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Technical note

Reliability of reflectance measures in passive filters

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HIGHLIGHTS

- Indigo carmine impregnated passive filters for evaluation of ozone concentration.
- Require only examination via reflectometer and calibration curve.
- Linear mixed models used to estimate latent reflectance.
- Method allows outlier detection and accommodation.
- Useful for sample size determination.

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ABSTRACT

Measurements of optical reflectance in passive filters impregnated with a reactive chemical solution may be transformed to ozone concentrations via a calibration curve and constitute a low cost alternative for environmental monitoring, mainly to estimate human exposure. Given the possibility of errors caused by exposure bias, it is common to consider sets of m filters exposed during a certain period to estimate the latent reflectance on n different sample occasions at a certain location. Mixed models with sample occasions as random effects are useful to analyze data obtained under such setups. The intra-class correlation coefficient of the mean of the m measurements is an indicator of the reliability of the latent reflectance estimates. Our objective is to determine m in order to obtain a pre-specified reliability of the estimates, taking possible outliers into account. To illustrate the procedure, we consider an experiment conducted at the Laboratory of Experimental Air Pollution, University of São Paulo, Brazil (LPAE/FMUSP), where sets of $m = 3$ filters were exposed during 7 days on $n = 9$ different occasions at a certain location. The results show that the reliability of the latent reflectance estimates for each occasion obtained under homoskedasticity is $k_m = 0.74$. A residual analysis suggests that the within-occasion variance for two of the occasions should be different from the others. A refined model with two within-occasion variance components was considered, yielding $k_m = 0.56$ for these occasions and $k_m = 0.87$ for the remaining ones. To guarantee that all estimates have a reliability of at least 80% we require measurements on $m = 10$ filters on each occasion.

1. Introduction

In the urban environment, both inhalable particulate matter and ozone have been identified as the two pollutants with the greatest impact not only on human health, but also on plants, buildings and on the ecosystem itself (WHO, 2006; Chiqueto and Silva, 2010).

In particular, ozone, a chemical compound with high oxidative potential and one of the least studied because of the difficulties with its monitoring and with the evaluation of its impact on health (WHO, 2006; Chiqueto and Silva, 2010), has demanded the attention of authorities and scientists. The methods and equipments recommended for its monitoring (CETESB, 2011) require high capital as well as installation and operation costs. Although precise time series behavior of the pollutant may be generated with this

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type of equipment, a good spatial resolution or the identification of black spots with high ozone concentration may not be feasible. Furthermore, the use of fixed monitoring stations in epidemiological studies generates pollutant exposure misclassification since they do not reflect personal behavior, habits and mobility characteristics.

Environmental monitoring of ozone by passive filters not only constitutes a cheaper and easy to use solution, but is also a reasonable alternative to quickly identifying areas with high concentrations of the pollutant. Given their simplicity (they do not require pumps or other devices), they may be used as personal and/or portable monitors for outdoor and indoor measurements. While generating less precise results, the combined use of passive filters with traditional monitoring networks could enrich the spatial and temporal knowledge of the pollutant behavior, improving the exposure characterization of epidemiological studies.

The use of passive filters impregnated with a reactive chemical solution that fades progressively during its exposure to ozone was proposed by Grosjean and Hisham (1992) and constitutes an indirect process for evaluating its concentration. The variation of reflectance, i.e., the fraction of the incident light flux reflected by the surface before and after environmental exposure can be determined by a reflectometer and used to predict the latent concentration of ozone in the exposure period via calibration models. Compared to other types of passive filters [see Koutrakis et al. (1993) or Krupa and Legge (2000), for example] that require chemical extraction after exposure, the use of a reflectometer saves time and eliminates chemical waste resulting from the extraction phase. In our study we simplified the impregnation process originally proposed by Grosjean and Hisham (1992), using only an indigo carmine solution (2 g of indigo carmine reagent diluted in 1000 mL of distilled water) eliminating the need for glycerol and methanol.

The possible contamination by other pollutants, however, requires a careful reliability evaluation. Given the possibility of errors caused by exposure bias, it is common to consider sets of m filters exposed during a certain period to estimate the latent reflectance on n different sample occasions.

