

UNIVERSITY OF BIRMINGHAM

Research at Birmingham

Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases

Delgado Saborit, Juana Maria; Alam, Mohammed; Godri Pollitt, Krystal J.; Stark, Christopher; Harrison, Roy

DOI:

[10.1016/j.atmosenv.2013.05.080](https://doi.org/10.1016/j.atmosenv.2013.05.080)

License:

Creative Commons: Attribution (CC BY)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Delgado Saborit, JM, Alam, M, Godri Pollitt, KJ, Stark, C & Harrison, R 2013, 'Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases', *Atmospheric Environment*, vol. 77, pp. 974-982. <https://doi.org/10.1016/j.atmosenv.2013.05.080>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Eligibility for repository : checked 01/04/2014

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

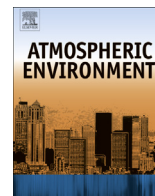
Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.



Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases[☆]



Juana Maria Delgado-Saborit^a, Mohammed S. Alam^a, Krystal J. Godri Pollitt^{a,b,1}, Christopher Stark^a, Roy M. Harrison^{a,*}

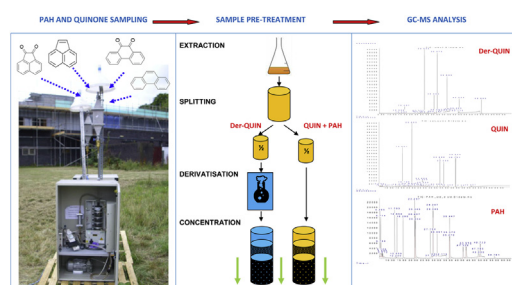
^aDivision of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

^bMRC-HPA Centre for Environment and Health, School of Biomedical & Health Sciences, King's College London 150 Stamford Street, London SE1 9NH, United Kingdom

HIGHLIGHTS

- An existing method was extended and validated to analyse larger number of quinones.
- Concentration of 17 PAH and 15 quinones have been determined.
- PAH and quinones were analysed from the same substrate air samples.
- Four quinone compounds are measured in the atmosphere for the first time.
- Particle–vapour relationships for quinones are assessed.
- New data for quinones in SRM are reported.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form
28 May 2013
Accepted 31 May 2013

Keywords:
Polycyclic aromatic hydrocarbons
Quinones
Oxygenated polycyclic aromatic hydrocarbons
OPAH
Partitioning
Standard reference material

ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are often measured in studies of atmospheric chemistry or health effects of air pollution, due to their known human carcinogenicity. In recent years, PAH quinone derivatives have also become a focus of interest, primarily because they can contribute to oxidative stress. This work reports concentrations of 17 PAH and 15 quinones measured in air samples collected at a trafficked roadside. Data are presented for four compounds not previously reported in ambient air: 2-methyl-1,4-naphthoquinone, 2,6-di-tert-butyl-1,4-benzoquinone, methyl-1,4-benzoquinone and 2,3-dimethylanthraquinone, and a large vapour phase component is measured, not analysed in most earlier studies. Analyses are reported also for SRM 1649a and 1649b, including many compounds (8 for SRM 1649a and 12 for SRM 1649b) for which concentrations have not previously been reported. This work assesses the vapour/particle phase distribution of PAHs and quinones in relation to their molecular weight, vapour pressure, polarity and Henry's Law constant, finding that both molecular weight and vapour pressure (which are correlated) are good predictors of the partitioning.

© 2013 The Authors. Published by Elsevier Ltd. All rights reserved.

[☆] This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author. Also at: Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, Jeddah 21589, Saudi Arabia. Tel.: +44 121 414 3494; fax: +44 121 414 3709.

E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

¹ Currently at: University of Toronto, Department of Chemical Engineering, Toronto, Canada.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of environmental pollutants containing two or more fused benzene rings. They exist ubiquitously in the environment and are formed through high-temperature incomplete combustion and pyrolysis of fossil fuels and other organic materials (Harrison et al., 1996). PAHs have been extensively studied since the mid 1970s owing to their potential mutagenic and carcinogenic properties (Giger and Blumer, 1974). Recently, increasing interest has been paid to oxygenated derivatives of PAHs, particularly quinones (Walgraeve et al., 2010), which contain two carbonyl groups in a fully conjugated dione structure. These oxygenated derivatives are reported as being more toxic than their parent PAHs, as they do not require enzymatic activation, therefore acting as direct mutagens and/or carcinogens (Pedersen et al., 2004, 2005; Walgraeve et al., 2010). Recently, the IARC has classified anthraquinone as a group 2B chemical, signifying its possible carcinogenicity to humans (Grosse et al., 2011). It has also been shown that exposure to 1,2-naphthaquinone induces mitochondrial production of H₂O₂, which mediates the expression of inflammatory genes (Cheng et al., 2012). There is sufficient evidence therefore, that quinones are toxic to both humans and the environment, despite the fact that the mechanisms underlying the toxicology are complex and far from fully understood.

Both gaseous and particulate matter (PM) associated quinones, like PAHs, may be released into the atmosphere through incomplete combustion processes in diesel (Layshock et al., 2010) and gasoline engines (Valavanidis et al., 2006; Jakober et al., 2007), incomplete combustion of waste (Sidhu et al., 2005) and biomass burning (Iinuma et al., 2007). Gaseous and heterogeneous atmospheric processing of PAHs can yield further quinone products via photochemistry and reactions with atmospheric oxidants (OH, NO₃ and O₃) or through biological transformation (Sasaki et al., 1997; Atkinson and Arey, 2007). However, quantitative data are limited on the relative importance of primary and secondary sources of quinones. Owing to their toxicity and persistence in the atmosphere, oxygenated-PAH (OPAH, hydroxylated, ketones and quinones) compounds are becoming key components in the analysis of PM (Wingfors et al., 2011).

Numerous studies have quantified PAH compounds in ambient gas and particle phase samples (Chang et al., 2006; Poster et al., 2006), while few studies have measured quinone concentrations (Walgraeve et al., 2010 and refs within). However, very few studies have characterised simultaneously both quinones and parent PAH compounds in the environment. For example, Wang et al. (2011) in a toxicity study of PM_{2.5} during the Beijing Olympic Games, utilised gas chromatography-mass spectrometry (GC-MS) to detect parent PAHs, while quantifying oxygenated-PAH (3 of which were quinones) and nitrated-PAH (NPAH) compounds using electron capture negative ion chemical ionisation (NICI) (Wang et al., 2011). Albinet and co-workers measured in Marseille and in a French Alpine area 15 PAH compounds using HPLC with fluorescence/UV detection, while determining simultaneously 17 NPAH and 9 OPAH compounds - 2 of them quinones - using GC-MS with NICI (Albinet et al., 2006, 2007a, 2007b, 2008a, 2008b). More recently, Wingfors et al. (2011) characterised the size distribution of aerosol and particle-bound PAH, OPAH, and n-alkanes in urban environments. They developed their method to measure 18 OPAHs (10 of which were quinones) using GC-MS, and found that only 6 of their target quinones met the detection criteria, exemplifying the difficulty in successfully detecting quinones (Wingfors et al., 2011).

