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The effect of degradation by gaseous oxidants on measured benzo[a]pyrene concentrations

Richard J. C. Brown
Andrew S. Brown

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Dr Richard J. C. Brown
Dr Andrew S. Brown
Analytical Science Division

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of NPLML by Mr Alan Brewin, Head, Analytical Science Division.

EXECUTIVE SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) are formed primarily as products of incomplete combustion and emitted from a number of anthropogenic and natural processes. Because they are toxic to human health, the allowable emissions and air concentrations of PAHs are limited by a number of national and international regulations and directives. In Europe benzo[a]pyrene (BaP) is subject to regulation by the European Commission's Fourth Air Quality Daughter Directive, as it exhibits the highest toxic equivalent value (toxicity multiplied by concentration) of common PAHs found in the ambient atmosphere. The target value for BaP in the PM₁₀ particulate fraction of ambient air is 1 ng/m³ calculated as an annual average at each monitoring station.

National air quality monitoring networks assess compliance against this target value. In the UK this is carried out by the UK PAH Monitoring Network operated by the National Physical Laboratory, on behalf of Defra. According to the European reference method size-fractionated air particulate is to be collected on to filter for periods of a day at a time. The PAHs in these filters are then extracted and analysed to obtain a monthly mass concentration in air. Studies have shown that PAHs are subject to on-filter degradation by gaseous ambient oxidants.

On-filter degradation may result in an underestimation of the BaP concentration in ambient air. However, there is currently no data to suggest what the effect of degradation on the annual average BaP concentration – the most important Directive compliance metric – might be. Therefore, this study, commissioned by the UK Department for Environment, Food and Rural Affairs, has:

- reviewed the current literature to assess the current understanding of on-filter benzo[a]pyrene degradation by oxidising gases and whether there is any published evidence to assess what the effect of degradation on annual average BaP concentrations might be;
- performed a re-analysis of existing data sets to assess the effect of degradation on annual average BaP concentrations;
- determined what the compliance implications are if the concentrations that would be obtained in the absence of degradation are extrapolated across the whole of the UK;
- made proposals about how to best deal with the expected losses of BaP, for instance as an input to advise any future revision of air quality directives;
- suggested the operation of a year-long parallel study with and without ozone denuders that would collect additional data to confirm the findings of this study.

This work suggests that BaP losses in the UK are likely to be in the range from 5 % for low BaP concentrations to 7 % for higher BaP concentrations and around 6 % at the target value. If these relatively low losses were confirmed by a year long field trial using ozone scrubbers, it is proposed that the uncertainty budget for the measurement could simply be expanded to accommodate this bias. Alternatively a correction could be made to the measured values (with or without an addition to the uncertainty budget) to account for the lost BaP.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	5
TABLE OF CONTENTS	6
1 INTRODUCTION.....	7
2 DEGRADATION OF PAHS.....	9
2.1 Overview	9
2.2 The factors affecting the extent of PAH degradation	10
2.2.1 Denuders	11
2.2.2 Spiked samples passive degradation	12
2.2.3 Passive degradation.....	12
2.2.4 Ozone concentration	12
2.2.5 Relative humidity.....	13
2.2.6 Size distribution and sources of particles.....	13
2.2.7 Filter type.....	13
2.2.8 Sampling duration	13
2.2.9 Summary.....	14
3 ADDRESSING THE DEGRADATION ISSUE.....	15
4 THE EFFECT OF DEGRADATION ON THE ANNUAL AVERAGE PAH CONCENTRATION IN THE UK: A NOVEL ASSESSMENT METHOD	17
4.1 Introduction	17
4.2 Parallel sampling at Harwell and Scunthorpe Town	17
4.3 Results of parallel sampling	19
5 MODELLING OF REACTION KINETICS	21
6 EFFECT ON THE ANNUAL AVERAGE VALUE	24
6.1 Extrapolation of degradation results to the whole of the UK.....	25
7 CONCLUSIONS.....	30
8 RECOMMENDATIONS.....	31
8.1 General Recommendations.....	31
8.2 Suggested future field trial.....	31
9 REFERENCES.....	33

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are formed primarily as products of incomplete combustion [1]. These organic pollutants which are formed of two or more fused benzene rings are ubiquitous in the environment and often have allergenic, mutagenic and carcinogenic effects. As the number of benzene rings comprising the PAH increases their vapour pressure decreases and so does their partition in ambient air between the vapour and particulate phase, such that two-ringed naphthalene is found almost exclusively in the vapour phase whereas five-ringed benzo[a]pyrene (BaP) is almost exclusively particulate-bound.

The prevalence of PAHs in ambient air and their toxicity has prompted the production of national and international legislation to regulate both emissions of these compounds from industrial facilities and limit the allowable concentration of these compounds in ambient air. In the UK both the European Commission's Fourth Air Quality Daughter Directive (4th DD) [2] and the UK Air Quality Objectives [3] apply. The 4th DD requires monitoring of BaP in the PM₁₀ particulate phase of ambient air at a number of sampling locations defined by the size of population centres and measured concentrations. BaP has been chosen as a 'marker' PAH compound for the PAH suite because: (a) it exhibits the highest toxic equivalent value (equal to concentration multiplied by toxicity per unit concentration) of common PAHs in air, and (b) the concentrations of PAHs are usually very highly correlated as they all originate from combustion processes, and hence if one is measured the concentration of others may be inferred. A target value for BaP of 1 ng/m³, expressed as an annual mean concentration at each monitoring station is to be achieved and maintained by the end of 2012. In addition, a set of six other PAHs also require measurement at a subset of locations in order to ensure that the relative PAH ratios remain constant (Figure 1). The UK objective for BaP, published prior to the target value decided upon by the 4th DD, is 0.25 ng/m³, expressed as an annual mean concentration at each monitoring station, which was to be achieved by the end of 2010.

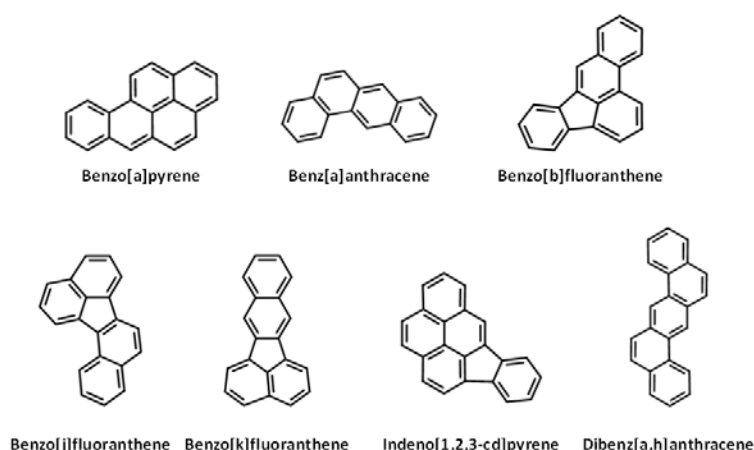


Figure 1. Structure of the seven PAHs specified by the Fourth Daughter Directive

Sampling of PAHs in the PM₁₀ phase takes place using samplers with size selective heads according to the European reference method EN 12341 [4]. The PM₁₀ is collected on quartz filters which are later analysed for PAH content. Furthermore the 4th DD specifies that daily sampling periods be used for PAH collection. In practice, the daily filter changing requirement means that samplers with automatic changeover facilities are essential, since it would be impractical to visit the station every day. Automatic changeover also allows filter to be exchanged at midnight ensuring that each sample covers an entire calendar day.

In the UK the requirements of the 4th DD with respect to PAHs are delivered by the UK PAH Monitoring Network which is currently operated by the National Physical Laboratory on behalf of Defra [5]. In 2011 the UK PAH Network comprised 31 monitoring stations (twenty in England, four in Scotland, four in Wales and three in Northern Ireland). In addition, co-located deposition samplers at two background stations (Harwell and Auchencorth Moss) measure PAHs in deposition in support of the requirements of the 4th DD, and two modified PM₁₀ samplers also collect vapour phase PAHs onto polyurethane foam at these same sites.

Every fortnight a local site operator attends each monitoring station to exchange the filter cartridges. The sampled filters are then returned to NPL where they undergo analysis for PAH content according to the European Reference method EN15549 [6].

2 DEGRADATION OF PAHS

2.1 Overview

It has been recognised for 25 years that PAHs are able to undergo on-filter reactions with oxidising gases in ambient air producing a sampling artefact [7]. PAHs in the vapour phase react predominantly with hydroxyl radicals. Particulate-bound PAHs are much more likely to undergo heterogeneous reactions such as photo-oxidation and reactions with ozone and nitrogen dioxide. In ambient air these reactions proceed relatively slowly because of the relatively low concentrations of the reactants. However once this particulate matter is trapped on a filter in much higher concentrations with air containing oxidising gases being constantly drawn through it these reactions can proceed much faster. The products of these oxidation reactions are oxy-PAHs, nitro-PAHs, nitro-oxy-PAH and hydroxy-PAHs. A proposed scheme for the ozonolysis of surface adsorbed pyrene to form hydroxypyrene is shown in Figure 2.