Our objective is to propose a protocol to evaluate the reliability of reflectance measurements that will be used in a calibration procedure to estimate the latent ozone concentration. With this objective, a pilot study conducted by the Laboratory of Experimental Air Pollution, University of São Paulo, Brazil (LPAE/FMUSP) exposed sets of $m = 3$ filters for a period of 7 days on $n = 9$ different sample occasions at a location where the State of São Paulo Environment Protection Agency (CETESB) had an ozone monitor. In each filter, reflectance was measured at the beginning and at the end of the exposure period. The difference between the two measurements (here simply called reflectance) is the variable of interest. The results of this pilot study will be used to design the calibration study. The protocol involves: a) identification of outlying reflectance values; b) computation of the reliability of each observation and of the mean of the observations on the same occasion; c) determination of the number of filters (m) required to obtain a pre-specified reliability of the latent reflectance estimate.

The paper is organized as follows: in Section 2 we present the proposed statistical model; in Section 3, we describe the analysis of the reliability of the measurements; in Section 4, we analyze the LPAE/FMUSP data; finally in Section 5, we present a brief discussion and some final considerations.

2. The model

A linear model with a random factor (see Pinheiro and Bates, 2004, for example) can be used to characterize studies as the one described above wherein m observations of the same characteristic are obtained for n different samples. In the passive filter example, the samples correspond to the $n = 9$ occasions, each with $m = 3$ filters being evaluated. The model is

$$y_{ij} = \mu + a_i + e_{ij}, \tag{1}$$

where μ is the latent reflectance across the population of occasions being sampled, a_i is a random variable representing the deviation between the latent reflectance for the ith occasion and the latent population reflectance, and e_{ij} is a random variable representing the difference between the observed reflectance for filter j on occasion i and the latent reflectance on occasion i, $i = 1, \ldots, n$ and $j = 1, \ldots, m$. The random variables a_i and e_{ij} are assumed to be independent, normally distributed with mean zero and constant variance. The variance of a_i, (between–occasions variance) is denoted by σ_a^2, and the variance of e_{ij}, (within-occasion variance) is denoted by σ^2.

Under this model, the fitted value of the reflectance on the ith occasion is

$$\hat{y}_{ij} = \bar{y}_{..} + k(\bar{y}_{i.} - \bar{y}_{..}) \tag{2}$$

where $\bar{y}_{..} = \sum_{i=1}^{n}\sum_{j=1}^{m} y_{ij}/N$, $N = m{\cdot}n$, $\bar{y}_{i.} = \sum_{j=1}^{m} y_{ij}/m$ and $k = \sigma_a^2/(\sigma_a^2 + \sigma^2/m)$, $i = 1, \ldots, n$ and $j = 1, \ldots, m$. The role of the shrinkage constant k is to accommodate possible outliers. Note that when m is large or when σ^2 is small in relation to σ_a^2 that is, when the observations within the same occasion are more homogeneous, k approaches 1 and the best predictor of the occasion latent reflectance is the mean of the observed responses on that occasion.

The parameters σ_a^2 and σ^2 are usually unknown and may be estimated by

$$\hat{\sigma}_a^2 = \frac{\text{MSA} - \text{MSE}}{m} \text{ and } \hat{\sigma}^2 = \text{MSE}, \tag{3}$$

where $\text{MSA} = \sum_{i=1}^{n} m(\bar{y}_{i.} - \bar{y}_{..})^2/(n-1)$ and $\text{MSE} = \sum_{i=1}^{n}\sum_{j=1}^{m}(y_{ij} - \bar{y}_{i.})^2/(N-n)$ represent, respectively, the between occasions mean square and the within occasions mean square from the Analysis of Variance (see Fisher and van Belle (1993), for example).

Appropriate index-plots of the conditional and marginal residuals, defined as $\hat{e}_{ij} = y_{ij} - \hat{y}_{ij}$ and $r_{ij} = y_{ij} - \bar{y}_{i.}$, respectively, are useful to verify the assumptions of model (1) as indicated in Nobre and Singer (2007) and Singer et al. (2014). Computer routines in R (R Development Core Team (2012)) based on *lme4* and *nlme* functions are being developed for this purpose and can be downloaded from www.ime.usp.br/~jmsinger/lmmdiagnostics.zip. With the proposed residual analysis it is possible to detect outlying observations as well as occasions with different reflectance variability. In such cases, an alternative is to consider a heteroskedastic model. This procedure will be illustrated in the analysis of the LAPAE/FMUSP data in section 4.

3. Analysis of the reliability of the measurements

To minimize the effect of exposure bias, it is recommended that m filters be exposed during a certain period to obtain a more reliable estimate of the latent reflectance on a given occasion.

A measure of the reliability of an observation is the intra-class correlation coefficient (Bartko, 1966; Fleiss, 1986; McGraw and Wong, 1996), also called intra-class correlation coefficient of reliability, given by:

$$\rho = \sigma_a^2\Big/\left(\sigma_a^2 + \sigma^2\right). \tag{4}$$