Service San Dimas Experimental Forest), which is located at an elevation of 800 m on the slopes of the San Gabriel Mountains and about 35 km northeast of Los Angeles. The surrounding vegetation is mostly chaparral and Coulter pine. The passive samplers were exposed to ambient air on the top of a trailer about 2 m above ground.

Ozone was measured by ultraviolet photometry (Model 1108, Dasibi Corp). Nitrogen dioxide was measured by chemiluminescence (Model 8840, Monitor Labs). Two sets of co-located instruments were operated for a 3-day period and yielded good agreement for both ozone (within ± 6% of mean value) and for NO_2 (within ± 8%). All NO_2 concentrations reported in this article have been corrected for PAN and PPN (see below), which are quantitative interferents when measuring NO_2 by chemiluminescence[8]. PAN and PPN were measured on-site by electron capture gas chromatography (EC-GC) as described elsewhere[7]. Calibration of the EC-GC involved the synthesis of pure PAN and PPN in n-dodecane, and side-by-side measurements of ppb levels of PAN (or PPN) in purified air by EC-GC and with a calibrated NO_x chemiluminescence analyzer[7]. The detection limits for PAN and PPN during the field measurements were 0.01 and 0.02 ppb, respectively.

Passive samplers

The passive samplers were prepared as previously described[1,2] and consisted of a modified 25 mm diameter polycarbonate dual filter holder (Nuclepore Corp.) a 25 mm diameter Whatman 41 paper filter coated with the colorant tested, and a 1.2 µm pore size PTFE Teflon filter (Sartorius) as the diffusion barrier. The colorant-coated paper discs were mounted in the dual holder downstream of the Teflon filter diffusion barrier. The Teflon filter was held in place by a polycarbonate ring cap and an ethylene-propylene rubber O-ring. With this configuration, the passive sampler sampling rate is given by $S = 60\ DA/L$, where S is the sampling rate (diffusion rate) in ml/min, D is the diffusion coefficient of the photochemical pollutant to be measured (units $cm^2\ sec^{-1}$), A is the sampling area (cm^2) of the colorant-coated filter, and L is the distance (cm) between the diffusion barrier (i.e., upstream Teflon filter) and the pollutant trap (i.e., the downstream colorant-coated filter). Using formaldehyde as the test pollutant, experimental measurements of the passive sampler sampling rate have been carried out: the measured sampling rate was 97 ± 9% of the value calculated from theory[4].

The compounds tested, and the composition of the filter coating solutions were as follows: curcumin (Aldrich, 1.0 mg in 100 ml ethanol + 1 ml glycerol), Disperse Blue 3 (Aldrich, 1.0 mg in 100 ml ethanol + 1 ml glycerol), 1-methyl perimidine (synthesized from 1, 8 diaminonapthathalene[9], 0.4 g in 100 ml ethanol) and phenoxazine (Aldrich, 1.0 g in 100 ml acetone + 1 ml glycerol). Curcumin and Disperse Blue 3 are colorants which fade upon exposure to ozone[10] and to NO_2[11]. Phenoxazine is a nearly colorless compound whose reaction with ozone lead to colored products[12]. Methylperimidine reacts with NO_2 to yield a colored nitroso or nitro product[9]. Indigo carmine-coated passive samplers[1,2] were included in all tests for comparison.

Color change measurements

Color changes were measured by reflectance spectroscopy using a portable color analyzer (model CR-121, Minolta Corp.). The spectral response of the instrument closely approximates the CIE colorimetric Standard Observer curves. The measured color change ΔE is given by $\Delta E^2 = \Delta L^2 + \Delta a^2 + \Delta b^2$, where L*, a* and b* are the CIE parameters for chromaticity (a*, b*) and brightness (L*), and ΔL, Δa and Δb are the differences between exposed and unexposed samples. The instrument is calibrated using a white reflector plate standard, and the light source standard is CIE illuminant C (pulsed xenon arc lamp, 6774 K). In comparisons involving ceramic color tile standards as well as thirty colorants airbrushed on watercolor paper or coated on Whatman 41 cellulose paper, excellent agreement has been obtained between the color parameters measured with the color analyzer and those calculated from the 380–700 nm spectra recorded with a Diano Match Scan II reflectance spectrophotometer[13,15]. The precision (relative standard deviations for triplicate measurements) in color change measurements using the color analyzer was 0–0.7% (color parameter L*), 0–12% (a*) and 0–22% (b*) for ceramic color tile standards and was ≤ 5% for ΔE measurements on colorant samples[13,15].

The uniformity in colorant coating was measured for each batch of filters. The corresponding relative standard deviations (RSD) were 3.7% for curcumin (ΔE_o= 97. 4 ± 3.6, n

= 28, where ΔE_o is the color difference between uncoated and coated filters), 4.0% for indigo carmine ($\Delta E_o = 39.5 \pm 1.6$, n = 33), 5.4% for 1-methylperimidine ($\Delta E_o = 18.5 \pm 1.0$, n = 32) and 16.6% for phenoxazine ($\Delta E_o = 3.0 \pm 0.5$, n = 24). Average RSD for triplicate color readings of unexposed filters were 0.22% for indigo carmine (n = 23), 1.8% for phenoxazine (n = 6), and 0.58% for 1-methylperimidine (n = 3). Average RSD for co-located passive samplers were 14% for Disperse Blue 3 (n = 8), 14% for indigo carmine (n = 19), 4% for phenoxazine (n = 4) and 6% for 1-methylperimidine (n = 1).