In order to improve the sensitivity for the detection of quinones, some studies have exploited derivatisation techniques. Cho et al. (2004) converted four quinones to their diacetyl derivatives using zinc and acetyl acetate, prior to detection by Gas Chromatography

Electron Impact Mass Spectrometry (GC-EIMS) (Cho et al., 2004). This derivatisation significantly improved the limits of detection, where their repeatability and reproducibility varied between 2 and 22%. Chung et al. (2006) expanded this methodology to measure 12 quinones, and reported that not all quinones could be converted to their diacetyl derivatives (Chung et al., 2006). Jakober et al. (2007) measured the emissions of 9 quinones from gasoline and diesel motor vehicles, using O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine derivatisation in conjunction with LC-MS (Jakober et al., 2006) and GC-MS (Jakober et al., 2007).

In this study we have applied and extended the methodology of Cho et al. (2004) to include 7 derivatised quinones in one fraction of the sample extract, while measuring 17 PAHs and 8 underivatised quinones in the second fraction. The modified methodology was validated by an analysis of urban dust (SRM 1649a and SRM 1649b) which resulted in excellent agreement with certified concentrations for PAHs and quinones (where available), and we report the first quantified values of 9 further quinones in certified urban dust samples. The methodology was also applied to provide the largest comprehensive measurement dataset for quinones and parent PAH compounds in both vapour and particulate phases from single denuder and filter collection media samples, from a trafficked site in Birmingham, UK.

2. Materials and methods

2.1. List of PAHs and quinones analysed

Seventeen PAHs and fifteen quinones (see Table S1) were analysed in vapour and particulate phase airborne samples. The sample extract was divided into two fractions in order to increase the sensitivity to quinones. The first portion was analysed for 17 PAHs and 8 quinones whilst the second was derivatised to analyse 7 quinones. Analysed PAHs are listed in Table S1, and the quinones, with abbreviations in Table 1.

2.2. Atmospheric sampling

Five days of samples were collected within the campus of the University of Birmingham at a trafficked site located 2 m away from the A38 road, which has an average annual daily flow of traffic of 28,000 vehicles. Five consecutive 24-h samples were taken from 11 to 15 January 2010.

The sampling train consisted of a denuder collecting the vapour phase upstream of a MOUDI collecting the particulate phase fraction, with a polyurethane foam (PUF) located at the end of the sampling train. The denuder was designed by Delgado-Saborit et al. (submitted for publication) and consists of a set of parallel metal plates coated with XAD-4 (Gundel et al., 1995) to trap the PAH and quinone gas-phase, with an experimental efficiency ranging 85–97%. The MOUDI 110R (MSP Copley Scientific, UK) collected size fractionated particle-phase PAH and quinones samples onto PTFE (polypropylene backed) 47 mm filters (Whatman, Maidstone, UK). The aerosol was collected in the size fractions 1.8–10 μm and <1.8 μm for 24 h at 30 L min⁻¹. Concentrations of particulate phase compounds reported in this work refer to the total sum of compounds on both filters and the PUF, which represents condensed phase material volatilising within the MOUDI. Field blanks were collected as a quality control/quality assurance measure (See Table S2), but no further correction was applied to the analysed concentrations.

2.3. Analytical determination

Details of the extraction and analysis using GC-MS are given in the Supplementary Information (SI).

Table 1
Experimental concentrations (mg kg⁻¹) of quinones and standard deviation in brackets in SRM 1649a and 1649b measured in this study and in the literature.

	SRM 1649a						SRM 1649b			
	This study	Cho et al. (2004) ^a	Mirivel et al. (2010) ^b	Albinet et al. (2006) ^b	Fernandez and Bayona (1992) ^b	Durant et al. (1998) ^b	This study	Layshock et al. (2010) ^b	Wingfors et al. (2011) ^b	NIST SRM 1649b
Number of replicates	N = 4	N = 12	N = 3	N = 6	N = 13 injections	N = 13 injections	N = 4	N = 3	N = 3	
Analytical instrument	GC–EI–MS	GC–EI–MS	UPLC–APCI–TOFMS	GC–NICI–MS	GC–EI–MS	GC–EI–MS	GC–EI–MS	GC–EI–MS	GC–EI–MS	
Derivatised quinones										
Benzoquinone (BQ)	0.87 (0.29)						0.79 (0.19)			
2,6-Di-tert-butyl-1,4-benzoquinone (2,6DTBQ)	0.12 (0.03)						0.09 (0.03)			
1,2-Naphthoquinone (1,2NQ)	0.24 (0.03)	0.19 (0.026)					0.34 (0.09)			
1,4-Naphthoquinone (1,4NQ)	0.29 (0.06)	0.24 (0.054)					0.39 (0.15)			
2-Methyl-1,4-naphthoquinone (2MNQ)	0.37 (0.17)						0.34 (0.12)			
Phenanthrenequinone (PQ)	1.22 (0.26)	1.18 (0.13)	1.133 (0.152)				1.51 (0.12)			
Anthracenequinone (AQ)	1.81 (0.24)	2.03 (0.192)	2.357 (0.183)	2.238 (0.363)	0.22 (0.04)	2.7 (0.12)	1.78 (0.22)	1.60 (0.11)	1.1 (0.02)	1.8
Benzo(a)anthracene-7,12-dione (7,12BaAQ)	2.44 (0.37)		3.442 (0.322)	8.459 (0.797)	7.465 (1.1)	2.4 (0.25)	3.37 (0.20)	2.20 (0.15)	8.9 (0.4)	3.6
Underivatised quinones										
Methyl-1,4-benzoquinone (M1,4BQ)	3.26 (0.32)						3.44 (0.24)			
Acenaphthenequinone (AceQ)	2.87 (0.46)						3.01 (0.14)			
2-Methylanthraquinone (2MAQ)	0.21 (0.11)		0.986 (0.125)				0.37 (0.14)			
2,3-Dimethylanthraquinone (2,3DMAQ)	0.14 (0.05)						0.14 (0.04)			
5,12-Naphthacenequinone (5,12NAQ)	2.50 (0.13)					1.8 (0.11)	2.81 (0.08)	3.16 (0.13)		
Benzo(a)pyrene-6,12-dione (6,12BaP)	0.39 (0.14)						0.50 (0.20)			
Benzo(a)pyrene-1,6-dione (1,6BaP)	0.88 (0.08)						0.79 (0.10)			

^a Quinones were derivatised.

