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Assessment of the effect of degradation by atmospheric gaseous oxidants on measured annual average benzo[a]pyrene mass concentrations

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HIGHLIGHTS

- ▶ A novel method for assessing the effect of on-filter degradation on benzo[a]pyrene (BaP) is presented.
- ▶ The method is based on using different sampling periods for ambient particulate matter.
- ▶ Assumed pseudo-first order reaction rate kinetics allow calculation of concentration in the absence of degradation.
- ▶ Effect on the measured annual average BaP concentration at two monitoring stations in the UK is estimated.

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ABSTRACT

A novel method for assessing the effect of degradation by atmospheric species on measured annual average benzo[a]pyrene (BaP) concentrations is presented. The method is based on assessing the difference in measured BaP mass concentrations using different sampling periods and extrapolation using assumed pseudo-first order reaction rate kinetics to produce the expected BaP mass concentration when theoretical sampling periods of zero duration are used – during which no degradation would be observed. The results suggest that the use of a one day sampling period as specified by the required reference method for BaP assessment in the UK may result in an underestimation of the annual average BaP mass concentration by approximately 6%. This is relatively small compared to the overall uncertainty of the measurement.

1. Introduction

Atmospheric pollutants that are harmful to human health and environmental sustainability, such as polycyclic aromatic hydrocarbons (PAHs), are routinely monitored by air quality measurements across the globe. In Europe, a target value for benzo[a]pyrene (BaP – as a marker for the suite of PAH compounds) in the PM_{10} particulate phase has been established, against which compliance is judged (European Commission, 2005). The target value is 1 ng m^{-3} as an annual average mass concentration at an individual monitoring station.

It has been recognised for over thirty years that, during sampling, BaP (and indeed all PAHs) collected on air filters can react with atmospheric gaseous oxidants moving through the filter, in particular ozone but also to a lesser extent nitrogen dioxide, hydroxyl radicals, NO_3 and N_2O_5, producing oxy- and nitroxy-PAH derivatives. This degradation can result in possible underestimation of the concentration of BaP in air (Pitts et al., 1978). This is of special concern as it may result in false negatives with respect to compliance with legislation (Creutznacher and Huber, 2002). The body of literature that has studied this process in the laboratory has provided an insight into how complex this reaction is (Menichini, 2009). The extent of BaP degradation has been shown to depend on a number of interacting factors such as the: concentration of gaseous oxidant, flow rate through the filter, filter material, temperature, relative humidity, composition of the particle to which the BaP is bound, extent of surface coverage of BaP on the particles and particle size (Nana-Owusua et al., 2004; Kahan et al., 2006; Kwamena et al., 2007; Cazaunau et al., 2010; Chu et al., 2010). A complex relationship with exposure time is also apparent with the collected BaP sometimes decaying to zero and sometimes reaching a non-zero plateau (Perraudin et al., 2007) – presumably because some BaP remains resistant to oxidation, perhaps because it is occluded or covered by other particles. Given this range of parameters it is not surprising that BaP losses from pre-loaded artifacts of anywhere between 0% and 100% have been observed in the laboratory (Menichini, 2009). In the field, degradation rates are even more complex to assess because of changes during sampling in temperature, relative humidity and oxidant concentration, and

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also the nature of the substrate. In addition the mass concentration of BaP in the air being sampled may be changing over time depending on the length of the sampling period. Faced with this complexity most field studies of BaP degradation have relied on the comparison of duplicate samplers where one sampler is unmodified and the other either has synthetic ozone introduced during sampling (Brorström et al., 1983) or operates with an ozone denuder incorporated into the sampler (Van Vaeck and Van Cauwenberghe, 1984; Creutznacher et al., 2005). Again a range of BaP loses have been observed (Tsapakis and Stephanou, 2003). These studies are not always entirely satisfactory because of the synthetic nature of either the introduction, or removal, of ozone from the system (Goriaux et al., 2006; Albinet et al., 2010) – indeed the performance of MnO_2 ozone denuders is known to be influenced by ambient humidity. Furthermore it is not clear that other gaseous atmospheric oxidants such as nitrogen dioxide and hydroxyl radicals are properly considered by these studies.

The introduction of the EC's Fourth Daughter Directive on Heavy Metals and PAHs in ambient air and, in support of this, the publication of the required reference method for the measurement of BaP in PM_{10}, EN15549 (European Committee for Standardization, 2008), made it clear that one day sampling periods were mandatory for BaP sampling in order to produce data in support of the implementation of this legislation – in part because of the known degradation of BaP sampled over longer timescales. However it still remained unclear what the likely effect on annual average BaP concentrations of using the one day sampling period would be. The UK was using fourteen day sampling periods until the new legislation. Subsequently, a new set of samplers was purchased and rolled out across the UK network in 2007 and 2008 (Conolly, 2011). During this change there was a period of parallel running at two monitoring stations where measured concentrations differed by an order of magnitude: Scunthorpe Town between 2007 and 2010 inclusive (a station very close to a steel works with a 2010 annual average BaP mass concentration of 1.30 ng m^{-3}) and Harwell between 2008 and 2010 inclusive (a rural station with a 2010 annual average BaP mass concentration of 0.12 ng m^{-3}). This parallel running was conducted by the operators of the UK PAH monitoring network (initially AEA Technology and subsequently the National Physical Laboratory) on behalf of the UK Department of Environment Food and Rural Affairs (Conolly, 2011; Brown et al., 2011). The data acquired during this period of parallel running presented an opportunity to assess the effect of different sampling periods on measured BaP concentrations.