RESULTS AND DISCUSSION

Ambient levels of photochemical oxidants

Field tests were carried out over the one-month period Aug. 9—Sept. 8, 1990 using co-located curcumin, Disperse Blue 3, 1-methylperimidine and phenoxazine passive samplers. The exposure duration was typically 3 days (see exact values in Table 1), thus yielding 10 consecutive sets of passive samples for each colorant tested. Also listed in Table 1 are the ambient concentrations of the photochemical oxidants ozone, NO_2, PAN and PPN averaged over the passive samplers' exposure duration, along with the corresponding cumulative oxidant doses (dose = product of oxidant concentration and exposure duration) calculated from the onset of the field test. While individual results are discussed in more detail elsewhere[16], it is relevant to mention here that the period studied did include several smog episodes, with 3 day-averaged ozone, NO_2, PAN and PPN levels of 40–88, 9–22, 3.0–8.6, and 0.5–1.5 ppb, respectively. During the 30-day period studied, ozone, NO_2, PAN and PPN accounted on the average for 78%, 15%, 6% and 1%, respectively (ppb basis) of the total oxidants. Not surprisingly in view of their common formation pathways, O_3, NO_2, PAN and PPN exhibited closely correlated diurnal and 3 day-averaged variations. This is illustrated in Figure 1, where cumulative 3-day increments in NO_2, PAN and PPN concentrations are plotted against the corresponding ozone concentrations. Linear regression analysis of this data set (Y = NO_2, PAN or PPN, X = O_3) yielded slopes,

Table 1 Ambient Levels And Cumulative Dose Of Photochemical Oxidants, Tanbark Flat, Ca, Aug. 9—Sept. 8, 1990

From	*To*	*Sampling duration, hrs.*	*Oxidant concentration, ppb*				*Cumulative oxidant dose, ppb. day*			
			O_3	*NO_2*	*PAN*	*PPN*	*O_3*	*NO_2*	*PAN*	*PPN*
8/9 16:30	8/12 14:00	69.5	84	12	4.4	0.7	256	36	13.2	2.1
8/12 16:00	8/15 12:39	68.6	42	22	3.6	0.5	378	102	24.0	3.6
8/15 16:25	8/18 12:11	67.8	66	15	6.2	0.9	576	147	42.6	6.3
8/18 16:11	8/21 11:38	67.4	40	12	3.0	0.4	696	183	51.6	7.5
8/21 15:00	8/24 10:38	67.6	63	17	5.7	1.0	885	234	68.7	10.5
8/24 14:25	8/27 11:11	68.8	49	10	4.0	0.6	1032	264	80.7	12.3
8/27 15:08	8/30 15:25	72.3	72	11	5.6	1.0	1248	297	97.5	15.3
8/30 18:38	9/2 11:18	64.7	88	9	8.6	1.5	1512	324	123.3	19.8
9/2 14:44	9/5 17:30	74.8	81	9	5.5	1.0	1755	351	140.1	22.8
9/5 20:30	9/8 10:20	61.8	81	9	5.5	1.0	1998	378	156.6	25.5