^b Quinones were not derivatised.

While half of the sample extract was blown down and analysed directly, a second half of the sample extract containing deuterated internal standards was derivatised following a modified version of the method described by Cho et al. (2004). Briefly, the extract was transferred to a conical glass test tube and concentrated under nitrogen to almost dryness. Acetic anhydride (200 μL) and zinc (100 mg) were added into the tube and were mixed using a vortex. The mixture was heated at 80 °C with a heating block for 15 min, mixing on a vortex every 5 min. Addition of acetic anhydride and zinc was repeated (equivalent amounts) and then followed by a second 15 min heating routine with vortex mixing at 5 min intervals. The samples were then cooled to room temperature. Pentane (3 mL) and 0.5 mL of water were added. The pentane layer was transferred into a second set of silanised conical glass test tubes. The sample was further concentrated under nitrogen to 100 μL . This concentrated sample volume was transferred to a 250 μL GC insert, further evaporated under nitrogen to dryness and reconstituted in 25 μL of recovery standard (i.e. p-terphenyl- d_{14}). Derivatised samples were stored in the GC inserter vials in a freezer at -20 °C until analysis.

3. Results and discussion

3.1. Analytical validation

Since the analytical methodology extends the previous Cho et al. (2004) method to include 15 quinones, and combines the extraction and analysis to analyse PAHs and quinones from the same substrate, the quality of the results of the modified methodology was validated by characterising: a) the effect of derivatisation on the additional quinones of our interest (Section 3.1.1 and Fig. S1); b) the recovery levels (Section 3.1.2 and Tables S3 and S4); c) the limits of detection (Section 3.1.2, Supplementary Information Section S1.4 and Table S2); d) the precision and accuracy (Section 3.1.2, Supplementary Information Section S1.5 and Table S3). The method was also validated characterising the concentrations of PAHs and quinones in two NIST standard reference materials as described in detail below (Section 3.1.3 and Table S5).

3.1.1. Derivatisation vs. non-derivatisation of quinones

Derivatisation is a procedure that has proven very useful in enhancing the sensitivity of analytical techniques to detect and quantify analytes (Rosenfeld, 2003; Cho et al., 2004; Chung et al., 2006). Cho et al. (2004) proposed a method to analyse four quinones, namely 1,2NQ, 1,4NQ, PQ and AQ, based on their diacetyl derivatives using zinc and acetyl acetate (Cho et al., 2004). Chung et al. (2006) extended this methodology to measure a larger number of quinones, but found that not all quinones investigated were fully converted to their diacetyl derivatives and did not show lower detection limits (Chung et al., 2006). A subset of the quinones were consequently measured underderivatised including AceQ, 2MAQ, 2,3DMAQ, 5,12NAQ, 7,12BaAQ and AQ. BQ and 2,6DTBQ, but were found to achieve improved sensitivities when acetylated (Chung et al., 2006).

In the current work, we have evaluated the measurement of 15 quinones in ambient samples, utilising the derivatisation methodology of Cho et al. (2004), and expanding the species measured by Chung et al. (2006) to include 2MNQ; M1,4BQ; 6,12BaP and 1,6BaP. The ions corresponding to the underderivatised and derivatised quinones were measured to assess the extent of derivatisation. All quinones were successfully derivatised at high concentrations (1000 $\text{pg } \mu\text{L}^{-1}$ –14,000 $\text{pg } \mu\text{L}^{-1}$), with the exception of 5,12NAQ and AceQ, in agreement with Chung et al. (2006) (see Fig. S1). At lower concentrations (0–1500 $\text{pg } \mu\text{L}^{-1}$, those expected in ambient air),

however, M1,4BQ; 2MAQ; 2,3DMAQ; 6,12BaP and 1,6BaP did not fully derivatise, consistent with results of Chung et al. (2006). 1,2NQ, 1,4NQ, and PQ were found to fully derivatise in agreement with previous studies (Cho et al., 2004; Eiguren-Fernandez et al., 2008) and we report the derivatisation of 2MNQ for the first time. These quinones were therefore analysed in their diacetylated form. Furthermore, it was found that in contrast to Chung et al. (2006), 7,12BaAQ and AQ were successfully derivatised, which might be attributed to the fact that our method involves two additions of the acetylation reagent and the catalyst, whilst the Chung et al. (2006) methodology only repeated the addition of the catalyst, but not the acetylation agent.

3.1.2. Analytical performance

To assess the recovery efficiency of the three analytical methods (i.e. derivatised quinones, underderivatised quinones and PAHs), 5 replicate PTFE filters, PUFs and denuders were spiked with 50 μL of standard solution containing all the natural standards and internal standards at a concentration of 200 $\text{pg } \mu\text{L}^{-1}$ and 1000 $\text{pg } \mu\text{L}^{-1}$, respectively. The spiked sample substrate (i.e. filters, PUFs and denuders) were extracted and analysed as described in the Experimental Section. Results appear in Table S3 and S4.

The average recovery for the PAH spiked standards (Table S3) was $99 \pm 12\%$ for the internal standards and $95 \pm 16\%$ for the natural standards, similar to those reported for GC–MS analyses of airborne PAHs elsewhere (Escriva et al., 1994; Vasconcellos et al., 2003; Bates et al., 2008; Zhu et al., 2009; Delgado-Saborit et al., 2010). The average recovery for the derivatised quinones was $107 \pm 11\%$ and $83 \pm 10\%$ for the internal and natural standards, respectively. The lower recovery of the natural standards in comparison to the PAH method is attributed to the additional derivatisation step. The levels of recovery of the internal standards are similar to those analysed by HPLC–APCI–ITMS (Jakober et al., 2006) and GC–MS (Fernandez and Bayona, 1992; Mosi et al., 1997; Cho et al., 2004; Chung et al., 2006). The average recovery levels of the underderivatised quinones were $88 \pm 7\%$ and $80 \pm 6\%$ for the internal and natural standards, respectively. Despite the lower recoveries for certain underderivatised quinones (60–96%), this method demonstrated good reproducibility (standard deviation of 2–15%), confirming that the underderivatised quinone methodology was deemed suitable (Harrad, 2005). The recovery values were calculated as part of the QA–QC protocols, but no further correction was applied to the results. Table S4 in the Supplementary Information presents the recovery levels calculated for denuders and PUF samples, which are consistent with recovery results calculated from filters (Table S3) as discussed above.