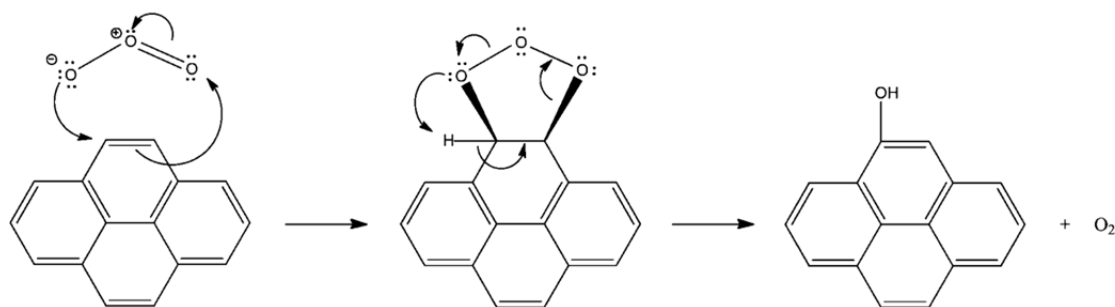


Figure 2. A proposed scheme for the ozonolysis of surface adsorbed pyrene to form hydroxypyrene (reproduced from [8]).

The implications of this for ambient air monitoring are that on-filter degradation of PAHs may result in lower PAH concentrations being measured than are actually present. This is qualitatively recognised by the 4th DD which requires daily sampling for PAH, whereas this is only recommended for metals in PM₁₀. However, despite knowledge of this degradation phenomenon it is not clear how much BaP is likely to be lost during sampling, and moreover, what the effect of this might be on the annual average. The effect of on-filter degradation may be clearly observed by examining annual average concentrations measured on the UK PAH Network either side of 2007, the year during which the sampler type changed from one taking 14 day-long samples to samplers that were compliant with the requirement of the 4th DD and took 24 hour samples. This is shown in Table 1. Even considering the increase in BaP emissions over this period from 3.0 tonnes to 3.3 tonnes [9] there was an average increase in concentration levels of 180 %. Despite taking into account any other mitigating factors, such as unusual meteorological conditions, it is clear that against a background of falling ambient concentrations in the years preceding 2006 [10] that sampling time has had a large effect on measured concentrations in the past. It may be assumed that this is as a result of the additional BaP degradation induced by the longer sampling times.

Monitoring Station	2004-2006 average (14 day samples) / ng m ⁻³	2008-2010 average (24 hour samples) / ng m ⁻³
Birmingham Tyburn	0.14	0.31
Bolsover	0.19	0.37
Cardiff Lakeside	0.079	0.24
Edinburgh St Leonards	0.041	0.13
Hazelrigg	0.054	0.090
High Muffles	0.033	0.10
Hove	0.090	0.24
Kinlochleven	0.28	0.28
Leeds Millshaw	0.15	0.39
Lisburn Dunmurry	0.56	1.02
Liverpool Speke	0.096	0.26
London Brent	0.11	0.20
London Crystal Palace	0.16	0.26
Newcastle Centre	0.080	0.19
Scunthorpe Town	0.61	2.07
Stoke Ferry	0.087	0.14

Table 1. Average annual BaP concentrations measured on the UK PAH Network in 2004 to 2006 and in 2008 to 2010, at stations with continuous operation over this period. As indicated the 2004-2006 data was based on 14 day samples whilst the 2008-2010 data was based on 24 hour samples.

The effect of the change in sampling times on measured concentrations is not as easily observable in UK wide statistics. This is because during the period when the Digitel samplers replaced Andersen samplers there was also a significant increase in the number of UK PAH Network monitoring stations as well as changes to existing locations. Only 16 of the current 31 UK PAH Network monitoring stations (the ones in Table 1) were measuring in 2004.

2.2 The factors affecting the extent of PAH degradation

The extent of PAH degradation has been shown to depend on a number of interacting factors such as the: PAH under consideration, concentration of gaseous oxidant, exposure to light, flow rate through the filter, temperature, relative humidity, composition of the particle to which the PAH is bound, extent of surface coverage of PAH on the particles and particle size. A complex relationship with exposure time is also apparent with the collected PAH sometimes decaying to zero and sometimes reaching a non-zero plateau – presumably because some PAH 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 artefacts of anywhere between 0 and 100 % have been observed in the laboratory [11]. In the field, degradation rates are even more complex to assess because of changes in temperature, relative humidity and oxidant concentration during sampling. 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 or operates with an ozone denuder on the sampler head. Again a range of BaP losses have been observed. These studies are not always entirely satisfactory because of the synthetic nature of either the introduction, or removal, of ozone from the system. Furthermore it is not clear that other gaseous atmospheric oxidants such as nitrogen dioxide and hydroxyl radicals are properly considered by these studies. The seminal review in this area (examining degradation by ozone) [11] and other investigations of the heterogeneous reactions of BaP with ozone [12,13,14,15] have summarised the experimental evidence in the literature in a number of areas and these are detailed below.

2.2.1 Denuders

Most denuders used in PAH degradation studies use ionic liquids, activated carbon or manganese dioxide as the active material to remove oxidising gases. These materials are usually present on the surface of a honeycomb support placed within the sampler head prior to the collecting filter. The most significant experiments performed with ozone denuders have not been in the laboratory but in the field collecting real samples where one sampler has been fitted with a denuder and one has not. The overwhelming majority of the literature points to losses of PAHs from those samplers not fitted with a denuder. However, the overall range of losses observed has been from 10 to 90 %, although most values were in the narrower range of between 20 and 55 % [16]. Interestingly, when several particulate phase PAHs were compared, BaP consistently showed the highest losses [17]. The efficiency of the denuders used is clearly also a key factor in these experiments. These have been found to range from 100 % to 60 % [17]. This is often because the number of denuder tubes within the device is insufficient for the sampler flow rate. More worryingly some efficiencies have been observed to drop off over time, by up to 10 % in one day. The denuders used for ozone removal seem to have no effect on the mass of PM₁₀ collected, and according to some literature also have the effect of removing more than 90 % of other reactive gases such as NO₂ [18].

The most significant study from a UK perspective was the portion of the CEN TC264 WG21 field trial conducted at Harwell [19]. This consisted of 24 one day samples taken between November 2004 and January 2005 using co-located samplers and analysed for BaP. The trial used 2 Andersen samplers (A), 2 Digitel samplers without ozone denuders (P-) and 2 Digitel samplers with ozone denuders (P+).

During this period there were only 15 daily samples where values were produced for both P+ and P- samplers. The average of the individual P+/P- ratios over these samples was 1.25. However, many of these samples represented very low ambient concentrations: 8 samples were less than 0.1 ng/m³ and 11 were less than 0.25 ng/m³, and the largest P+/P- ratios were observed for these lowest concentrations. Hence the ratio of the average P+ concentration over all 15 samples to the average P- concentration over all 15 samples is only 1.08, as a result of the dominance of the higher

concentration samples. (As we will demonstrate later, this value is very similar to our assessment of the underestimate of the BaP using historical UK PAH Network data).

As an additional point of interest, Andersen samples produced concentrations 9 % higher than Partisol samples for the 8 samples where values for each are available. However, the average concentrations for these samples was only 0.13 ng/m³ and so these differences, at the 0.01 ng/m³ level, are not significant with respect to the measurement uncertainty.

2.2.2 Spiked samples passive degradation

BaP artificially loaded onto filters generally showed greater losses than comparable experiments with real samples [20]. In some cases a day long exposure to ambient ozone concentrations resulted in losses of up to 75 %. As noted later this may be a function of the fact that the degradation characteristics of particulate-bound PAHs are significantly different to those that are not particulate bound. The faster degradation rates observed for spiked samples are thought to be a function of the easy accessibility of artificially added BaP to oxidant gases, as compared to particulate-bound BaP which may not be on the surface of the particle. Furthermore the surface coverage of PAHs on particulate matter seems to have a very large influence on the degradation observed, with higher surface coverage resulting in faster degradation rates – a further indication that BaP not on the surface of the particulate matter decays at a slower rate.

2.2.3 Passive degradation

Degradation under passive exposure conditions has also been reported to be high, with losses of up to 80 % observed [21]. However, this is thought to be related to the unrealistically high concentration of ozone and BaP used. Under realistic conditions, degradation owing to passive exposure is unlikely to be a factor. This is probably due to the relatively short time periods which the filters are left in the sampler after automatic changeover, and the fact that the filters are stacked tightly against each other, restricting exposure to ozone. Together with passive degradation we may also consider briefly the effects of particulate residence time in the atmosphere. The further away the sampler from the source of emission, the longer the time the PAHs have to be degraded by similar passive mechanisms to those discussed above, and also by exposure to sunlight, prior to sampling. Regardless of the extent of degradation by this mechanism, which we would expect to be small for passive ozone degradation but larger for exposure to sunlight, it is not a factor we need to consider in regard to compliance with the EC Directive since, as the legislation refers to as-sampled air.