The aims of this paper are two-fold: (1) to present a novel, entirely field-based method to assess degradation of on-filter BaP based only on variations in sampling period with no synthetic variables being introduced, and (2) to determine what the effect of degradation of on-filter BaP might be on the annual average recorded at monitoring stations using one day sampling periods. We are not aware of any other literature on either of these two aims, or of any attempts to describe the real-time degradation kinetics of on-filter BaP being continuously collected on a filter – although three studies (Schauer et al., 2003; Sanderson and Farant, 2005; Lammel et al., 2010) have indirectly compared samples collected over different sampling periods this was not the main motivation for these studies and they did not observe any influence of sampling duration on BaP degradation.

2. Materials and methods

Air samples were taken at Scunthorpe Town (2007–2010) and Harwell (2008–2010) using co-located Andersen GPS-1 (fitted with a continuous flow measurement facility) and Digitel DHA-80 (fitted with a continuous flow measurement facility and rain jar) samplers, sampling for a period of 336 h (14 days) and 24 h between filter changes, respectively, at calibrated flow rates of nominally 5.4 $m^3 h^{-1}$ and 30 $m^3 h^{-1}$, respectively, such that the difference in the total sampled volumes over the different periods was a factor of 2.52. Sampler flows were calibrated every quarter and not observed to change significantly when compared to the uncertainty of the flow measurement. Taking into account the difference in filter sizes between the two samplers, the volume of air sampled (and hence the PM loading) per area of filter during each sampling period differs only by a factor of 1.16 with the 24 h Digitel samples exhibiting the higher of the two values. The particulate matter size fraction sampled was nominally PM_{10}, although it is acknowledged that the Andersen samplers as deployed may have sampled size fractions slightly in excess of this. Quartz fibre filters were used, with field blanks being taken for each sampler every quarter. After being sampled in the Digitel sampler, filters were changed automatically and stored in a cooled, close-packed stack of 14 sampled and unsampled filters within the sampler body such that it is assumed that the rate of degradation by diffusion of gaseous oxidants (which is anyway much lower than for active sampling (Menichini, 2009)) was negligible. We also assume that over the sampling periods in question the filters in each sampler are exposed to the same changes in temperature, relative humidity, gaseous oxidant concentration etc. The sampled filters were sent to an analytical laboratory accredited to ISO 17025 (International Standardisation Organisation, 2005) to perform the analysis required by EN15549 – in this case soxhlet extraction followed by extract concentration with rotary evaporation and analysis using gas chromatography–mass spectrometry. Blank and field blank levels were routinely below the detection limit for the method. (BaP was quantified as this is the compound covered by the European target value. In future work it would be useful to quantify other PAHs that are mentioned in the European legislation but not covered by a target value.) Results were reported as a mass of BaP collected every quarter (i.e. over approximately 91 Digitel sampling periods and 6–7 Andersen sampling periods). These masses were then divided by the corresponding volume of air sampled to produce a mass concentration in air. The annual mean is then given as the arithmetic mean of these four quarterly values.

3. Results and discussion

3.1. Results of parallel sampling

The results of the study, together with some other meteorological and ambient pollutant parameters known to influence the rate of BaP degradation are given in Tables 1 and 2. There is no strong correlation between the parameters displayed apart from the expected correlation between the two sets of BaP concentrations, and some anti-correlation between ozone and BaP concentrations. This anti-correlation is not a direct cause and effect relationship but is simply a result of the opposing seasonal trends in ozone concentrations (higher in summer as a result of meteorological variations) and BaP concentration (higher in winter as a result of changing fuel usage often correlated with ambient temperature (Brown et al., 2011)). This is proved by the apparent lack of correlation between ozone concentration and the ratio of the BaP concentration measured using each sampler, and highlights the highly complex nature of the degradation process under real field conditions. The average concentrations measured over the study period at Harwell (0.093 and 0.055 ng m^{-3} for 24 h and 336 h samples, respectively) and Scunthorpe Town (1.86 and 0.90 ng m^{-3} for 24 h and 336 h samples, respectively) are consistent with their site types (Harwell – rural, and Scunthorpe Town – urban industrial) and with concentrations measured by the UK PAH Network at these sites in recent years (Brown et al., 2011). However, it is clear