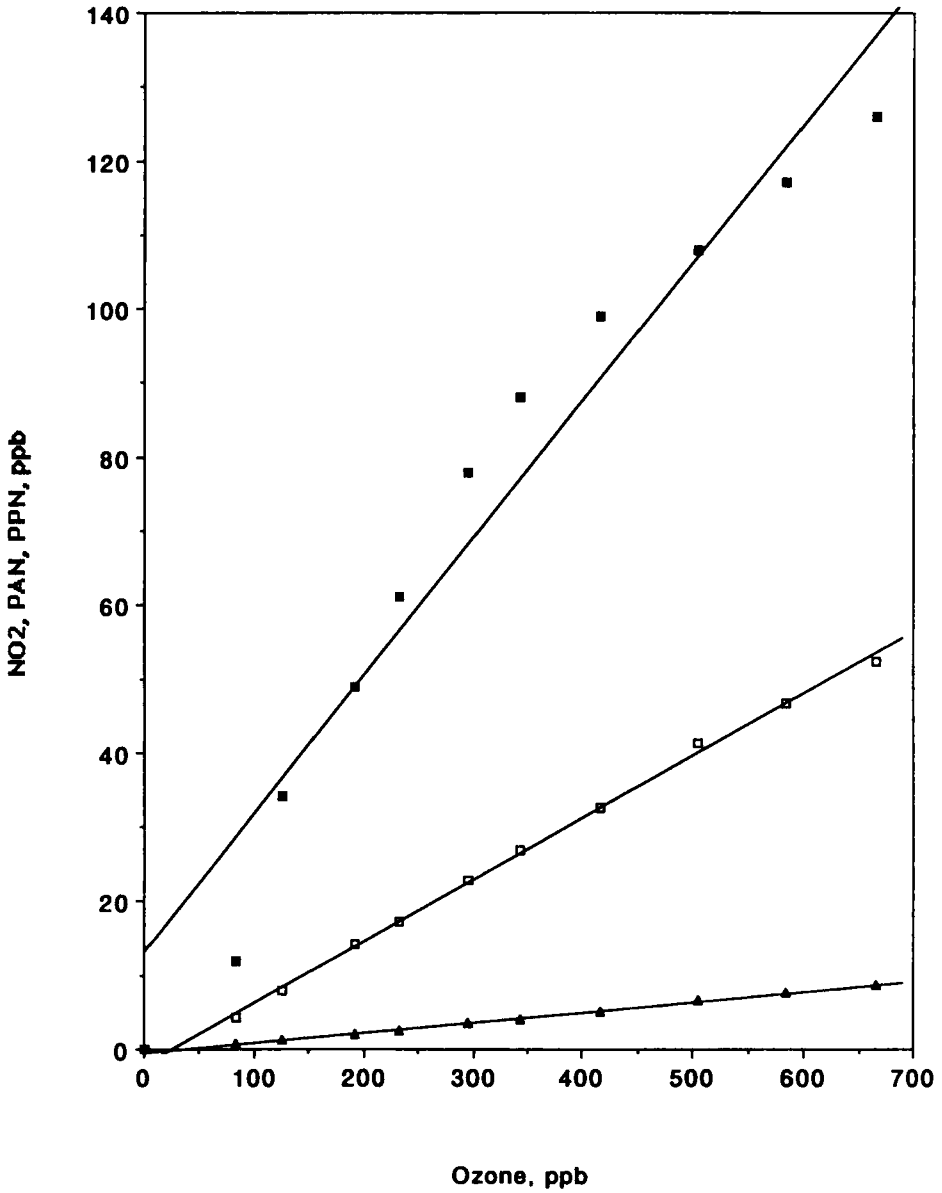

Figure 1 Scatter plots of cumulative NO_2 (top, solid squares), PAN (middle, open squares) and PPN concentrations (bottom, solid triangles) vs cumulative ozone concentrations, Tanbark Flat, CA, Aug. 9—Sept. 8, 1990. Linear regression parameters are given in the text.

intercepts and correlation coefficients of 0.186 ± 0.016 and 13.2 ± 6.4 (R = 0.970) for NO_2, 0.083 ± 0.001 and -2.07 ± 0.46 (R = 0.99) for PAN, and 0.0138 ± 0.0002 and ± 0.55 ± 0.07 (R = 0.999) for PPN, respectively.