2.2.4 Ozone concentration

There is general agreement in the literature that there is a positive correlation between ozone concentration and the extent of BaP degradation. Early literature studies pointed to linear relationships between these two quantities from which it might be possible to estimate BaP losses by measuring ozone concentrations [20,22]. However, as the literature has proliferated in this area, the simplicity of this relationship has been called into question and there is now more general agreement that degradation rate is actually controlled by a number of complex environmental conditions which

may change from sample to sample and across different stations and pollution climates. Hence whilst the general correlation between extent of degradation and ozone concentration is still valid the relationship is considerably more complex than previously thought [23].

2.2.5 Relative humidity

Despite relatively little literature in this area there appears to be consensus that the degradation rate of BaP increases with increasing humidity [24,25]. However, the main effect of humidity is to compromise the performance of ozone scrubbers used during the sampling of PM₁₀. In this way, increases in relative humidity would have a similar effect in increasing the degradation rate of collected BaP since increased concentrations of ozone would pass through the denuder.

2.2.6 Size distribution and sources of particles

Studies have suggested that BaP degradation may be particularly rapid on diesel and soot particles, most likely owing to their large specific surface area and high adsorptive capacity [26]. Losses of up to 87 % have been observed for filters loaded with diesel particulates exposed to ozone – although the concentration of ozone used in this study was one order of magnitude higher than would usually be expected. Conversely, and importantly, other studies have shown that BaP bound to salt particles do not undergo any degradation at all in the presence of ozone [15].

2.2.7 Filter type

Relatively little literature exists examining the effect of filter type on degradation kinetics, but the two identifiable studies failed to find any evidence of an effect of the use of different materials on degradation [27,28]. This is perhaps not surprising since filter materials are usually chosen to be relatively inert and therefore would not be expected to play a significant part in altering the rate of reaction. Furthermore, the filter material is quickly covered by the first layer of particulate matter collected after which it cannot have any direct effect on degradation reactions.

2.2.8 Sampling duration

Evidence from spiked samples indicates that degradation of BaP occurs within the first few hours of sampling. However, in a real situation where the BaP is entirely particulate-bound and additional particulate matter is continually being added to the filter, the situation is clearly more complicated. Whilst some studies noticed degradation after two hours sampling [17] other studies recorded significant losses only when samples were exposed for longer than 24 hours (a 14 % loss of BaP was observed). Literature studies which compared paired sampling periods of 24 and 72 hr and 1 and 14 days did not see a significant influence on BaP loss [18,29]. The variation observed may well be associated with the complex influence of other environmental parameters during each experiment and in addition any variation in the performance of the ozone denuders used in the studies. Furthermore, it is clear from the data presented in Table 1 that sampling time has been indirectly observed to have an effect on measured concentrations on the UK PAH Network. Indeed, variation of sampling time represents an interesting mechanism by which to explore the kinetics of the degradation process, and is one that is expanded on below.

2.2.9 Summary

Of the sixteen studies that have specifically examined the on-filter degradation of BaP by ozone, all but two have concluded that loss of BaP during sampling is an artefact which cannot be ignored. When considering only field sampling campaigns carried out under real conditions, mean BaP losses were typically in the range 20 to 50 %. However, the degradation reactions have been shown to be extremely complex and depend on a number of other factors that are likely to vary between different samples and across different locations. What is clear from the literature is that the most relevant studies in the field are of very limited duration: 3 to 15 days for most campaigns; hence these results may not be extrapolated to whole seasons, let alone to the whole year. None of these studies quantify the effect of ozone degradation on the annual mean, and more work would be required to assess this. In particular, there have been no reports of a field trial using samplers with and without ozone denuders that covered a whole calendar year.

3 ADDRESSING THE DEGRADATION ISSUE

In recent years the ozone degradation problem has been considered at length by the European Committee for Standardisation working group that is responsible for drafting standard methods for the measurement of PAHs in ambient air – CEN TC264 WG21 [30]. One solution proposed by the working group has been to use an ozone denuder within the particulate sampler, between the size selective head and the collecting filter [31]. Such denuders are generally manufactured from manganese dioxide or activated charcoal, and have a honeycomb structure. The density of the channels within the honeycomb needs to be sufficient to allow the ozone to be efficiently removed by sideways diffusion perpendicular to the direction in which the air is actively drawn through the denuder. These devices have been shown to be highly efficient in removing ozone under controlled conditions, and do not remove significant quantities of particulate matter from the gas stream. However, problems still exist with these denuders and most importantly their efficiency is affected by humidity. As the humidity rises the denuders remove less ozone from the air passing through and furthermore this effect appears to be cumulative such that the denuders do not recover after exposure to humidity, presumably because of adsorption of water to the surface of the denuder. As a consequence, the denuders have to be ‘recharged’ regularly by heating them in an oven – possibly after as little as three days sampling – making operation of a network using them considerably more expensive. In addition the denuders themselves are expensive because they are not currently being mass-produced and they are also very fragile introducing additional operational issues with transportation to and from the monitoring stations.

Because of the lack of validation of the current denuder technology and the expense and complexity of implementation for air quality monitoring networks, WG21 have decided not to make the ozone denuder a normative requirement at the current time. Furthermore, because the denuder interacts with the sampling system as defined by EN12341 it is possible that such an arrangement would be required to provide a formal equivalence demonstration for the sampling of PM₁₀ mass – even if only as a variation on a theme [32]. In addition, these denuders generally only remove ozone such that any remaining degradation caused by nitrogen dioxide or other gaseous oxidants may not be eliminated.

An alternative approach to the PAH degradation issue is to measure the oxy- and nitro-PAHs which are the products of degradation. Indeed some of these oxy- and nitro-PAH analogues exhibit higher toxicities than regular PAHs– for example 6-nitrochrysene and 1,6-dinitropyrene are known carcinogens with toxicity equivalents 10 times higher than BaP [33,34]. Unfortunately this is not a trivial task since each PAH may produce multiple oxy- and nitro-derivatives which will necessarily occur at lower concentrations in the collected particulate matter than the parent PAH. In addition, oxy-PAHs may be produced directly from combustion so it would be challenging to deconvolute contributions from direct emission and degradation. Measurement of these compounds in air is not currently undertaken routinely by laboratories operating air quality networks, and as such these are currently considered as specialist research-based measurements. Moreover, until a thorough assessment of the current concentrations of all these compounds in air is performed it will not be clear which, if any, might be suitable marker compounds for air quality monitoring. CEN TC264

WG21 are currently drafting a report on oxy- and nitro-PAH in ambient air which should provide additional information on the topic.

A further option to avoid ozone degradation would be to use automatic instruments analysing the collected particulate matter using thermal desorption gas chromatography-mass spectrometry that could use very short sampling periods, possibly of one hour or less. This would eliminate most degradation problems. Whilst producing very promising results [35] the thermal desorption technique does not currently conform to the reference method and has not been shown to be equivalent and so is not considered a viable alternative in the short term.

4 THE EFFECT OF DEGRADATION ON THE ANNUAL AVERAGE PAH CONCENTRATION IN THE UK: A NOVEL ASSESSMENT METHOD

4.1 Introduction

Discussions at CEN TC264 WG21 have speculated that the effect on the annual average concentrations of PAHs may be less than that observed during individual studies in the literature since BaP concentrations are generally highest in the winter when ozone concentrations, and therefore degradation rates, are lowest, and lowest in the summer, when ozone and degradation rates may be highest. Since average BaP concentrations are dominated by values measured during the winter months this may point to reduced effects of degradation on the annual average. Similarly, judicious timing of filter changeover just prior to dawn allows the sampling to access the longest periods of low ozone overnight prior to sample changeover, thereby minimising the effects of degradation. For air quality network purposes however, it is convenient to change filters at midnight in order to ensure that each filter covers a calendar day. No studies in the literature have examined either of these topics. Below we describe a novel assessment of the effect of degradation by all oxidising compounds of the annual average B[a]P value.

4.2 Parallel sampling at Harwell and Scunthorpe Town

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 PM₁₀, EN15549, made it clear that one-day sampling periods were mandatory in order to produce data in support of the implementation of this legislation. This was 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 when a new set of samplers was purchased and rolled out across the UK network in 2007 and 2008. 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. 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 analysis of the data produced during this period of parallel running 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.



Figure 3. Andersen GPS-1 (left) and Digitel DHA-80 samplers at Auchencorth Moss, similar to the samplers used at Scunthorpe Town and Harwell.

