PERFORMANCE CHARACTERISTICS OF PALMES DIFFUSION TUBES USED FOR MEASUREMENT OF NITROGEN DIOXIDE OUTSIDE RESIDENTIAL SITES

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Abstract

As part of a largescale indoor survey of nitrogen dioxide (NO_2) in the Los Angeles area, 120 residences were randomly selected from more than 400 homes participating during a winter sampling period. For the 102 homes agreeing to participate, one NO_2 diffusion tube was placed outside on the north side of the house and another was placed outside six feet above the ground. The latter sampler was placed on a pole away from building structures and vegetation, and covered by an opaque cup. A network of 19 chemiluminescence monitors was used to provide interpolated measures of outdoor NO_2 concentrations for each residence. Nitrogen dioxide interpolated from the chemiluminescence monitors was better correlated with NO_2 measured at the sampling poles than on the north face of the home (r^2=0.65 and 0.51, respectively). Implications for characterizing NO_2 outside residences are discussed.

Introduction

Palmes-type diffusion tubes have been used in surveys of indoor air quality to characterize ambient NO_2 levels outside residential sampling locations. These ambient measurements have been utilized in statistical and physical models to determine factors influencing indoor NO_2 concentrations. The precision and accuracy of Palmes tubes used in this application have not been described. Several factors have been identified that would influence outdoor diffusion-sampler measurements including wind, sunlight, moisture, and vegetation. Since outdoor NO_2 is a major factor influencing indoor NO_2 concentrations, it is important that ambient NO_2 be carefully characterized in studies of indoor nitrogen dioxide (1).

Approximately 600 homes were randomly selected from the Los Angeles Basin to identify factors influencing variability in indoor residential concentrations of NO_2 (1). The survey protocol called for outdoor NO_2 to be characterized using a Palmes-type diffusion sampler located in a northern location at the side of the house in order to avoid direct sunlight. Following spring and summer sampling periods during 1984, unreasonably low outside NO_2 concentrations measured at several residences raised concern about potential interferences for outside monitors or the possibility that outside tubes were not properly uncapped to initiate sampling. The low outside concentrations were inconsistent with weeklong average concentrations calculated from nearby ambient NO_2 monitors operated by the South Coast Air Quality Management District (1). This inconsistency led to the following experiment to determine the accuracy of the original placement protocol.

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Methods

One hundred twenty participants were chosen at random from the main study. Each household had one Palmes tube placed in the original position at the side of the house. A siting protocol for a second outdoor tube was developed in order to minimize the potential for interferences and wind effects. This second outdoor tube was placed inside an opaque plastic cup that was set five feet off the ground on a wooden stake. The plastic cup shielded the sampling tube from sunlight and wind, and the stake was placed away from the direct influence of shrubbery and away from the side of the house. All tubes were constructed and analyzed by the University of Wisconsin.

Values for NO_2 at the house-side and stake were compared with one another, and with NO_2 values interpolated from chemiluminescence readings taken at stations operated by the South Coast Air Quality Management District (SCAQMD). Hourly values from 19 SCAQMD stations were averaged for the sampling week and concentration isopleths were drawn by hand. Residences were assigned NO_2 values according to their location within the concentration isopleths.

Results

Of the 120 households randomly selected to participate, 18 refused and the tubes for 9 were lost in the field. Therefore, results are presented for 93 homes. Average concentrations of NO_2 measured at the homes were generally lower than those concentrations measured at the SCAQMD stations (Table 1).

Table 1: Nitrogen dioxide concentration measurements at two locations outside the homes and interpolated values from the South Coast Air Quality Management District

	NO_2 ($\mu g/m^3$)	
Location	Mean (S.E.)	Median
Stake	92.7 (3.9)	99.5
House-Side	99.3 (4.4)	102.5
SCAQMD	120.3 (3.0)	117.0

Regression analyses and inspection of scatterdiagrams were conducted for all paired comparisons. Figure 1 shows the house-side to stake values along a 1:1 line. A clear pattern of outliers was observed with 5 to 10% of the pairs found with one member of the pair having a value near zero. This pattern suggests that the outliers represent diffusion tubes that had never been uncapped by a household occupant. Outliers were identified in this manner for each paired comparison and regressions computed with and without outliers present (Table 2).

