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Application of passive diffusion tubes to short-term indoor and personal exposure measurement of NO_2

M. R. Heal[1*], M. A. O'Donoghue[1], R. M. Agius[2] and I. J. Beverland[2]

[1] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.*

[2] *Department of Public Health Sciences, Medical School, University of Edinburgh, Teviot Place, Edinburgh, EH8 9AG UK.*

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* Corresponding author:

Dr. Mathew R. Heal, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K.
Tel: +44 (0)131 650 4764
Fax: +44 (0)131 650 4743
email: m.heal@ed.ac.uk

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Abstract

Palmes-type passive diffusion tubes were shown to be as accurate in measurement of indoor NO_2 during short-term (2 and 3-day) exposures as during 1-week exposures. The statistical limit of detection for cumulative NO_2 in 2 and 3-day exposure was 150 (nL/L).h. Mean coefficient of variation for duplicate 2 and 3-day exposures was < 13 %. A pilot study measuring personal, indoor (living room) and outdoor (just outside the home) NO_2 over 3 days for 8 volunteers demonstrates the feasibility and reliability of using passive diffusion tubes for short-term personal exposure measurements, and confirms the necessity of obtaining actual exposure profiles for a specific sub-population.

Introduction

The suggestion of links between air pollution and adverse health outcomes (e.g. the frequency and severity of asthma attacks) is well-documented (DoH 1997). A panel study by Schwartz (1990) has shown associations between respiratory symptoms and outdoor concentrations of NO_2. In contrast to the majority of air pollutants, ambient concentrations of NO_2 have not decreased over the past few years (DoH 1997).

Epidemiological studies that rely on a fixed outdoor monitoring site to estimate personal exposure to air pollution are often weakened because of: i) uncertainties in spatial variation of concentration across the study area, ii) the relatively short time spent outdoors, and, iii) the presence of specific indoor sources of air pollution. The latter factor is important in many instances for personal exposure to NO_2 because of gas cookers, gas and oil-fuelled space heaters and cigarette smoke (Melia et al. 1978).

To investigate causal relationships between NO_2 at sub-acute levels and health outcomes, it is therefore necessary to quantify directly personal exposure of specific individuals, particularly in regard to susceptible sub-populations. Passive diffusion samplers of both tube-type design (Palmes et al. 1976) and badge-type design (Yanagisawa and Nishimura 1982) have been developed for NO_2 measurement and since these are cheap, unobtrusive and permit simultaneous deployment, have been used in a number of personal exposure studies (Hoek et al. 1984; Quackenboss et al. 1986; Spengler et al. 1994). Although the badge sampler has been used in 2-day exposures (Spengler et al, 1994), passive diffusion tubes (PDT) have previously been assumed to require an exposure of at least one week, which masks the potential influence of shorter-term variation in exposure. Shorter sampling duration is essential for studies of personal exposure to NO_2 and health (Schwartz 1990).

The tube-type sampler is now used widely in networks for measuring ambient NO_2. In the work reported here we show that ordinary PDTs are as precise and accurate when deployed over short-term accumulations of just two to three days, at domestic indoor concentrations of NO_2, as for 1-week exposures. We demonstrate that PDTs can be applied equivalently for outdoor, indoor and personal sampling on this timescale using a small cohort pilot study.

Experimental Details

Standard acrylic passive diffusion tubes (length 7.1 cm, internal diameter 1.08 cm) from Gradko International were used. Following exposure, NO_2 is extracted as nitrite ion (NO_2^-) from the triethanolamine adsorbent and quantified colorimetrically using a Greiss-Saltzmann reagent. The average concentration of NO_2 at the mouth of the tube during the exposure is calculated from the diffusion uptake rate of the sampler (Palmes et al. 1976).