Limits of detection, precision and accuracy were assessed. Full details are in the Supplementary Information. To summarise, sample detection limits for the quinones varied widely, from 3 pg m^{-3} for 2-methyl-1,4-naphthoquinone to 168 pg m^{-3} for 5,12-naphthacenequinone. Precisions ranged from 2.1% to 20.3%, but were mostly better than 10%, and accuracy (defined as the difference between the true quantity and the analytical results, normalised by the true quantity) ranged from 2.7% to 13.4% and was hence very good (see Table S3).

3.1.3. Standard reference material analysis

Four samples (1 mg) of NIST certified Urban Dust Standard Reference Material (SRM 1649a and 1649b) (SRM-1649a, 2007; SRM-1649b, 2009) were analysed to validate the accuracy and the precision of the methodology. The mass of the SRMs was accurately measured using a balance with 1 μg precision and normalised to the mg kg^{-1} concentrations. Experimental concentrations of PAHs were compared with the certified concentration using a

one-sample *t*-test (SPSS 17.0). Statistically significant differences were not observed between the certified and analysed values ($p > 0.05$) for all PAHs in both standards, with the exception of B[k]F ($p < 0.05$). B[k]F was generally found to be higher in concentration in all the experimental dataset (see SI, Table S5). This compound is the second peak of two proximate chromatography peaks. The resolution factor for B[b]F and B[k]F, could indicate that the latter part of the first peak (B[b]F) may be partially integrated within the second consecutive peak (B[k]F), leading to the statistically significant difference of $p < 0.05$. Overall, the mean experimental concentrations obtained in this study for both SRM 1649a and 1649b were in excellent agreement with the certified concentrations and similar to those reported elsewhere (Crimmins and Baker, 2006; Delgado-Saborit et al., 2010).

Table 1 compares the concentrations of quinones measured in SRM 1649a and 1649b, using the methodology described in this study, with the limited literature and certified values. Although no certified concentrations were available for the quinones studied for SRM 1649a, AQ and 7,12BaAQ concentrations were available for SRM 1649b. The measured concentrations of AQ and 7,12BaAQ found in SRM 1649b in this study are in excellent agreement with the certified concentrations. Species concentrations for the two SRMs analysed are expected to be very similar, according to the preamble to the two NIST certificates (SRM-1649a, 2007; SRM-1649b, 2009); which is demonstrated by the analyses completed for the PAH compounds (see Table S5). The quinone concentrations measured in both SRMs are also similar (see Table 1), which demonstrates the accuracy and precision of this methodology. The measurements reported here are in good agreement with Cho et al. (2004), who also analysed quinones in their derivatised form. The concentration for the most widely reported quinone, AQ, is in very good agreement with most of the literature, but in contrast to Fernandez and Bayona (1992) who measured 2 quinones utilising gel permeation chromatography coupled to normal phase liquid chromatography (Fernandez and Bayona, 1992). Those authors indicated that their lowest recoveries corresponded to the OPAH measured but did not report recovery values.

The concentration of the underderivatised quinones in SRM 1649a and 1649b (shown in Table 1) are the first measurements reported, with the exception of 5,12NAQ. The concentrations of 5,12NAQ determined in SRM 1649a and 1649b are in reasonable agreement with the scarce literature. In essence, the limited information within the literature for the concentrations of quinones analysed in SRM 1649a and 1649b, means that the results reported in this study do not only demonstrate the methodology's applicability, but also enlarges the database of quantified quinone compounds for cross comparison.

In addition, the small standard deviation reported for all quinones (Table 1), and PAHs (SI, Table S5), not only shows that mass of SRM analysed is homogeneous, but also highlights that our method is suitable for the determination of a large list of PAH and quinone compounds from the same analytical matrix.

3.2. Concentrations of PAHs and quinones in ambient air

Five days of ambient air samples were collected, extracted and analysed from a trafficked site in Birmingham. Table 2 shows a breakdown of the average concentration measured for individual pollutant species. Four compounds (2-methyl-1,4-naphthoquinone, 2,6-di-tert-butyl-1,4-benzoquinone, methyl-1,4-benzoquinone and 2,3-dimethylantraquinone) were detected which have not been reported previously in ambient air. Although the general trends of the PAH concentrations obtained are in good agreement with previous measurements at the same site, they are consistently

Table 2

Average ambient concentrations of PAHs, derivatised and underderivatised quinones in the particulate and gas phases, including PUF measurements collected for five days.

PAHs (pg m ⁻³)	Average concentration			
	Denuder	Filters	PUF	Total
Acenaphthylene	10,100	160	100	10,360
Acenaphthene	8600	300	100	9000
Fluorene	7000	480	110	7590
Phenanthrene	17,200	840	150	18,190
Anthracene	4000	250	51	4301
Fluoranthene	10,000	1400	75	11,475
Pyrene	14,000	1350	65	15,415
Benzo(a)anthracene	3300	440	40	3780
Chrysene	3000	850	71	3921
Benzo(b)fluoranthene	220	500	25	745
Benzo(k)fluoranthene	70	560	24	654
Benzo(e)pyrene	35	260	10	305
Benzo(a)pyrene	35	180	7	222
Indeno(1,2,3-cd)pyrene	40	430	9	479
Dibenz(a,h)anthracene	40	240	7	287
Benzo(ghi)perylene	30	440	7	477
Coronene	10	350	B.D.L ^a	360
∑(PAHs) (ng m ⁻³)	77.7	9.0	0.85	87.6
Derivatised quinones (pg m⁻³)				
Benzoquinone	1500	55	97	1652
2,6-Di-tert-butyl-1,4-benzoquinone	2400	1900	100	4400
1,2-Naphthoquinone	3200	90	84	3374
1,4-Naphthoquinone	1700	65	33	1798
2-Methyl-1,4-naphthoquinone	1700	80	25	1805
Phenanthraquinone	4600	1800	215	6615
Anthracenequinone	640	340	90	1070
Benzo(a)anthracene-7,12-dione	80	500	B.D.L ^a	580
∑(derivatised-OPAHs) (ng m ⁻³)	15.8	4.8	0.64	21.3
Underderivatised quinones (pg m⁻³)				
Methyl-1,4-benzoquinone	2300	60	55	2415
Acenaphthenequinone	470	65	46	581
2-Methylantraquinone	2900	500	75	3475
2,3-Dimethylantraquinone	150	130	35	315
Benzo(a)anthracene-7,12-dione	80	500	B.D.L ^a	580
5,12-Naphthacenequinone	90	250	B.D.L ^a	340
Benzo(a)pyrene-6,12-dione	B.D.L ^a	B.D.L ^a	B.D.L ^a	B.D.L ^a
Benzo(a)pyrene-1,6-dione	10	80	B.D.L ^a	90
∑(underderivatised-OPAHs) (ng m ⁻³)	6.0	1.6	0.21	7.9
∑(OPAHs) (ng m ⁻³)	21.8	6.4	0.85	29.1