Air samples were taken at Scunthorpe Town (2007-2010) and Harwell (2008-2010) using co-located Andersen GPS-1 and Digitel DHA-80 samplers (Figure 3 shows similar samplers side-by-side at Auchencorth Moss), sampling for a period of 336 hours (14 days) and 24 hours between filter changes, respectively, at calibrated flow rates of nominally $5.4 \text{ m}^3 \text{ h}^{-1}$ and $30 \text{ m}^3 \text{ h}^{-1}$, respectively, such that the difference in the total sampled volumes over the different periods was a factor of 2.52. 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 hour 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 (although the vast majority of particulate phase PAHs exist in the PM_{10} phase and below). After being sampled in the Digitel sampler, filters were changed automatically and stored in a 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) was assumed 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 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. Results were reported as a mass of BaP collected every quarter (i.e. over approximately 91 Digitel sampling periods and 6 to 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.

4.3 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 2 and 3.

Time Period	BaP Conc. (14d samples) / ng m ⁻³	BaP Conc. (24h samples) / ng m ⁻³	Ratio 24h samples / 14d samples	Average ozone / nmol/mol (b)	Average Ambient Temp. / °C (d)	Calculated value of k' / h ⁻¹
2007 Q1	0.84	1.0	1.19	55.3	6.4	0.0012
2007 Q2	0.4	1.3	3.25	68.0	12.3	0.011
2007 Q3	1.1	0.63	0.57 (a)	47.6	14.6	-
2007 Q4	1.2	1.7	1.42	40.8	7.5	0.0024
2008 Q1	0.4	1.8	4.50	60.0	5.7	0.016
2008 Q2	2.8	8.0	2.86	80.5	11.3	0.0090
2008 Q3	0.95	2.0	2.11	48.9	15.3	0.0057
2008 Q4	0.89	0.78	0.88	40.0	6.5	-
2009 Q1	0.89	1.4	1.57	50.1	4.6	0.0032
2009 Q2	1.7	3.4	2.00	78.4	11.9	0.0052
2009 Q3	0.27	1.0	3.70	47.9 (c)	15.3	0.013
2009 Q4	0.5	1.2	2.40	45.5	7.1	0.0070
2010 Q1	0.93	1.7	1.79	57.6	2.8	0.0043
2010 Q2	0.7	1.2	1.78	73.1	10.7	0.0042
2010 Q3	0.18	0.67	3.72	56.4	15.1	0.013
2010 Q4	0.94	1.2	1.29	53.3	4.7	0.0017
2007 Annual	0.81	1.33	1.64	54.7	8.7	0.0035
2008 Annual	1.26	3.15	2.50	57.4	9.7	0.0075
2009 Annual	0.84	1.75	2.08	55.5	9.8	0.0056
2010 Annual	0.69	1.20	1.74	60.1	8.3	0.0040

Table 2. Average quarterly (Q) and annual BaP concentrations for the two different sampling times and other parameters measured at Scunthorpe Town. (a) Extreme outlying value not included in subsequent analysis. (b) Taken from High Muffles monitoring station approximately 50 miles away. (c) Value from Ladybower monitoring station, approximately 50 miles away, because of no data available being from High Muffles for that quarter. (d) Taken from Bradford meteorological station, approximately 50 miles away. The annual average values are averages of the data from the four relevant quarters above. The values of k' , calculated using equation (5) (below), are also given.

Period	BaP Conc. (336h samples) / ng m ⁻³	BaP Conc. (24h samples) / ng m ⁻³	Ratio 24h samples / 336h samples	Average ozone / nmol/mo l (a)	Average Ambient Temp. / °C (b)	Calculated value of k' / h ⁻¹
2008 Q1	0.042	0.13	3.10	53.9	6.9	0.010
2008 Q2	0.011	0.027	2.45	62.7	11.4	0.0072
2008 Q3	0.019	0.032	1.68	45.8	16.3	0.0037
2008 Q4	0.11	0.16	1.45	37.7	7.2	0.0026
2009 Q1	0.082	0.17	2.07	44.6	5.3	0.0056
2009 Q2	0.020	0.031	1.55	61.6	13.5	0.0031
2009 Q3	0.012	0.028	2.33	46.1	17.1	0.0067
2009 Q4	0.079	0.11	1.39	45.1	8.6	0.0023
2010 Q1	0.11	0.18	1.66	50.4	4.4	0.0036
2010 Q2	0.030	0.043	1.42	68.4	13.3	0.0024
2010 Q3	0.0055	0.012	2.18	52.6	16.8	0.0061
2010 Q4	0.14	0.20	1.41	38.5	5.6	0.0024
2008 Annual	0.046	0.087	1.92	50.0	10.4	0.0049
2009 Annual	0.048	0.085	1.76	49.4	11.1	0.0041
2010 Annual	0.071	0.108	1.52	52.5	10.0	0.0029

Table 3. Average quarterly and annual BaP concentrations for the two different sampling times and other parameters measured at Harwell. (a) Data taken from co-located ozone monitoring station. (b) Taken from the Oxford meteorological station approximately 10 miles away. The annual average values are averages of the data from the four relevant quarters above. The values of k' , calculated using equation (5) (below), are also given.

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) [5]. 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.

5 MODELLING OF REACTION KINETICS

It is not practical to take into account all the variations in atmospheric parameters that are occurring during sampling when modelling the kinetics of the degradation reaction, save for the consideration that they affect each sampler equally. Therefore we consider a simplified average model which assumes all parameters, including gaseous oxidant concentration and BaP collection rate, are constant (and equal to their average during the period considered). Previous studies have shown that the degradation of BaP by ozone may be described by a pseudo-first order rate equation [13,14,15], thus:

$$\frac{d[\text{BaP}]}{dt} = -k'[\text{BaP}] \quad (1)$$

where $[\text{BaP}]$ is the mass of BaP on the filter, and k' is the pseudo-first order rate constant such that $k' = k[\text{O}_3]$, where k is the second order rate constant and $[\text{O}_3]$ is the concentration of ozone (analogous equations could be used for any other gaseous oxidants). This model has been shown to work well for artefacts loaded with a known quantity of BaP subsequently exposed to ozone, to which no further BaP is added [12]. For the collection of real samples onto air filters the situation is more complex. This is because whilst the collected BaP continues to decay at a rate k' , new BaP from the air is continually collected onto the filter at a rate h which itself subsequently decays. Hence we may approximate the real sampling situation as:

$$\frac{d[\text{BaP}]}{dt} = -k'[\text{BaP}] + h \quad (2)$$

Recognising that $[\text{BaP}] = 0$ when $t=0$, because no BaP is present on the filter at the start of sampling, integration of this expression between $t=0$ and $t=t$ yields:

$$[\text{BaP}]_t = \frac{h(1 - e^{-k't})}{k'} \quad (3)$$

where $[\text{BaP}]_t$ is the mass of un-decayed BaP remaining on the filter at time t . Since, the total mass of BaP deposited onto the filter after time t is given by $[\text{BaP}]_{t,\text{tot}} = ht$, we may define the fraction of the mass of un-decayed BaP remaining on the filter after time t , to the total mass deposited on the filter after time t , as $f_t = [\text{BaP}]_t / [\text{BaP}]_{t,\text{tot}}$, such that:

$$f_t = \frac{1 - e^{-k't}}{k't} \quad (4)$$

It is interesting to note from equation (4) that the parameter f_t is independent of the collection rate of BaP onto the filter under the assumption of constant collection rate and first order decay kinetics. Figure 4 plots f_t at a function of t for various values of k' .

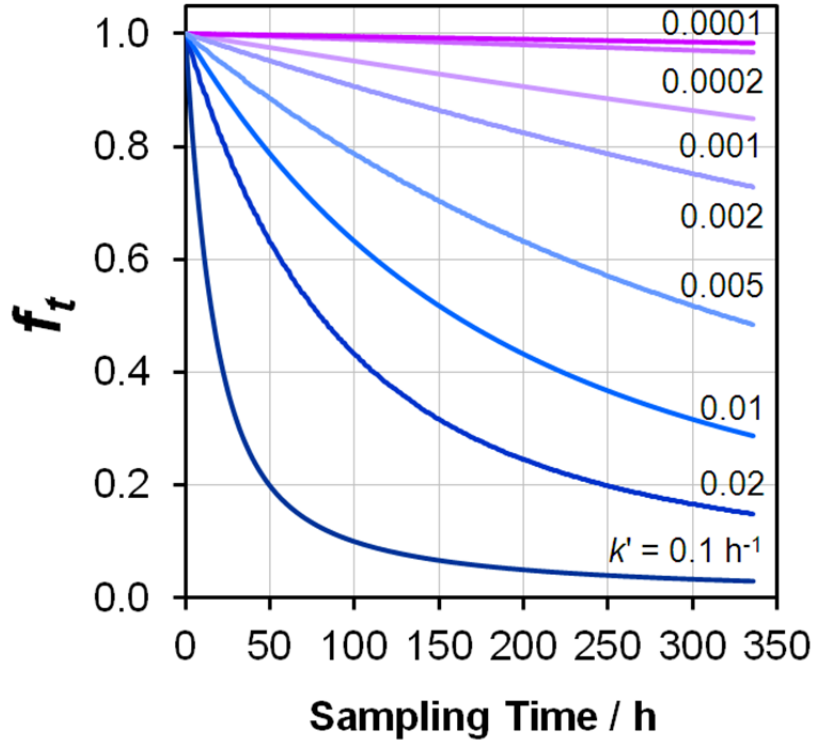


Figure 4. Plot of f_t as a function of sampling time for various values of k' (in units of h^{-1}) as indicated on the plot, from equation (4).