PDT accuracy in short term exposures was investigated by consecutively exposing tubes for combinations of 2, 3, 4 or 5 day periods in parallel with 1-week exposures. (In two instances, 1-week actually corresponded to 6 and 8 days). The majority of tubes were exposed in the laboratory, but for one week tubes were also exposed in the kitchen of a domestic residence containing a gas cooker. Tubes were always deployed in duplicate to assess measurement precision over these short exposures. Indoor and fridge-stored unexposed tubes were analysed for every exposure and never exceeded the limit of detection (see below).

The personal exposure pilot study used 8 volunteers (A-H), aged over 60. All subjects were non-smokers and resident within the city limits of Edinburgh, UK (~ 450,000 inhabitants). Simultaneous personal, indoor (living room) and outdoor (immediately outside the home) PDT exposures of 3-days were undertaken for each subject, spread over a 3 week period in August 1997. Personal tubes were attached at shoulder level on the subjects at all times or placed on a nearby table overnight and during bathing. Each subject maintained an activity diary of 15 minute resolution throughout.

Results of short-term indoor PDT exposure evaluation

Precision

Figure 1 shows the scatter plot of PDT duplicate precision (random assignment within each pair) for all exposure periods in the study. (Concentrations of NO_2 are expressed in units of nL/L which is equivalent to part per billion, ppb, as an atmospheric volume mixing ratio). The correlation coefficient between replicates of 2 and 3-day exposure was r = 0.89 ($P < 0.001$, n = 23). For comparison, the correlation coefficient between replicates of 6, 7 and 8-day exposure was also 0.89 ($P < 0.001$, n = 11). The mean coefficient of variation (c.v.) between duplicates of 2 and 3-day exposures was 12.6 % (s.d. = 11.0 %), whilst for 6, 7 and 8-day exposure replicates mean c.v. was 6.1 % (s.d. = 5.5 %). Precision for 1-week exposures compares extremely favourably with previous outdoor studies, e.g. 5-8 % (Atkins and Lee 1995), 10 % (Shooter et al. 1997) or 8 % (van Reeuwijk et al. 1998). Although precision is lower for the very short indoor exposures, it remains acceptable given the low cumulative exposures measured (< ~500 (nL/L).h). Campbell (1988) reports a precision of ~ 10 % for 28-

day exposure at 3 nL/L (2000 (nL/L).h), deteriorating to ~ 30 % for concentrations around 0.5 nL/L (340 (nL/L).h).

Limit of detection

Five point calibration graphs of nitrite standards, appropriate to the low levels of accumulated nitrite, were used for each set of analyses of exposed PDTs. The expression,

$$y = c + 3.s_{y/x}$$

where c is the intercept and $s_{y/x}$ the standard error in the regression, was used to calculate a limit of detection (l.o.d.) from each calibration curve (Miller and Miller 1993). The worst-case l.o.d. value, of all calibration curves used, was 20 ng NO_2^-, equivalent to cumulative exposure of 150 (nL/L).h. It is possible to detect considerably lower values of nitrite, but the above formula provides equal confidence against false reporting. Our l.o.d. is a factor of two lower than the usually quoted detection limit of 300 (nL/L).h for a passive diffusion tube (Boleij et al. 1986).

To exceed the limit of detection of 150 (nL/L).h in a 2-day exposure requires greater than 3 nL/L mean ambient NO_2. All indoor measurements in this study exceeded 6 nL/L. A 2-day exposure is therefore of sufficient duration if errors associated with the analytical technique are the limiting factor. An important contributor to analytical error in the calibration graphs was intrinsic variability in absorbance between different cuvettes in the dual-beam spectrometer.

Short-term versus 1-week accuracy

Figure 2 compares exposure-averaged NO_2 concentration derived from cumulative NO_2 from consecutive short-term PDT exposures totalling one week (the vast majority of short-term exposures are 2 and 3 days) with the exposure-averaged NO_2 concentration from a 1-week placement in parallel with the short-term placements. Means of replicate exposures are used. The data point at around 30 nL/L NO_2 corresponds to exposures in a kitchen with a gas cooker and illustrates the impact of such an indoor source on concentration of NO_2.