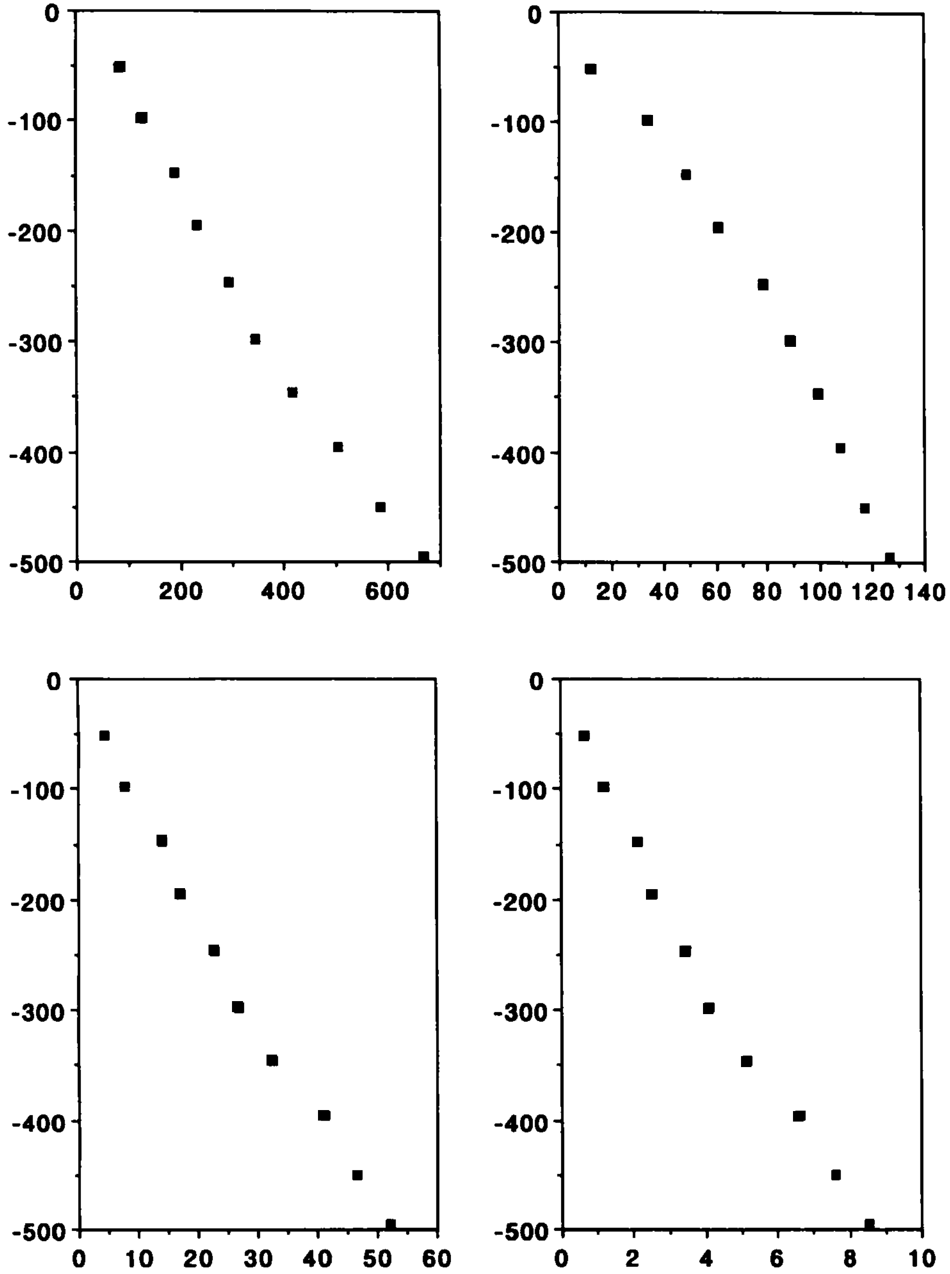

Figure 2 Cumulative color change (ΔE units) for curcumin passive sampler vs cumulative ambient concentration of ozone (upper left), NO_2 (upper right), PAN (lower left) and PPN (lower right)

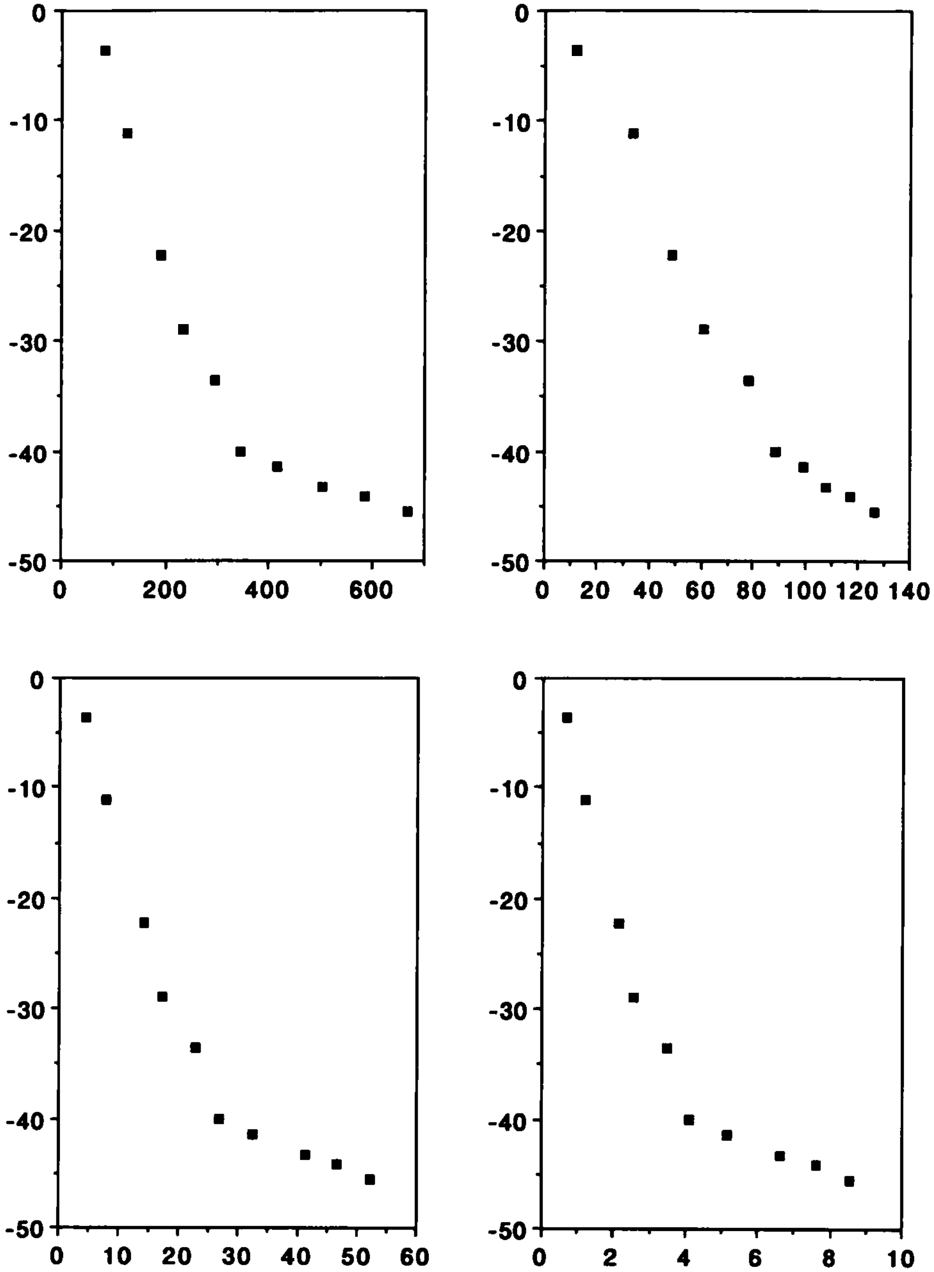

Figure 3 Cumulative color change (ΔE units) for Disperse Blue 3 passive sampler vs cumulative ambient concentration of ozone (upper left), NO_2 (upper right), PAN (lower left) and PPN (lower right)