The absolute value of f_t is unknown because there is no way of knowing or directly measuring k' under these real field conditions. However, the ratio of the measured values of BaP using different sampling times (from Table 1) yields f_a/f_b : the value of f_t after a sampling period a compared to that after a sampling period b , where $a < b$. Substituting expressions for f_a and f_b into equation (4) and taking a ratio of these expressions we obtain:

$$\frac{f_a}{f_b} = \frac{b(1 - e^{-ak'})}{a(1 - e^{-bk'})} \quad (5)$$

This relationship may then be solved to give k' using numerical methods such as the Generalised Reduced Gradient algorithm (as implemented in Microsoft Excel's 'Solver' function and used in this paper). The values of k' obtained using equation (5) for the quarterly samples, and their respective annual averages, considered in this study are given in Tables 2 and 3. The average values determined at Harwell and Scunthorpe Town monitoring stations using this process were 0.0040 and 0.0052 h^{-1}

respectively. These values are in general at least an order of magnitude slower than most experimentally obtained results in the laboratory [12,14,15], probably as a result of the continual deposition of new PM onto the filters acting to cover existing BaP which would otherwise be subject to degradation processes. These reduced reactions rates are consistent with observations in the literature where they have been taken to indicate that BaP is efficiently oxidised on the surface of particles on time scales of minutes to hours while physical shielding is expected to prevent a rapid BaP degradation in the bulk of particles and on the surface of particles subsequently covered by newly sampled PM [17]. The value of k' determined may then be used to provide absolute values for f_a and f_b from equation (4) which gives the proportion of BaP lost during sampling periods a and b . The value of f_a may then be compared against f_0 – a theoretical sampling period of zero time when no sample degradation will occur – whose value is by definition 1. This yields the additional mass of BaP expected on the filter in the absence of degradation, as $f_0/f_a = 1/f_a$.

For the 24 hour and 336 hour sampling periods considered in this study the relationship between f_{24}/f_{336} and $1/f_{24}$ is shown in Figure 5. It is noticeable that the sensitivity of $1/f_{24}$ to changes in the f_{24}/f_{336} ratio is relatively low. This provides added confidence in the final output of the analysis since, as discussed below, even quite large spreads in the experimentally determined f_{24}/f_{336} ratio will have a relatively minor effect on variations in the underestimation of the annual average concentration based on the $1/f_{24}$ metric.

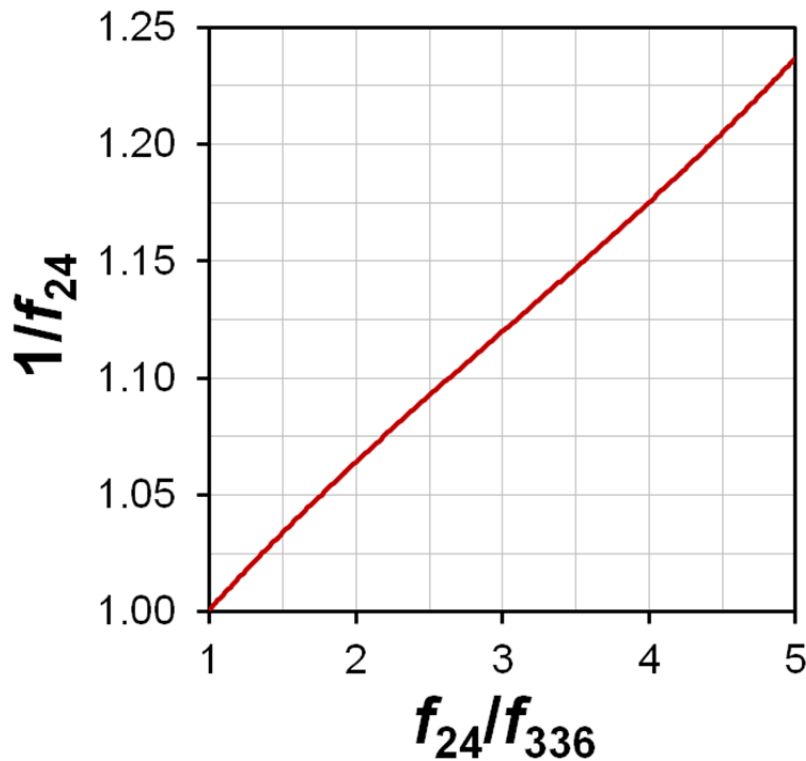


Figure 5. The relationship between f_{24}/f_{336} and $1/f_{24}$, from equation (5).

6 EFFECT ON THE ANNUAL AVERAGE VALUE

We have considered the average observed f_{24}/f_{336} value at both monitoring stations. This indicates that at Scunthorpe approximately 6 % of the BaP collected was lost when using a one day sampling period, and 53 % was lost when using a fourteen day sampling period. At Harwell approximately 5 % of the BaP was lost when using a one day sampling period, and 45 % was lost when using a fourteen day sampling period. The range of $1/f_{24}$ values at Scunthorpe Town and Harwell was calculated using the mean f_{24}/f_{336} value at each station and double the standard error on the mean of this value (to approximate an expanded uncertainty at the 95 % confidence interval) as input parameter into equation (4). The results indicate that in the absence of any degradation the actual annual average values at Scunthorpe and at Harwell would be (6.4 ± 2.3) % and (4.9 ± 1.4) % higher than those values recorded using the one day sampling period mandated by the European reference method. It is noteworthy that in relative terms these underestimations show no significant difference despite them relating to locations where the annual average mass concentrations differ by more than an order of magnitude, and where there are also some differences in the average meteorological and ambient pollutant parameters measured. The average predicted BaP degradation profiles as a function of sampling time at both stations are shown in Figure 6. In absolute terms this underestimation would correspond to an increase in annual average mass concentrations at Scunthorpe Town from 1.86 ng m^{-3} to 1.98 ng m^{-3} and at Harwell from 0.093 ng m^{-3} to 0.098 ng m^{-3} .

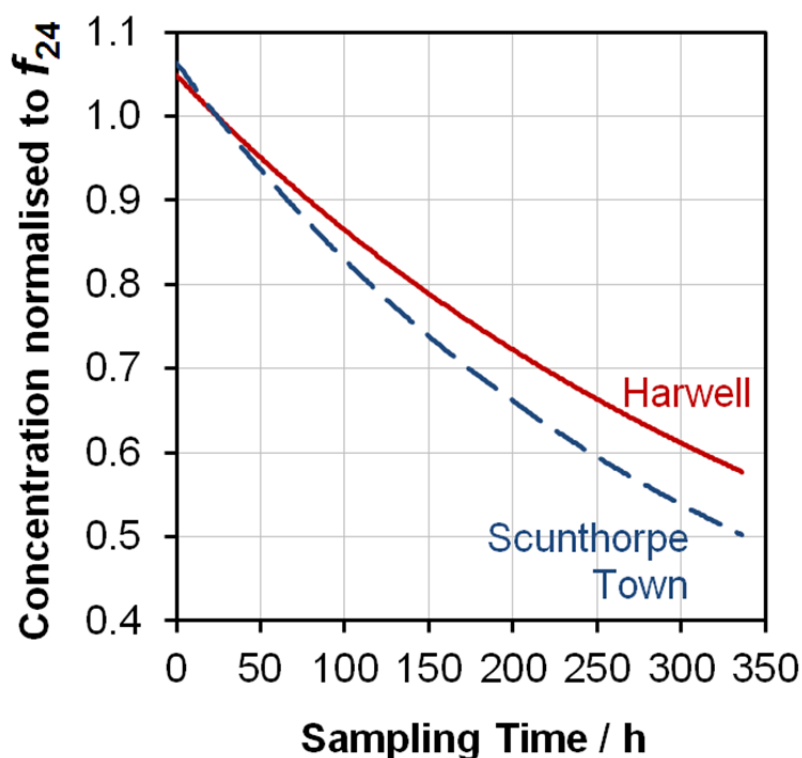


Figure 6. Average BaP degradation profiles calculated for the monitoring stations considered in this study, with the measured concentration normalised to the value of f_{24} at each station.