There is good agreement between 1-week and short-term derived NO_2 concentrations. The correlation coefficient of $r = 0.98$ is very highly significant ($P < 0.001$) and the relationship does not differ significantly from 1:1. We conclude that exposure-averaged NO_2 concentrations derived from 2 and 3-day exposures of PDTs are as accurate as NO_2 concentrations derived from 1-week exposures.

Results from 3-day personal exposure measurements using PDTs

Results for 3-day personal, indoor and outdoor NO_2 for the 8 recruits are shown in Figure 3. The median NO_2 personal exposure for the 8 subjects (exposure periods not concurrent across all subjects) was 13.7 nL/L (range 13 - 22 nL/L), which compares with a median indoor concentration of 13.2 nL/L (range 10 - 17 nL/L), and a median outdoors concentration of 16.8 nL/L (range 9 - 19 nL/L).

Personal exposure for all 8 subjects as a group is intermediate between indoor and outdoor concentrations but is very much closer to the former, as expected given the far greater time spent indoors. From the activity diaries, the average time spent indoors at own home for all subjects is 74 % (range 64 - 91 %). Residences A, C, D, E and G have gas cookers, but the indoor measurements do not indicate any elevated indoor NO_2 in the main living room for any subject during the measurement period. All residences except that of subject F have gas heating but the study was carried out in the middle of summer when heating is unlikely to have been used. The average ratio of indoor to outdoor NO_2 is 0.91 which confirms that indoor NO_2 reflects outdoor NO_2 in the absence of specific indoor sources of NO_2 (Weschler et al. 1994).

Indoor NO_2 accounts for 54 % of the variation in personal NO_2. The relationship is not significant ($P > 0.05$) and suggests that, although sample size is small, indoor NO_2 is not a suitable measure of variation in specific personal exposure. Variation of an individual subject's personal exposure to NO_2 outside the limits of indoor and local outdoor NO_2 concentration is rationalised by reference to the personal activity diaries. For example, a high personal exposure to NO_2 was noted for subject D who had spent two hours within the enclosed Edinburgh central railway station, whereas a low personal exposure was observed for subject H who had spent considerable time at a golf course. These observations illustrate why the personal exposure results in Figure 3 do not necessarily fall in the range between the indoor and local outdoor NO_2 but are determined also by exposure elsewhere and why it is inappropriate to take a single value to represent the exposure of a population.

It would have been informative to compare these individual measurements with the appropriate short-term exposure-averaged NO_2 concentration measured by the fixed-site chemiluminescence analyser at Princes Street Garden in the city centre of Edinburgh (operated as part of the UK Department of Environment Automated Urban Network). Data from the city-centre site are used to estimate exposure in current epidemiological time-series studies in Edinburgh (Prescott et al. 1998). Unfortunately the continuous analyser for NO_2 was in-operative for the same three-week period over which PDT measurements were obtained. By way of crude comparison, NO_2 concentrations from the city-centre analyser averaged over the two 3-day periods prior to, and the two 3-day periods after, the PDT trial were 19, 34, 19 and

19 nL/L, respectively. These concentrations exceed NO_2 measured outside all subject residences and it is reasonable to assume that this is also likely to have been the case during the period of data collection. Since subject residences are in more suburban localities the result is not surprising, but again illustrates the point that a single city-centre monitoring site is a poor surrogate for individual exposures.

Although, previous work on NO_2 passive diffusion tubes (Heal et al. 1998) has demonstrated an intrinsic tendency of PDTs to measure concentrations between NO_2 and total NO_x (= NO + NO_2), this is significant only in the presence of large local sources of NO and oxidant (mainly ozone) to convert NO to NO_2. For both indoors, and outdoors in suburban localities not adjacent to busy roads, overestimation of true NO_2 in this way by PDT is likely to be negligible.