Table 2: Regression analyses for comparison of NO_2 ($\mu g/m^3$) measured outside on house-side and on stake placed elsewhere in yard

Comparisons	Pairs	Dependent Variable	r^2	Intercept (S.E.)	Slope (S.E.)	Standard Error of the Estimate
House-Side to Stake NO_2						
All Data	89	Stake	0.27	45.2 (9.0)	0.47 (0.08)	32.5
Outliers Removed	74	Stake	0.69	27.7 (6.2)	0.68 (0.05)	13.4
SCAQMD to House-Side NO_2						
All Data	89	House-Side	0.18	26.1 (17.2)	0.61 (0.14)	37.9
Outliers Removed	80	House-Side	0.51	20.1 (10.2)	0.74 (0.08)	20.0
SCAQMD to Stake NO_2						
All Data	92	Stake	0.14	35.4 (15.5)	0.48 (0.13)	35.0
Outliers Removed	83	Stake	0.65	23.3 (6.6)	0.66 (0.05)	14.4

In total, 15 outliers were identified by examination of residual plots. Removal of these outliers greatly improved the quality of fit. In 12 of the cases either the house-side or stake value was low, while the other value recorded a realistic concentration. In three of the cases measurements for both of the outside Palmes tubes was near zero.

Discussion

Even following removal of obvious outliers, the correlation between two Palmes tubes placed in different locations at the same site was not very high. In fact, the correlation between the two tubes was not much higher than the correlation between either tube and the concentrations estimated from the SCAQMD monitoring network. This suggests unidentified sources of variability in outdoor Palmes tube readings. It also suggests that outdoor tube measurements may be substituted with fixed-site estimates when values are suspected of being erroneous. There is also some evidence, from higher correlation with fixed-site estimates determined from the monitoring network, that Palmes tubes placed away from structures and potential interferences (i.e. vegetation) may provide more precise values.

The specific sources of variability in NO_2 concentration measured by Palmes tubes at outdoor residential locations have not been determined. In a companion study, Palmes tubes located at the SCAQMD stations were found, in general, to be both accurate and precise (2) and were described by the following overall regression equation:

$$\text{CHEMILUMINESCENCE} = 5.9 + 0.93 \text{ PALMES}, \quad r^2 = 0.83 \tag{1}$$

Lower concentrations may be expected at residential sites since the SCAQMD monitors, by virtue of their location, will generally be more affected by mobile-source emissions of oxides of nitrogen. Artificially low or high measurements may result when a Palmes tube sampler is placed on the side of house. The effective diffusion path-length could be lengthened by dead airspace, or shortened by increase wind speed at building edges. Further, it is possible that interfering materials at the side of the house or in vegetation could reduce the accuracy of measurements. In several cases we suspect that the volunteer household member did not uncap one or more of the Palmes tubes to initiate sampling.

Regardless of the source of imprecision and inaccuracy there are several important implications for surveys of indoor air quality. Since indoor NO_2 is dependent on outdoor NO_2, failure to account for variation in outdoor concentrations could lead to erroneous interpretations of indoor measurements. This study also suggests that outdoor Palmes samplers should be located away from building structures and vegetation. Additionally, measurements of NO_2 made at ambient monitoring stations by chemiluminescence monitors may be substituted for suspect outdoor concentrations measured by Palmes tube samplers located at the residential site.

References

1. Wilson, A.L., Colome, S.D., Baker, P.E., and Becker, E.W. Residential indoor air quality characterization study of nitrogen dioxide. Vols. 1-3. Los Angeles: Southern California Gas Company, 1986.

2. Wilson, A. L., Colome, S.D., Baker, P.E., Cunningham, S.J., Becker, E. W., and Bope, W.G. Comparison of passive and chemiluminescence monitors for determining one-week average nitrogen dioxide concentrations. Proceedings of the Fourth International Conference on Indoor Air Quality and Climate, Berlin, FRG, 1987.