The observed relative increase in the BaP concentration in the absence of BaP degradation as compared with use of the European reference method one day sampling period are approximately equal to one tenth of the maximum allowable expanded uncertainty of the measurement (*i.e.* 50 %). It is proposed that this contribution from BaP degradation during sampling could be added to the uncertainty budget calculated for these measurements – although, in most cases the effect on the overall uncertainty will be small. Alternatively the degradation measured during such experiments could be used to provide a bias correction factor to amend the measured annual average value. Furthermore, with such small losses predicted for a one day sampling period, it is doubtful whether the extensive use of ozone scrubbers across national air quality networks would be cost effective. However, similar measurements made in other European locations may have resulted in much higher BaP degradations as a result of the significantly lower ozone concentrations in the UK as compared to the rest of continental Europe [36].

The technique presented is proposed as a novel solution to assess BaP degradation under real conditions based only on changes in the sampling period, which by definition takes proper account of all ambient parameters. Any future similar studies should try and make the sampling regimes as similar as possible, and include as many different sampling periods as possible. However, because sampling times by definition will vary during such a comparison, there will always be a trade-off between equalising either the flow rate or the sample particulate loading during the measurement, since both parameters may affect the degradation observed.

6.1 Extrapolation of degradation results to the whole of the UK

Having determined the extent of degradation at the two test stations it may be possible to extrapolate these results across the whole of the UK, though such an extrapolation will have a large uncertainty associated with it. This is because there are only two data points from which to extrapolate across a large range, and the BaP degradation process is a complex process depending on many variables, for most of which we have no data. However, the uncertainty in these extrapolations can only be represented by the data available, and we should be aware this may be an underestimate.

The two relevant parameters we have data for are PAH concentrations and ozone amount fractions. Using the data derived at Harwell and Scunthorpe Town, and its uncertainty, an extrapolation of the expected increase in the annual average BaP concentration in the absence of degradation has been performed across the concentration range. This is displayed in Figure 7. An extrapolation over a range of concentrations is considered valid since we know from laboratory studies that degradation has been shown to depend on BaP concentration and as fractional surface coverage of BaP on the particulate matter to which it is attached.

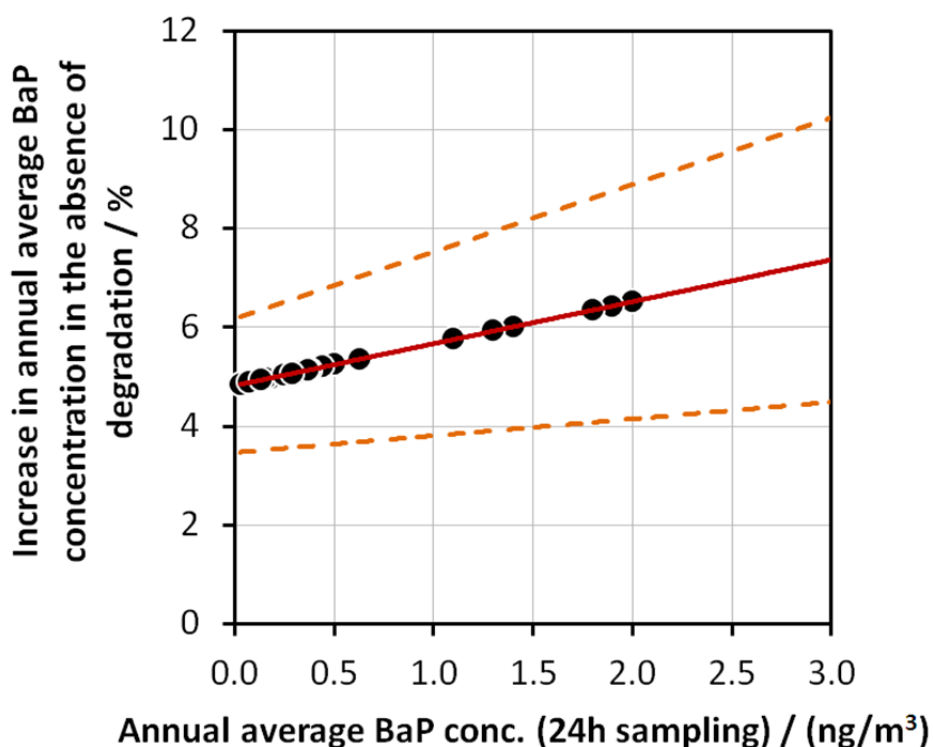


Figure 7. Predicted increase in the annual average BaP concentration in the absence of degradation as a function of the annual average BaP concentration measured using 24 hour sampling. The red line indicates the calculated relationship, with the orange dashed lines indicating the uncertainty in this value at the 95 % confidence level. The black circles represent the annual average BaP concentrations measured on the UK PAH Monitoring Network in 2010.

The increase in the annual average BaP concentration in the absence of degradation show a small sensitivity to the measured concentration using 24h sampling. This reflects the relatively similar $1/f_{24}$ values obtained at the two stations where parallel sampling was carried out. An examination of the effect on the BaP concentration measured on the UK PAH Monitoring Network in 2010 shows expected increases of between 4.8 and 6.5 % in the absence of degradation, with stations measuring higher concentrations showing the larger changes. The compliance status of the stations on the UK PAH Network using the highest values predicted from Figure 7 (at the upper 95 % confidence interval) is shown in Figure 8.

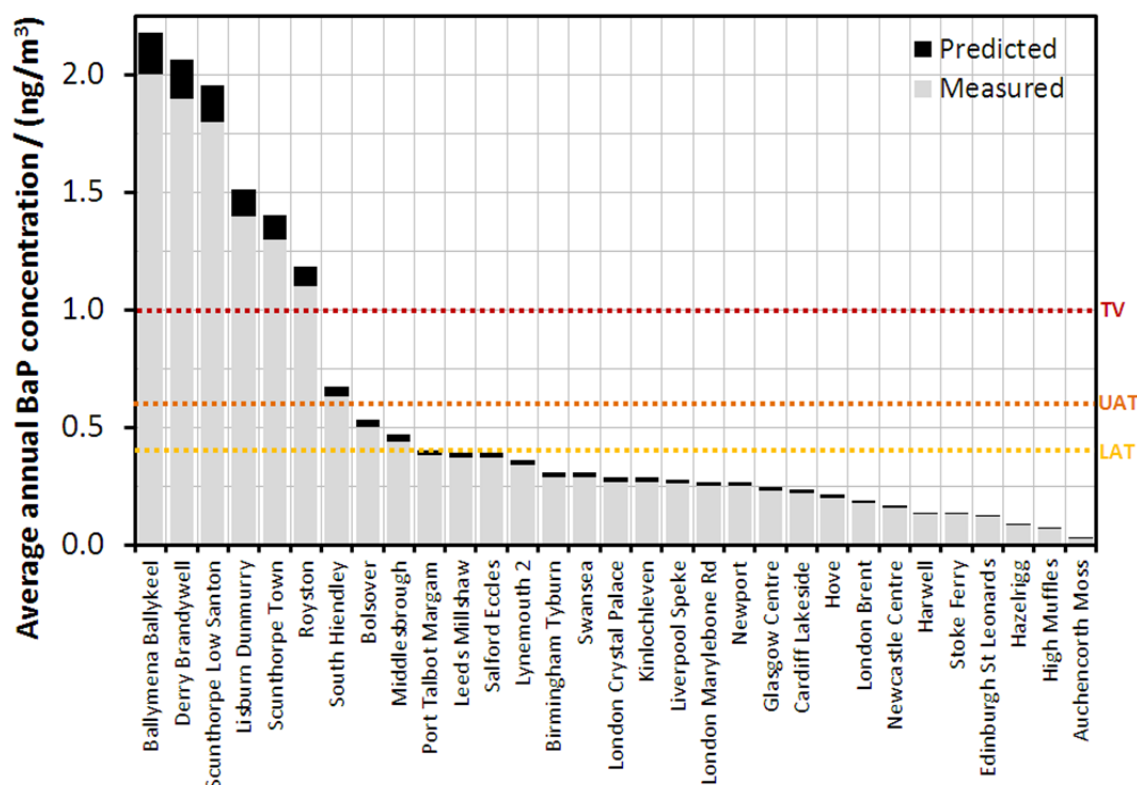


Figure 8. The annual average BaP concentration measured on the UK PAH Monitoring Network in 2010 (grey bars) and the additional predicted BaP which would have been measured in the absence of degradation (black bars). The target value (TV), upper assessment threshold (UAT) and lower assessment threshold (LAT) are indicated.

The likelihood of any additional exceedences of target values or assessment thresholds as a result of the additional predicted BaP which would have been measured in the absence of degradation are of course a function of the original measurement values. However, for the values measured in 2010 examination of Figure 8 demonstrates that adding on BaP lost due to degradation would have resulted in only one additional exceedence of a target value or assessment threshold. The concentration at Port Talbot Margam increased from 0.38 to 0.41 ng/m³ thereby exceeding the lower assessment threshold. It is likely that there would be one or two of these instances in every year – although this depends strongly on the distribution of concentration values obtained.