Conclusions

By exercising care during preparation, storage and analysis, Palmes-type passive diffusion tubes have been shown to be accurate and precise in short-term (2 and 3-day) measurement of indoor NO_2. A short-term exposure is important since exposure during a specific period may not reflect the longer-term average at that particular locality. For example, people are likely to spend time in areas, e.g. the kitchen, specifically when peak concentrations occur which leads to a higher exposure than calculated using time-weighted exposures constructed from weekly average concentrations. Conversely, at night, people are likely to be under-exposed to NO_2 compared with bedroom average since time spent in the bedroom is likely to be when gas appliances are switched off.

The successful outcome of this study, in conjunction with the very low unit cost of the PDT and the relatively minor inconvenience to the wearer, should now provide considerable impetus to more extensive use of passive diffusion tubes for the assessment of personal exposure to NO_2 within specific target populations. A 2 or 3-day exposure is particularly appropriate since some epidemiological studies report strongest associations of health outcomes with 3-day antecedent average air pollutant concentration, rather than with same-day concentration (Prescott et al. 1998). In addition, 2-day exposures permit a comparison of personal exposure between weekday and weekend.

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Figures

Figure 1: Concentrations of NO_2 obtained from duplicate indoor PDT exposures. For 2 and 3-day exposures, correlation coefficient, r = 0.89 (n = 23); for 6, 7 and 8-day exposures, r = 0.89 (n = 11).