Color change vs. oxidant concentration

The four compounds tested exhibited a gradual change in color in response to increasing ambient concentrations of photochemical oxidants. For curcumin (Figure 2) and Disperse Blue (Figure 3), this color change was a gradual decrease (fading), i.e. loss of chromophore. For phenoxazine, a colorless compound, the observed color increase resulted from the formation of one or more colored oxidation products (Figure 4). For 1-methylperimidine (Figure 5), the observed color change resulted from oxidation of the yellow-colored starting material to one or more orange/red reaction products. These color changes have been characterized in detail by recording 380–700 nm reflectance spectra of curcumin, Disperse Blue 3, 1-methylperimidine and phenoxazine before and after exposure to a mixture of photochemical oxidants[17].

Color change vs oxidant dose

For quantitative measurements of photochemical oxidants using colorant-based passive samplers, it is necessary to establish relationships between measured color changes and oxidant dose. Such relationships can be readily obtained from the color change vs. oxidant concentration data of the type shown in Figures 2–5. Although curve-fitting polynomial equations can be obtained to describe the non-linear regions of the plots shown in Figures 2–5, as we have done previously when measuring ozone with indigo carmine passive samplers[2], we limit here our analysis to the linear region of the data for each colorant tested. The linear regression parameters thus obtained are listed in Table 2, and the corresponding plots of color change vs total oxidants dose are shown in Figure 3. In turn, the regression parameters given in Table 2 can be used as calibration factors to calculate, for the four compounds tested, ambient oxidants concentrations from the measured color change and the known exposure duration.

The results shown in Figure 3 indicate that, if one wants to obtain data that are within the linear region of the color change vs oxidant dose curve, different compounds can be selected as a function of specific field applications. For ambient measurements in regions experiencing low levels of photochemical oxidants, and/or for short-term measurements, it is preferable to use those compounds that are most oxidant-fugitive, i.e. those with the highest slopes in Figure 3

Table 2 Cumulative Color Change Vs Cumulative Total Oxidants Concentration: Linear Regression Parameters

Colorant used in passive sampler	*Slope ± one std deviation (a)*	*correlation coefficient*	*n (b)*
Curcumin	0.200 ± 0.00	0.997	10
Disperse Blue 3	0.0283 ± 0.0004	0.991	6
1-methylperimidine	0.0381 ± 0.0004	0.997	7
phenoxazine	0.0935 ± 0.0003	0.998	8

(a) Y = color change, ΔE units; X = oxidants concentration, ppb (O_3 + NO_2+ PAN + PPN). Linear regressions forced through origin.

(b) from linear regions of curves shown in Figures 2–5.