^a B.D.L – Below instrument detection limit (see Table S2 for details on instrument limit of detection).

lower. This reflects an improvement in air quality within Birmingham, as reported also by Delgado-Saborit et al. (2010).

The concentrations of quinone species measured in this study are compared with concentrations reported in the literature measured during the cold months (Table 3) in the particulate and vapour phases, when available. Comparison of concentrations with earlier work is not straightforward, as most previous studies have sampled only the particulate phase. Compounds with similar particle-associated concentrations (filter + PUF in our study) are: 1,2NQ, 1,4NQ, AceQ, AQ, 2MAQ, 7,12BaAQ, 5,12NAQ and 1,6BaPQ. In the case of BQ, reported concentrations of the particle phase in Athens considerably exceeded that which we attribute to the particle phase, although the overall concentration (particle + vapour) is similar. Measurements of PQ in our work exceed the other published data. The only measurement of similar magnitude to ours is from Fresno, CA (Chung et al., 2006) in winter, where generally high concentrations were experienced. The data show clearly the importance of the vapour fraction (collected by the denuder) that has not been accounted for in most previous studies.

Table 3 Comparison of individual quinone concentrations (pg m^{-3}) measured in this study in winter with those reported in the literature during the cold period (winter and autumn periods).

Reference	Geographical location	Site description	Season	Substrate	BQ	1,2NQ	1,4NQ	AceQ	PQ	AQ	2MAQ	7,12BaAQ	5,12NAQ	1,6BaPQ
This study	Birmingham, UK	Traffic roadside	Winter	Denuder Particulate Total	1500 153 1652	3200 174 3374	1700 98 1798	470 111 581	4600 2015 6615	640 430 1070	2900 575 3475	80 500 580	90 250 340	10 80 90
Bayona et al. (1994)	Barcelona, Spain	Urban	Winter	TSP						21–26		05–10		
Niederer (1998)	Basel, Switzerland	Traffic roadside	Autumn	TSP						28–2676		32–782	12–312	
Schnelle-Kreis et al. (2001)	Munich, Germany	Urban background	All	PM10						510–1470		160–850		
Yassaa et al. (2001)	Algiers, Algeria	Urban	Winter	TSP						1000				
Castells et al. (2003)	Barcelona, Spain	Urban	Winter	TSP						65–310	184–218	112–132	60	
Schnelle-Kreis et al. (2005)	Munich, Germany	Urban background	Winter	PM2.5						1460		150		
Valavanidis et al. (2006)	Athens, Greece	NS	All	TSP	1030	310	150		80					
Lintelmann et al. (2006)	Munich, Germany	Urban background	All	PM10	470	167	74		57					
Chung et al. (2006)	Fresno, CA, USA	Residential roof	All	PM2.1	1123	157			71	228				
Sienra (2006)	Santiago Chile, Chile	Urban	Winter	TSP		1100	150	450	114–480	470	920	1000	930	1,4–62
Albinet et al. (2006)	Solliers, France	Rural	Winter	PM10			130–270	13.7	9.7	670–1580	300–1120	620–1370	800–1430	
Albinet et al. (2008a)	Chamonix Valleys, France	Rural	Winter	PM10						150–9930		30–3030		
				PM50						150–1420		130–270		
				PM10 + gas						570–3600				
Mirivel et al. (2010)	Douai, France	Urban background	Winter	PM10					57–182	75–657	61–843	530	2	
Wingfors et al. (2011)	Kabul, Afghanistan	Urban, background	Autumn	PM10		40–550				1100–5100	160–3300	1500–6500		

3.3. Vapour and particulate-phase partitioning of PAHs and quinones in ambient air

Fig. 1 illustrates the percentage of vapour and particulate phases (i.e. the sum of all the MOUDI stages) for each species to enable the comparison of vapour/particle phase distribution, as a function of increasing relative molecular weight (MW). The lower MW PAH were mainly found in the vapour phase, whilst heavier PAHs were present in the particle phase. Similarly, the derivatised quinones (low MW) were mainly found in the vapour phase, whilst the majority of heavier underderivatised quinones were present mainly in the particulate phase. Table 2 shows the concentrations measured in the PUF located downstream of the filter, indicating that the higher concentrations measured in this substrate are related with the more volatile species (i.e. species with three or less rings). This is consistent with the work of Wilson et al. (1995), where they found that appreciable amounts of the more volatile species volatilised off from particles collected in the filter, and were captured in a backup sorbent XAD-2 trap (Wilson et al., 1995).

Fig. 2 presents the gas-particle phase distribution of PAH and quinones according to the respective molecular weight (Fig. 2a) in which a sigmoidal logistic curve using 4 parameters was fitted using SigmaPlot 12.0. The sigmoidal curve fitted for PAHs and quinones was compared with that reported by Albinet et al. (2008b). The result is consistent with Albinet et al. (2008b), who reported that <10% of the 2- and 3-ring PAHs (MW < 200) and 2-ring quinones (MW < 180) were mainly found in the particulate phase, whilst >70% of the 5-ring PAH (MW > 252) and 4-ring quinones (MW > 240) were present in the particulate phase. On the other hand, the partitioning of the 4-ring PAH and 3-ring quinones differs from data reported by Albinet et al. (2008b). In the present study, the base of the sigmoidal curve for PAH extends until MW < 220, which implies that <20% of the 4-ring PAHs (202 < MW < 228) were present in the particulate phase, whilst the same compounds reported by Albinet et al. (2008b) can be found in the particulate phase ranging from 20% to 90%. Likewise, the comparison of the particle phase distribution of 3-ring quinones in this study differs from that reported by Albinet et al. (2008b). The sigmoidal curve fitted to our data presents a less steep slope, which does not reach a plateau at 100%. Therefore the 3-ring quinones are distributed in both particle and vapour phases in a different proportion to that reported by Albinet et al. (2008b), whose data fits a more steep sigmoidal curve reaching a 100% plateau for quinones with MW > 240. These differences may relate to external conditions, such as different temperatures during sampling. These were -4 ± 4 °C during the Albinet et al. (2008b) study, whilst temperatures ranged 1–4 °C in our study.