The effect of ozone on measured BaP concentrations has also been extrapolated over a range of ozone amount fractions. Because of the significantly seasonal variation in ozone (higher in summer, lower in winter) and BaP (generally higher in winter and lower in summer, except near to industrial emissions sources) the data in Tables 2 and 3 have been examined on a quarterly basis. The result of this analysis is shown in Figure 9.

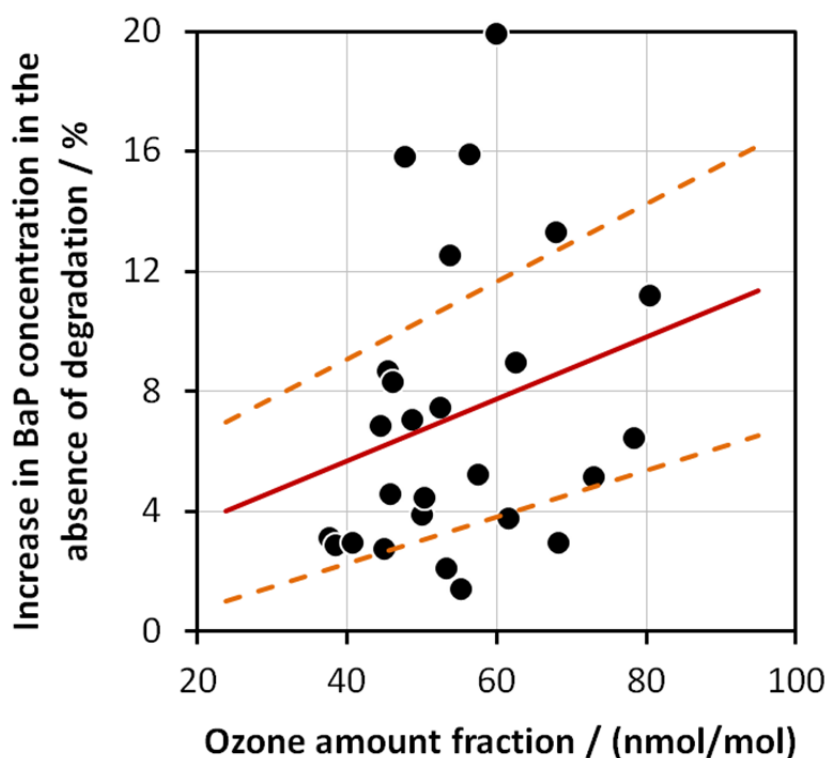


Figure 9. Predicted increase in the BaP concentration in the absence of degradation as a function of the ozone amount fraction measured during the sampling period. The red line indicates the linear best fit relationship through this data (albeit with a low correlation coefficient), with the orange dashed lines indicating the uncertainty in this fit at the 95 % confidence level – calculated by considering the maximum uncertainties from the measurements of BaP in the field.

The best fit relationship in Figure 9 is very weak – a correlation coefficient $R^2 < 0.1$. This is most probably an indication that ozone is one of only a number of factors affecting BaP degradation during sampling. However, there is some limited evidence from this plot that degradation may increase with ozone concentration. Over the range of annual average ozone amount fractions we might expect to observe with the UK (20-30 nmol/mol at urban traffic locations up to 70-80 nmol/mol at rural background locations [37]) we observe a range of increases in BaP concentrations from approximately 4 to 10 % – slightly higher than the values seen in Figure 7. However, the median observed value in Figure 9 is 5.8 % - very similar to the mid-range extrapolated values in Figure 7 – not entirely surprising since these extrapolations are based on the same data set.

When considering the implications of Figure 9 we should remember that the monitoring stations with the highest PAH concentrations are likely to experience mid to low level ozone concentrations [37]. Specifically these are in Northern Ireland - urban background locations with annual averages in the range 40-50 nmol/mol and urban industrial locations in South Wales, the Midlands and North East England again experiencing averages in the range 40-50 nmol/mol and maybe on occasions 50-60 nmol/mol. Under these circumstances the range of BaP increases observed would match those predicted in Figure 7. At the rural background station where annual average ozone may be in the

range 70-80 nmol/mol the PAH concentrations are extremely low and the predicted increase in BaP in the absence of degradation is large in relative terms but small in absolute concentrations.

7 CONCLUSIONS

It is clear from the published literature [11] that on-filter degradation by oxidising gases imposes a significant artefact during the measurement of BaP in ambient air. This is particularly important since this may mean that a negative systematic bias is imposed on measurements made in support of European legislation. Evidence from the change in sampling duration on the UK PAH network has supported the observation that the requirement in the 4th DD for a maximum of one day sampling times may have reduced any bias observed.

A review of the literature has shown that the rate of BaP degradation is dependent on the interaction of a number of parameters, not solely the concentration of ozone. Whilst studies of on-filter BaP in the field have been more limited, it is clear that the situation is even more complex because of the introduction of a number of confounding and variable environmental parameters. In addition, given the very short timescales of any field trials carried out it is not possible to extrapolate from the current literature what the effect of on-filter degradation on the annual average might be. Furthermore, the technologies that have been proposed to solve the degradation problem, such as ozone denuders, are not currently robust enough and have not been sufficiently validated for routine use in the field. In addition, the use of these would increase considerably the expense for operating air quality networks for PAH measurement.

Data collected from the UK PAH Network during a period of parallel running of the old and new UK PAH Network samplers at Harwell and Scunthorpe Town which used different sampling times have been reanalysed. This exercise has not only provided an estimate of the BaP which is likely to have been lost by the use of fourteen day sampling periods as opposed to the now mandated one day sampling period – at least half of the BaP collected – but also provided an estimate of the BaP still lost as a result of the one day sampling period. This was estimated to be between 5 and 6 % of the annual average at both locations – despite the measured concentrations at these locations being substantially different. It has been demonstrated that this value is low enough that even if an extrapolated correction was applied to all measurement concentrations during 2010 no additional monitoring stations would have exceeded the target value of 1 ng/m³.

Despite the useful output of this initial study there may be value in undertaking a year-long field trial at a UK Network station, using parallel samplers taking one day samples, one fitted with the ozone denuder technology and one without, to assess practically the effect of degradation on the annual average. Both samplers should be operated in the usual UK PAH Monitoring Network manner. Such a trial would provide the first field data on the effect on the BaP annual mean concentration of the use of ozone scrubbers.

8 RECOMMENDATIONS

8.1 General Recommendations

The following recommendations are made, based on the work conducted in this report:

- It is likely that the percentage of BaP lost over a year's sampling in the UK is small, perhaps between 5 and 7 %. It is recommended that the uncertainty of the BaP concentration measurement should incorporate this contribution. Even with this expansion to the uncertainty budget we would not envisage any measurement failing to meet the 50 % data quality objective for maximum allowable expanded uncertainty specified in the 4th DD. In future, if all Member States had performed such assessments, it would be better to correct BaP annual average to account for BaP degradation.
- It is recommended that the method outlined in this study be raised with AQUILA. The benefits of this will be two-fold. First, it will show that the UK have been proactive in addressing this issue and will provide evidence to show the extent of degradation in the UK pollution climate. Second, it will support the opinion within CEN TC264 WG21 that fitting ozone denuders to PAH samplers across Europe is unnecessary and expensive, not least because the denuder may not be fully effective.

8.2 Suggested future field trial

Despite the useful output of this initial study it is recommended that Defra undertake a year-long field trial at a UK Network station, using parallel samplers taking one day samples; one fitted with the ozone denuder technology and one without. Data from such a study would enable the assessment of the effect of degradation on the annual average when employing ozone denuders in the field.

We would recommend that the field trial was performed at an existing UK PAH Network station recording high BaP levels. Scunthorpe Town would be a suitable station and has the added advantage of being the location of the previous parallel study between the Andersen and Digitel samplers. Because of this there is already room within a secure cage to site an additional Digitel sampler. Furthermore it will be possible to compare directly the results of any field trial with the sampling time study performed in this report as this was also conducted at Scunthorpe Town.

The field trial should involve sampling over a whole year using two co-located Digitel samplers – one without any ozone denuder (the current UK PAH Network sampler) and one with an ozone denuder fitted. Defra already own the retrofitted Digitel head required to house the ozone denuder and several manganese oxide ozone denuder cartridges. An ozone analyser of the same type used on the current automatic urban and rural network (AURN) should be installed at the station and should be maintained and serviced to the same quality standards as other AURN site for the period of the comparison. This will help to determine whether variation in ambient ozone concentration is a

significant factor in observed degradation. In addition, simple meteorological parameters such as temperature and relative humidity will also be collected.

Daily samples should be taken with each sampler as per the existing reference method. The local site operator should visit site every week to change the denuder cartridge, and change the filters every other week. Sampled filters will be sent back to NPL where they will be analysed using the reference method in the same way all other UK PAH Network samplers are treated. In addition the ozone denuder cartridges will be sent to NPL where they will be recharged by being heated at 150 °C for a 24 hour period, after which they will be ready for use on site again.