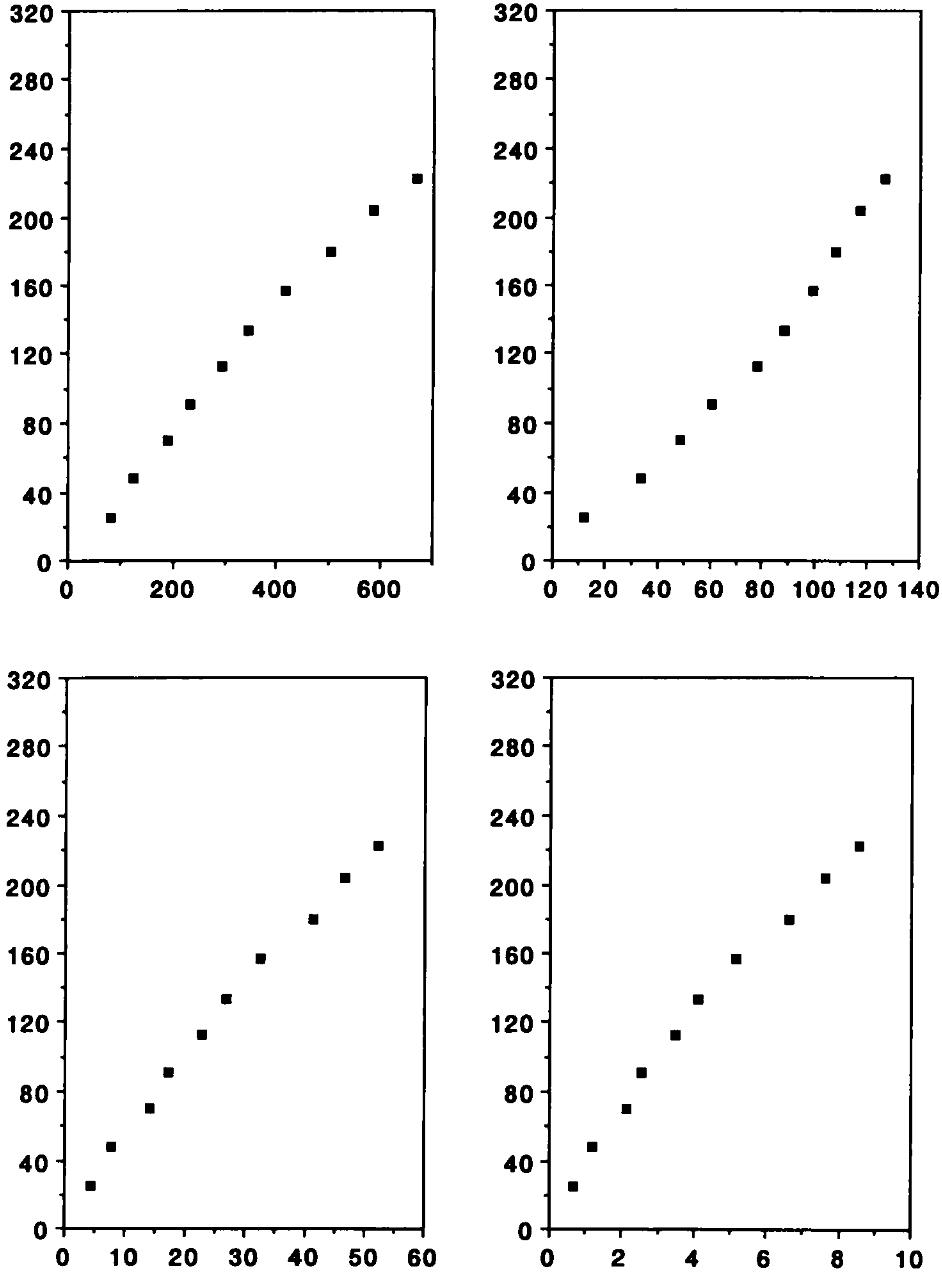

Figure 4 Cumulative color change (ΔE units) for phenoxazine passive sampler vs cumulative ambient concentration of ozone (upper left), NO_2 (upper right), PAN (lower left) and PPN (lower right)

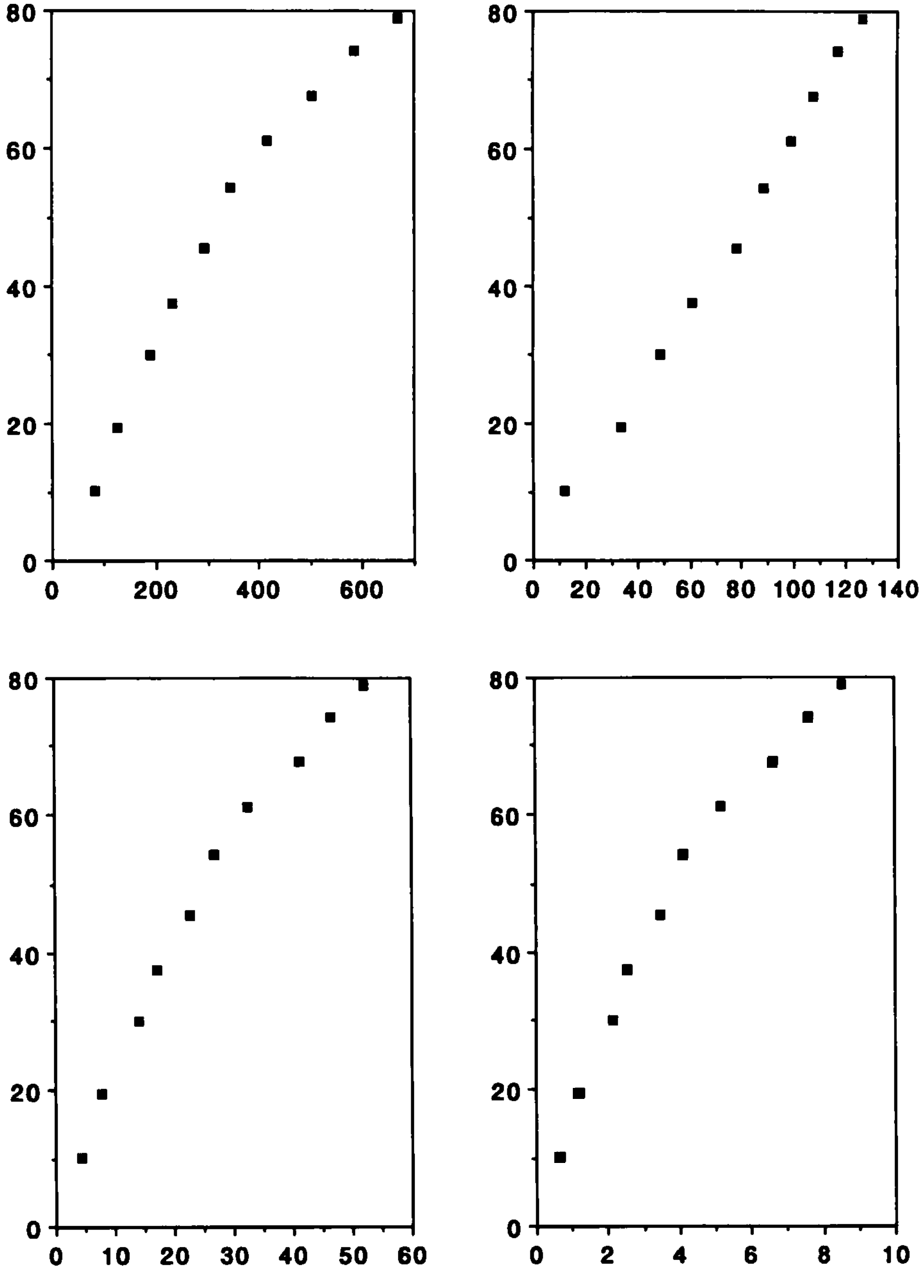

Figure 5 Cumulative color change (ΔE units) for 1-methylperimidine passive sampler vs cumulative ambient concentration of ozone (upper left), NO_2 (upper right), PAN (lower left) and PPN (lower right)