Fig. 1 shows that a larger percentage of particulate phase for PQ, AQ and 2,6DTMQ was observed in comparison to PAHs of similar molecular weights. This indicates that these quinones are less volatile than their PAH counterparts with similar molecular weights (e.g. PQ, MW = 208 g mol^{-1} , Ps = 3.11×10^{-4} Pa vs. Pyr, MW = 202 g mol^{-1} , Ps = 1.93×10^{-3} Pa). Further analysis of the physico-chemical properties of PAHs and quinones, namely molecular mass, vapour pressure as a measure of volatility; octanol–water partitioning coefficient (log Kow) as a measure of polarity and Henry's Law constant as a measure of the tendency to partition to the aqueous phase was performed to disentangle which properties predict better the particle-phase partitioning (Fig. S2). This analysis showed that the trend between vapour pressure and molecular weight was similar for PAHs and quinone species. On the other hand, the correlation between log Kow and the molecular weight showed a different pattern for PAHs and quinones. The heavier the compound, the larger the log Kow; with PAHs always showing larger log Kow than quinones for similar molecular

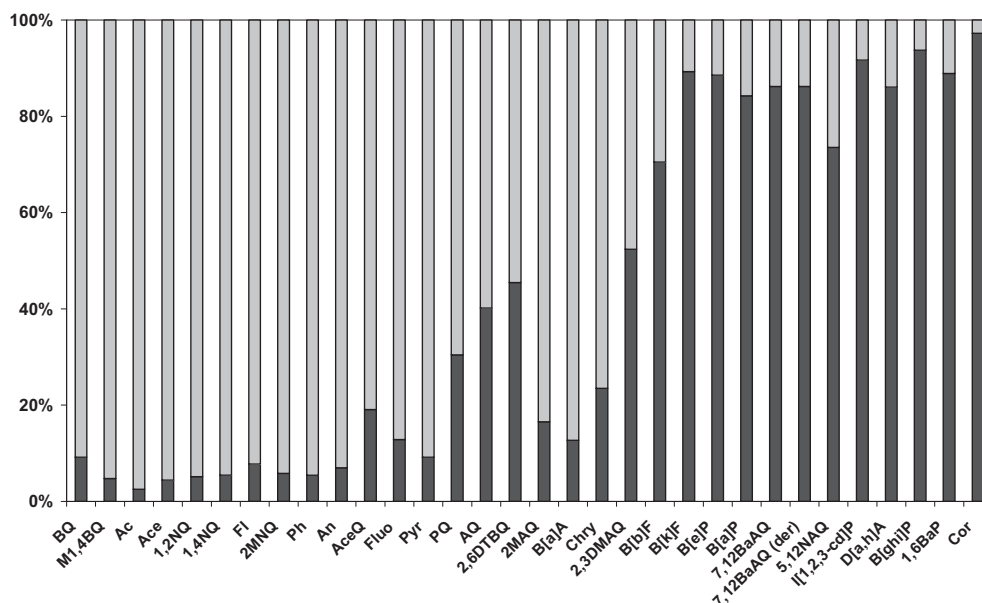


Fig. 1. Percentage of species found in particulate (black) and vapour phase (light grey) over a temperature range of 1–4 °C. Increasing relative molecular mass from left to right.

weights. This is consistent with quinones being more polar than their parent PAHs due to the C=O bond. The values of log Kow are proportional to the values of the octanol–air partitioning coefficient (log Koa) (Lohmann and Lammel, 2004). The PAH show much higher Henry's Law constants than the quinones (Fig. S2d), due to the higher aqueous solubility of the latter.

Fig. 2 shows also the distribution of particle/vapour phase for PAHs and quinones according to vapour pressure (Fig. 2b),

log Kow (Fig. 2c) and Henry's Law constant (Fig. 2d). SigmaPlot 12.0 was used to fit sigmoidal logistic curves using 4 parameters for the case of vapour pressure and log Kow, whilst an exponential curve was fitted for the Henry's Law constant, for PAHs and quinones. Perhaps surprisingly, despite differing physico-chemical properties of the two groups of substances, molecular weight is a remarkably good predictor of vapour pressure (Fig. S2a), and both properties are good predictors of