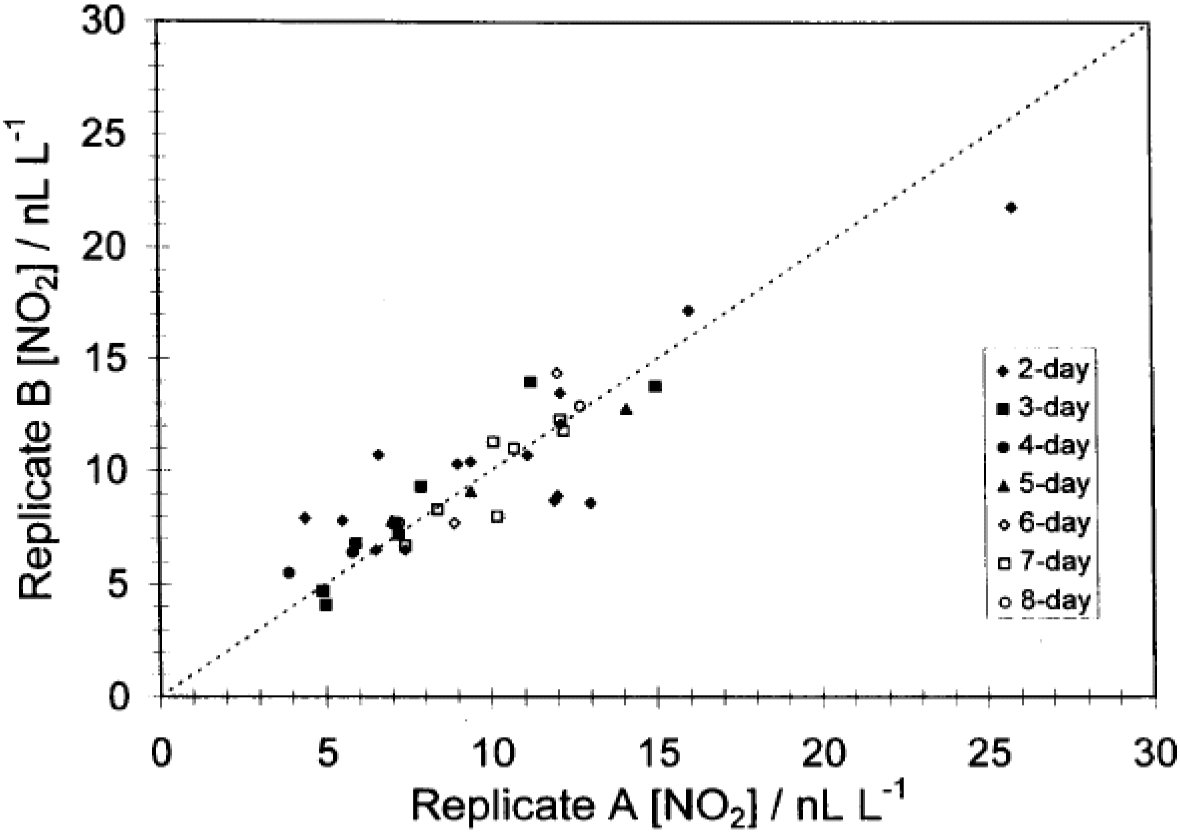

Figure 2: Regression of 1-week PDT NO_2 concentrations on 1-week PDT NO_2 derived from cumulative parallel short-term exposures of 2, 3 and/or 4 days.

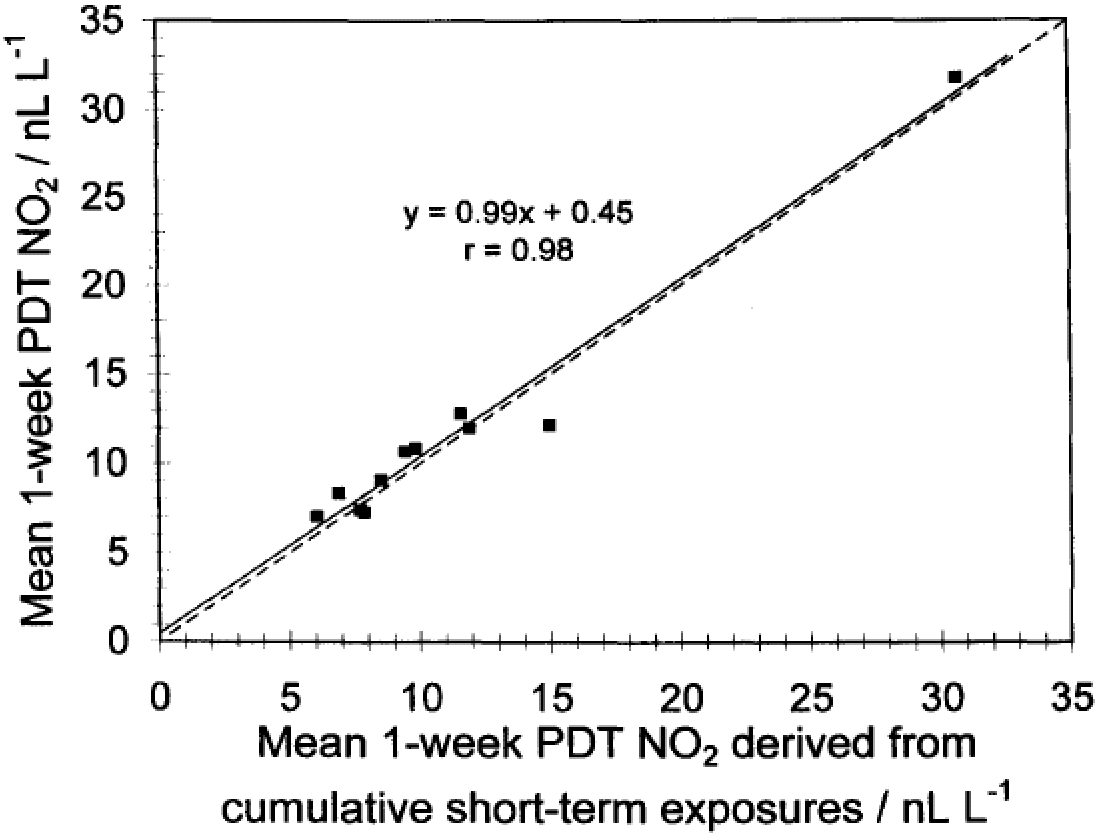

Figure 3: Indoor, personal and outdoor NO_2 exposures of 3 days on 8 subjects.