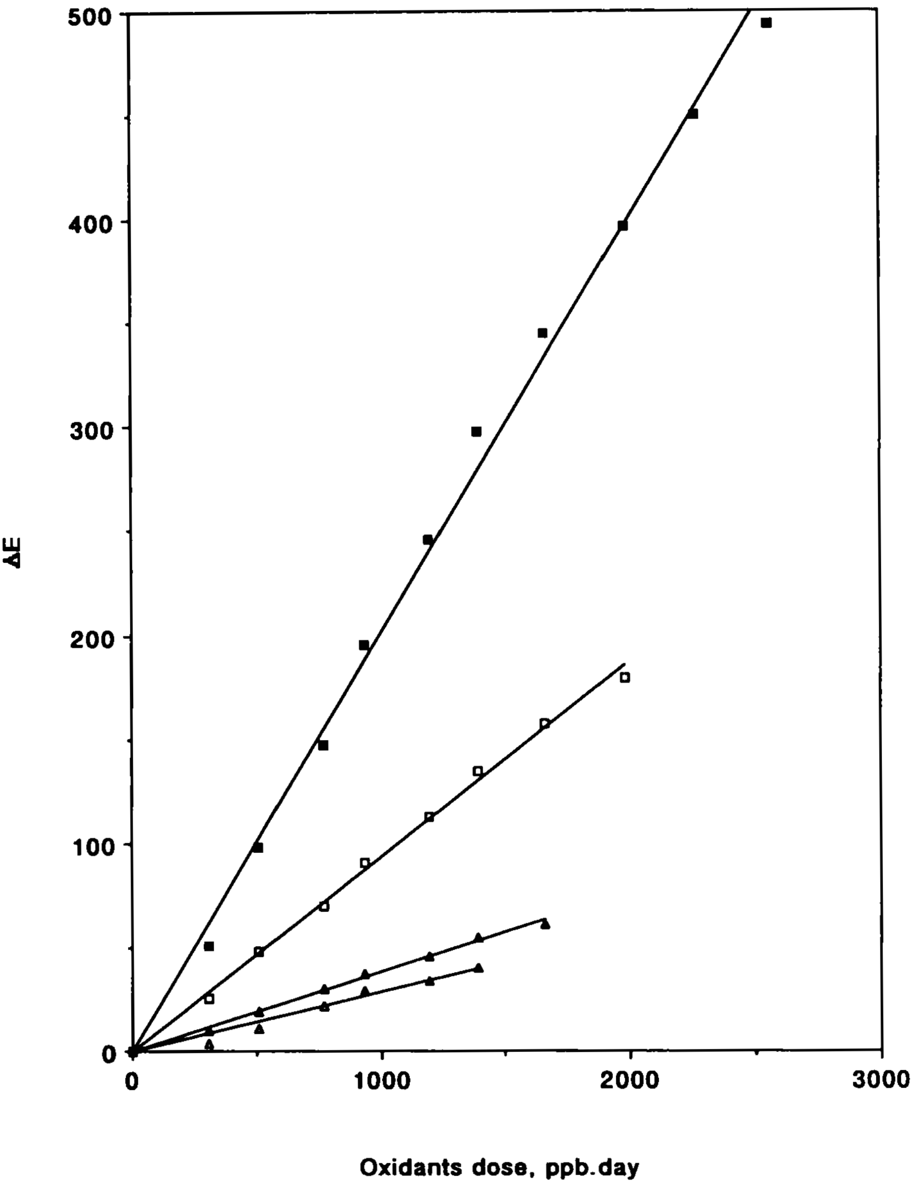

Figure 6 Cumulative color change (ΔE units) versus cumulative total oxidants dose (O_3 + NO_2 + PAN + PPN) for curcumin (top, solid squares), phenoxazine (open squares), 1-methylperimidine (solid triangles) and Disperse Blue 3 (bottom, open triangles). Linear regression parameters are given in Table 2.

(curcumin, phenoxazine). Conversely, the less ozone-fugitive compounds (1-methyl perimidine, Disperse Blue 3) may be used for longer-term measurements especially in regions experiencing higher levels of photochemical oxidants.