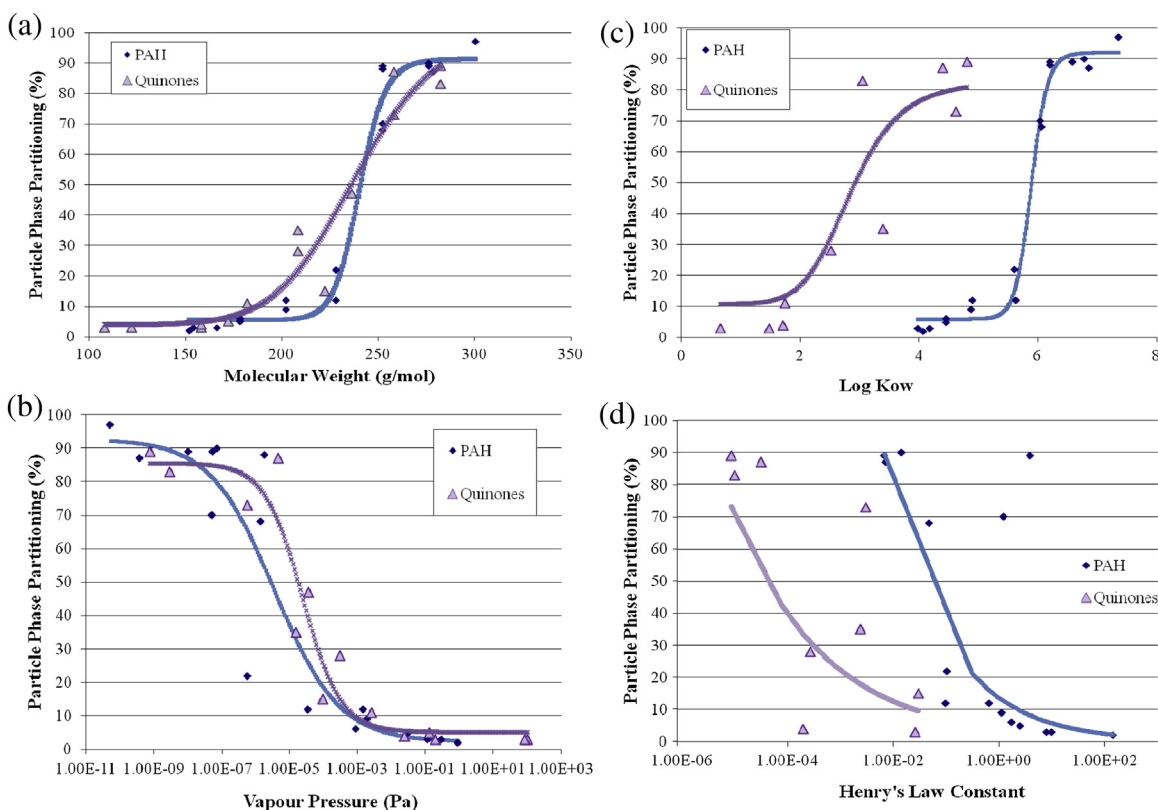


Fig. 2. Percentage of species found in the particulate phase according to (a) molecular weight; (b) vapour pressure; (c) logarithm of octanol–water partitioning coefficient (log Kow); and (d) Henry's Law constant. The curves represent the sigmoidal curve (a–c) and exponential curve (d) fitting to the points. See Section 3.3 for further details.

gas-vapour partitioning for both groups of compounds (Fig. 2a and b).

4. Conclusions

This study has performed a comprehensive analysis of PAHs and quinones from the same sampling media. The analytical method uses a modification of existing analytical methodologies for the determination of PAHs and quinones in air, and includes quinones previously not reported. To ensure the appropriate performance of the analytical methodology for the extended list of quinones measured in this study, thorough quality assurance tests have been performed, including characterisation of the limits of detection, precision and accuracy. The method has been validated with the analysis of two Standard Reference Materials, for which concentrations of some quinone species are reported for the first time. The concentrations of PAHs and quinones in the gas and particulate phase in a traffic impacted scenario have been characterised and compared with concentrations reported in the literature. This work considerably extends the field measurement data on quinones by analysing for compounds not previously reported in the atmosphere, and measuring the vapour phase component. The physico-chemical properties affecting the gas/particle phase distribution have been studied for PAHs and quinones. Both molecular weight and vapour pressure explain the similar trend observed in both PAHs and quinones.

Acknowledgements

The funding by the UK Natural Environment Research Council is gratefully acknowledged (grant reference number NE/F016581/1). The underlying research materials for this study, i.e. data used, can be accessed via email requesting information to j.m.delgadosaborit@bham.ac.uk.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.05.080>.

References

- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2006. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *Journal of Chromatography A* 1121, 106–113.
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2007a. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): concentrations and sources. *Science of the Total Environment* 384, 280.
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., 2007b. Sampling precautions for the measurement of nitrated polycyclic aromatic hydrocarbons in ambient air. *Atmospheric Environment* 41, 4988–4994.
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezou, J.L., 2008a. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys – part 1: concentrations, sources and gas/particle partitioning. *Atmospheric Environment* 42, 43–54.
- Albinet, A., Leoz-Garziandia, E., Budzinski, H., Villenave, E., Jaffrezou, J.L., 2008b. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys – part 2: particle size distribution. *Atmospheric Environment* 42, 55–64.
- Atkinson, R., Arey, J., 2007. Mechanisms of the gas-phase reactions of aromatic hydrocarbons and PAHs with OH and NO₃ radicals. *Polycyclic Aromatic Compounds* 27, 15–40.
- Bates, M., Bruno, P., Caputi, M., Caselli, M., de Gennaro, G., Tutino, M., 2008. Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. *Atmospheric Environment* 42, 6144.
- Bayona, J.M., Casellas, M., Fernandez, P., Solanas, A.M., Albaiges, J., 1994. Sources and seasonal variability of mutagenic agents in the Barcelona city aerosol. *Chemosphere* 29, 441–450.
- Castells, P., Santos, F.J., Gaiceran, M.T., 2003. Development of a sequential supercritical fluid extraction method for the analysis of nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in urban aerosols. *Journal of Chromatography A* 1010, 141–151.
- Chang, K.F., Fang, G.C., Chen, J.C., Wu, Y.S., 2006. Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004. *Environmental Pollution* 142, 388–396.
- Cheng, W.-Y., Currier, J., Bromberg, P.A., Silbajoris, R., Simmons, S.O., Samet, J.M., 2012. Linking oxidative events to inflammatory and adaptive gene expression induced by exposure to an organic particulate matter component. *Environmental Health Perspectives* 120, 267–274.
- Cho, A.K., Di Stefano, E., You, Y., Rodriguez, C.E., Schmitz, D.A., Kumagai, Y., Miguel, A.H., Eiguren-Fernandez, A., Kobayashi, T., Avol, E., Froines, J.R., 2004. Determination of four quinones in diesel exhaust particles, SRM 1649a, and atmospheric PM_{2.5}. *Aerosol Science and Technology* 38, 68–81.
- Chung, M.Y., Lazaro, R.A., Lim, D., Jackson, J., Lyon, J., Rendulic, D., Hasson, A.S., 2006. Aerosol-borne quinones and reactive oxygen species generation by particulate matter extracts. *Environmental Science & Technology* 40, 4880–4886.
- Crimmins, B.S., Baker, J.E., 2006. Improved GC/MS methods for measuring hourly PAH and nitro-PAH concentrations in urban particulate matter. *Atmospheric Environment* 40, 6764.
- Delgado-Saborit, J.M., Aquilina, N., Baker, S., Harrad, S., Meddings, C., Harrison, R.M., 2010. Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples. *Analytical Methods* 2, 231–242.
- Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2013. Use of a versatile high efficiency parallel denuder for the sampling of PAH in ambient air: gas and particle phase concentrations, particle size distribution and artefact formation. *Environmental Science & Technology* (submitted for publication).
- Durant, J.L., Lafleur, A.L., Plummer, E.F., Taghizadeh, K., Busby, W.F., Thilly, W.G., 1998. Human lymphoblast mutagens in urban airborne particles. *Environmental Science & Technology* 32, 1894–1906.
- Eiguren-Fernandez, A., Miguel, A.H., Di Stefano, E., Schmitz, D.A., Cho, A.K., Thurairatnam, S., Avol, E.L., Froines, J.R., 2008. Atmospheric distribution of gas- and particle-phase quinones in Southern California. *Aerosol Science and Technology* 42, 854–861.
- Escriva, C., Viana, E., Molto, J.C., Pico, Y., Manes, J., 1994. Comparison of four methods for the determination of polycyclic aromatic hydrocarbons in airborne particulates. *Journal of Chromatography A* 676, 375–388.
- Fernandez, P., Bayona, J.M., 1992. Use of off-line gel-permeation chromatography normal-phase liquid-chromatography for the determination of polycyclic aromatic-compounds in environmental-samples and standard reference materials (Air particulate matter and marine sediment). *Journal of Chromatography* 625, 141–149.
- Giger, W., Blumer, M., 1974. Polycyclic aromatic-hydrocarbons in environment – isolation and characterization by chromatography, visible, ultraviolet and mass-spectrometry. *Analytical Chemistry* 46, 1663–1671.
- Grosse, Y., Baan, R., Secretan-Laubay, B., El Ghissassi, F., Bouvard, V., Benbrahim-Tallaa, L., Guha, N., Islami, F., Galichet, L., Straif, K., 2011. WHO International Agency for Research on Cancer Monograph: carcinogenicity of chemicals in industrial and consumer products, food contaminants and flavourings, and water chlorination byproducts. *Lancet Oncology* 12, 328–329.
- Gundel, L.A., Lee, V.C., Mahanama, K.R.R., Stevens, R.K., Daisey, J.M., 1995. Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. *Atmospheric Environment* 29, 1719.
- Harrad, S., 2005. Technical Report: Summary of Analytical Methods and Associated Quality Assurance/quality Control (QA/QC) Procedures for Semi-volatile Organic Compounds. Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham.
- Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology*, 825–832.
- Iinuma, Y., Brueggemann, E., Gnauck, T., Mueller, K., Andreea, M.O., Helas, G., Parmar, R., Herrmann, H., 2007. Source characterization of biomass burning particles: the combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat. *Journal of Geophysical Research-Atmospheres* 112.
- Jakober, C.A., Charles, M.J., Kleeman, M.J., Green, P.G., 2006. LC-MS analysis of carbonyl compounds and their occurrence in diesel emissions. *Analytical Chemistry* 78, 5086–5093.
- Jakober, C.A., Riddle, S.G., Robert, M.A., Destaillets, H., Charles, M.J., Green, P.G., Kleeman, M.J., 2007. Quinone emissions from gasoline and diesel motor vehicles. *Environmental Science & Technology* 41, 4548–4554.
- Layshock, J.A., Wilson, G., Anderson, K.A., 2010. Ketone and quinone-substituted polycyclic aromatic hydrocarbons in mussel tissue, sediment, urban dust, and diesel particulate matrices. *Environmental Toxicology and Chemistry* 29, 2450–2460.
- Lintelmann, J., Fischer, K., Matuschek, G., 2006. Determination of oxygenated polycyclic aromatic hydrocarbons in particulate matter using high-performance liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A* 1133, 241–247.
- Lohmann, R., Lammel, G., 2004. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: state of knowledge and recommended parametrization for modeling. *Environmental Science & Technology* 38, 3793–3803.