The output of the study will be a report providing monthly average values measured with and without ozone scrubbing, and an assessment of whether there is any correlation between the extent of degradation and any of the other parameters measured. The effect of ozone degradation on the annual average BaP concentration will also be properly assessed for the first time.

This trial would not only provide additional practical evidence to support the findings of this report but will also provide a greater understanding of the strengths and limitations of the use of ozone denuders in the field.

If the scope of the study was to be expanded to include some laboratory work it could also encompass an assessment of the effectiveness of the ozone denuder in removing ozone after different periods of sampling in the field – something that has previously not been determined. Further laboratory based work could be aimed at determining the efficiency of heating systems placed within the head of the Digitel in decreasing the humidity of the sampled ambient air and quantifying the increase in lifetime of the denuder cartridges that this causes.

9 REFERENCES

1. European Commission, Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH): Position Paper. Office for Official Publications of the European Communities, Luxembourg, 2001.
2. Directive 2004/107/EC of the European Parliament and the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, Official Journal of the European Union, 2005, L23, 3-16.
3. The Air Quality Strategy for England, Scotland, Wales and Northern Ireland, Department for Environment, Food and Rural Affairs in partnership with the Scottish Executive, Welsh Assembly Government and Department of the Environment Northern Ireland, Cm 7169 NIA 61/06-07, HMSO, 2007.
4. European Committee for Standardisation, EN12341:1999 Air quality - Determination of the PM10 fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods, CEN, Brussels, 1999.
5. A. S. Brown, D. M. Butterfield, R. J. C. Brown, P. Hughey, K. J. Whiteside, S. L. Goddard, M. Williams, Annual Report for 2010 on the UK PAH Monitoring and Analysis Network, NPL Report AS 62, August 2011, NPL, Teddington.
6. European Committee for Standardisation, EN15549:2008 Air quality - Standard method for the measurement of the concentration of Benzo[a]pyrene in ambient air, CEN Brussels, 2008.
7. J. N. Pitts Jr., K. A. Van Cauwenberghe, D. Grosjean, J. P. Schmid, D. R. Fritz, W. L. Belser Jr., G. B. Knudson, P. M. Hynds, Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. *Science*, 1978, 202, 515–519.
8. S. N. Chu, S. Sands, M. R. Tomasik, Ozone Oxidation of Surface-Adsorbed Polycyclic Aromatic Hydrocarbons: Role of PAH-Surface Interaction, *J. Am. Chem. Soc.*, 2010, 132, 15968-15975
9. UK National Atmospheric Emissions Inventory, <http://naei.defra.gov.uk/>.
10. UK-AIR: Air Information Resource, <http://uk-air.defra.gov.uk/>.
11. E. Menichini, On-filter degradation of particle-bound benzo[a]pyrene by ozone during air sampling: A review of the experimental evidence of an artefact, *Chemosphere*, 2009, 77, 1275-1284.
12. M. Cazaunau, K. Le Menach, H. Budzinski, E. Villenave, Atmospheric Heterogeneous Reactions of Benzo[a]pyrene, *Z. Phys. Chem.*, 2010, 224, 1151-1170.
13. T. F. Kahan, N.-O.A. Kwamena, D. J. Donaldson, Heterogeneous kinetics of polycyclic aromatic hydrocarbons on organic films, *Atmos. Env.* 2006, 40, 3448-3459.
14. E. Perraudin, H. Budzinski, E. Villenave, Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles, *J. Atmos. Chem.*, 2007, 56, 57-82.
15. N.-O. A. Kwamena, J. A. Thornton, J. P. D. Abbatt, Kinetics of surface bound benzo[a]pyrene and ozone on solid organic and salt aerosols, *J. Phys. Chem. A*, 2004, 108, 11626-11634.
16. H. Creutzmacher, K. Huber, Ozon-Querempfindlichkeit bei der Immissionsmessung von schwebstaubakkumuliertem Benzo[a]pyren (Interference of ozone with measurements of particle bound benzo[a]pyrene in ambient air). *Gefahrst. Reinhalt. Luft*, 2002, 62, 319–324.
17. M. Tsapakis, E. G. Stephanou, Collection of gas and particle semi-volatile organic compounds: use of an oxidant denuder to minimize polycyclic aromatic hydrocarbons degradation during high-volume air sampling. *Atmos. Environ.*, 2003, 37, 4935–4944.
18. C. Schauer, R. Niessner, U. Pöschl, Polycyclic aromatic hydrocarbons in urban air particulate matter: decadal and seasonal trends, chemical degradation, and sampling artifacts, *Environ. Sci. Technol.*, 2003, 37, 2861–2868.
19. European Committee for Standardisation, CEN/TC 264/WG 21 Final Report Project BC/CEN/01/34.1.3 Field Validation Experiments, February 2006, CEN, Brussels.

20. R. W. Coutant, L. Brown, J. C. Chuang, R. M. Riggin, R. G. Lewis, Phase distribution and artefact formation in ambient air sampling for polynuclear aromatic hydrocarbons, *Atmos. Environ.*, 1988, 22, 403–409.
21. J. N. Pitts Jr., D. M. Lokensgard, P. S. Ripley, K. A. Van Cauwenberghe, L. Van Vaeck, S. D. Shaffer, A. J. Thill, W. L. Belser Jr., “Atmospheric” epoxidation of benzo[a]pyrene by ozone: formation of the metabolite benzo[a]pyrene-4, 5-oxide, *Science*, 1980, 210, 1347–1349.
22. J. Peters, B. Seifert, Losses of benzo[a]pyrene under the conditions of high volume sampling. *Atmos. Environ.*, 1980, 14, 117–119.
23. M. Goriaux, B. Jourdain, B. Temime, J. L. Besombes, N. Marchand, A. Albinet, E. Leoz-Garziandia, H. Wortham, Field comparison of particulate PAH measurements using a low-flow denuder device and conventional sampling systems. *Environ. Sci. Technol.*, 2006, 40, 6398–6404.
24. U. Pöschl, Formation and decomposition of hazardous chemical components contained in atmospheric aerosol particle, *J. Aerosol Med.* 2002, 15, 203–212.
25. U. Pöschl, T. Letzel, C. Schauer, R. Niessner, Interaction of ozone and vapour with spark discharge soot aerosol particles coated with benzo[a]pyrene: O₃ and H₂O adsorption, benzo[a]pyrene degradation, and atmospheric implications. *J. Phys. Chem. A*, 2001, 105, 4029–4041.
26. L. Van Vaeck, K. Van Cauwenberghe, Conversion of polycyclic aromatic hydrocarbons on diesel particulate matter upon exposure to ppm levels of ozone. *Atmos. Environ.* 1984, 18, 323–328.
27. D. Grosjean, K. Fung, J. Harrison, Interactions of polycyclic aromatic hydrocarbons with atmospheric pollutants. *Environ. Sci. Technol.*, 1983, 17, 673–679.
28. J. N. Pitts Jr., H. R. Paur, B. Zielinska, J. Arey, A. M. Winer, T. Ramdahl, V. Mejia, Factors influencing reactivity of polycyclic aromatic hydrocarbons adsorbed on filters and ambient POM with ozone. *Chemosphere*, 1986, 15, 675–685.
29. E. G. Sanderson, J. P. Farant, J.P., Atmospheric size distribution of PAHs: evidence of a high-volume sampling artefact. *Environ. Sci. Technol.*, 2005, 39, 7631–7637.
30. European Committee for Standardisation, Technical Committee 264 Air Quality, <http://www.cen.eu/CEN/Sectors/TechnicalCommitteesWorkshops/CENTechnicalCommittees/Pages/TCStruc.aspx?param=6245&title=CEN%2FTC>
31. H. Creutzmacher, M. Cipolloni F. Löffler, The use of an ozone scrubber to eliminate the ozone interference on sampling of benzo[a]pyrene: effects and new developments, *Gefahrst. Reinhalt. Luft*, 2005, 65, 437-442.
32. Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, Report by an EC Working Group on Guidance for the Demonstration of Equivalence, European Commission, January 2010.
33. S. Lundstedt, P. A. White, C. L. Lemieux, Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites, *Ambio*, 2007, 36, 475-485.
34. World Health Organisation, Environmental Health Criteria 229: Nitrogenated Polycyclic Aromatic Hydrocarbons, WHO, Geneva, 2003.
35. L. van Drooge, I. Nikolova, P. P. Ballesta, Thermal desorption gas chromatography-mass spectrometry as an enhanced method for the quantification of polycyclic aromatic hydrocarbons from ambient air particulate matter, *J. Chromatography A*, 2009, 1216, 4030-4035
36. European Environmental Agency. Air Quality in Europe – 2011 Report; Publications Office of the European Union: Luxembourg, 2011.
37. Air Quality Expert Group, Ozone in the United Kingdom, Defra Publication, London, 2009.