Consistency with laboratory tests and compound selectivity

Since ambient levels of O_3, NO_2, PAN and PPN during our study were highly correlated, see Figure 1, it is not possible from the field measurements alone to estimate the relative selectivity of the compounds tested towards one or more of the oxidants present in ambient air. Thus, it is useful to examine relevant literature data to verify consistency and to provide clues as to selectivity. No laboratory tests are available for PPN, but two types of studies have been carried out that involved the four compounds studied here and their color changes when exposed to O_3, NO_2 and PAN. In the first study, a passive sampler identical to that we employed in this work was used to expose curcumin and phenoxazine to ozone alone in purified air[1]. Both compounds exhibited color changes. The linear regions of the color change vs ozone dose plots were 600 ppb. day for curcumin and 500 ppb. day for phenoxazine. The ratio of the slopes of the color change vs ozone dose curves (linear regions) was 2.5 (phenoxazine/curcumin). These results are entirely consistent with those obtained in this study.

In the second type of study (Table 3), the four compounds were exposed to ozone alone, NO_2 alone, PAN alone and to a mixture of oxidants (O_3 + NO_2 + PAN) in purified air[1,14,15]. These studies, however, did not involve the use of passive samplers but involved direct exposure of the compounds coated on Whatman 41 paper. One set of experiments (1) involved short-term exposures and involved oxidant doses that are relevant to those we measured in ambient air in this study. The second set of experiments involved long-term

Table 3 Color Change Vs Oxidant Dose: Summary Of Relevant Literature Data

Oxidant (reference)	*dose ppb. day*	*Color change, ΔE units*			
		Curcumin	*Disperse Blue 3*	*1-methyl perimidine*	*phenoxazine*
Ozone (1)	150	8.4	9.4		18.5
NO_2(1)	300	3.8			18.8
PAN (14)	140	0.6	0.3	1.2	5.0
	300	1.7	0.3	2.1	12.9
	700	2.2	0.4	2.2	16.4
Oxidant mixture					
(O_3 + NO_2 + PAN) (15)	O_3 = 140 NO_2 = 260 PAN = 90	1.5	2.6	2.9	25.1
	O_3 = 270 NO_2 = 430 PAN = 170	2.1	3.2	3.5	31.9
	O_3 = 440 NO_2 = 690 PAN = 270	3.3	3.6	4.6	33.0

exposures (12 weeks), thus resulting in much higher oxidant doses[14,15]. For these experiments, only the results obtained during the first few weeks of exposure and corresponding to oxidant doses relevant to ambient air are listed in Table 3. From the results in Table 3, it is evident that all four compounds yield color change when exposed to the oxidants tested, i.e. O_3, NO_2 and PAN, either singly or as a mixture in purified air. Some trends in selectivity are also apparent (e.g. Disperse Blue 3 towards NO_2, phenoxazine towards PAN) and may lead to future applications of single oxidant measurements using passive samplers.

Interferences from other air pollutants

The four compounds selected for this study have been previously tested for their fugitiveness towards formaldehyde[13] and sulfur dioxide[18]. A control experiment involving exposure to purified air alone was also included[13]. These studies involved direct exposure (no passive sampler was included) for 12 weeks on Whatman 41 paper. The corresponding results are summarized in Table 4 for the first week(s) of exposure, i.e those corresponding to pollutant doses that are relevant to ambient air. The data in Table 4 show no color change for formaldehyde. For one compound, 1-methylperimidine, a modest color change was observed after exposure to about 100 ppb. day of SO_2. Ambient levels of SO_2 during our study were ≤ 2ppb and thus made a negligible contribution, if any, to the observed color changes for 1-methylperimidine during our field tests.

Detection limits

Detection limits can be calculated from the slopes of the color change vs oxidant dose shown in Figure 3 and using a signal to noise ratio of 3 for the corresponding color change measurements, which are uncertain within 0.5 ΔE units. The detection limits thus obtained are 8 ppb. day (1 ppb. week, 0.25 ppb. month, etc.) for curcumin, 16 ppb. day for

Table 4 Color Change Vs Pollutant Dose For Potential Interferents

Pollutant (reference)	*dose, ppb. day (number of weeks of exposure)*	*Color change, ΔE units*			
		Curcumin	*Disperse Blue 3*	*1-methyl perimidine*	*phenoxazine*
none (purified air, control test) (13)	0 (1)	0.9	0.3	1.4	1.1
	0 (2)	0.8	0.4	1.6	2.3
	0 (12)	2.7	1.8	5.1	8.9
formaldehyde (13)	740 (1)	0.9	0.2	0.8	0.6
	2,100 (2)	1.3	0.2	1.3	1.8
	10,200 (12)	2.0	1.2	5.2	10.4
sulfur dioxide (18)	320 (1)	0.2	0.9	1.4	0.8
	690 (2)	1.2	1.0	3.3	1.3
	5,270 (12)	2.6	0.5	6.7	7.2

phenoxazine, 40 ppb. day for 1-methylperimidine, and 54 ppb. day for Disperse Blue 3. While the four compounds tested are suitable for passive sampling of ambient photochemical oxidants, the selection of one compound should involve other considerations besides detection limit, e.g. the linear region of the dose-response curve as discussed earlier. In addition, it has been shown earlier for passive sampling of ozone[1] that the sampling rate can be increased or decreased substantially by simply replacing the upstream Teflon filter with other diffusion barriers, thus extending the dynamic range of the passive sampler as a function of desired sampling duration and other project objectives.

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