- Mirivel, G., Riffault, V., Galloo, J.-C., 2010. Simultaneous determination by ultra-performance liquid chromatography-atmospheric pressure chemical ionization time-of-flight mass spectrometry of nitrated and oxygenated PAHs found in air and soot particles. *Analytical and Bioanalytical Chemistry* 397, 243–256.
- Mosi, A.A., Reimer, K.J., Eigendorf, G.K., 1997. Analysis of polyaromatic quinones in a complex environmental matrix using gas chromatography ion trap tandem mass spectrometry. *Talanta* 44, 985–1001.
- Niederer, M., 1998. Determination of polycyclic aromatic hydrocarbons and substitutes (nitro-, oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. *Environmental Science and Pollution Research* 5, 209–216.
- Pedersen, D.U., Durant, J.L., Penman, B.W., Crespi, C.L., Hemond, H.F., Lafleur, A.L., Cass, G.R., 2004. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. *Environmental Science & Technology* 38, 682–689.
- Pedersen, D.U., Durant, J.L., Taghizadeh, K., Hemond, H.F., Lafleur, A.L., Cass, G.R., 2005. Human cell mutagens in respirable airborne particles from the Northeastern United States. 2. Quantification of mutagens and other organic compounds. *Environmental Science & Technology* 39, 9547–9560.
- Poster, D.L., Schantz, M.M., Sander, L.C., Wise, S.A., 2006. Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods. *Analytical and Bioanalytical Chemistry* 386, 859–881.
- Rosenfeld, J.M., 2003. Derivatization in the current practice of analytical chemistry. *Trends in Analytical Chemistry* 22, 785–798.
- Sasaki, J., Aschmann, S.M., Kwok, E.S.C., Atkinson, R., Arey, J., 1997. Products of the gas-phase OH and NO₃ radical-initiated reactions of naphthalene. *Environmental Science & Technology* 31, 3173–3179.
- Schnelle-Kreis, J., Gebefugi, I., Welzl, G., Jaensch, T., Kettrup, A., 2001. Occurrence of particle-associated polycyclic aromatic compounds in ambient air of the city of Munich. *Atmospheric Environment* 35, S71–S81.
- Schnelle-Kreis, E., Sklorz, M., Peters, A., Cyrus, J., Zimmermann, R., 2005. Analysis of particle-associated semi-volatile aromatic and aliphatic hydrocarbons in urban particulate matter on a daily basis. *Atmospheric Environment* 39, 7702–7714.
- Sidhu, S., Gullett, B., Striebich, R., Klosterman, J., Contreras, J., DeVito, M., 2005. Endocrine disrupting chemical emissions from combustion sources: diesel particulate emissions and domestic waste open burn emissions. *Atmospheric Environment* 39, 801–811.
- Sienra, M.R., 2006. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. *Atmospheric Environment* 40, 2374–2384.
- SRM-1649a, 2007. Urban Dust/Organics. National Institute of Standards and Technology. U.S. Department of Commerce, Gaithersburg, MD. https://www-s.nist.gov/srmors/view_detail.cfm?srm=1649A.
- SRM-1649b, 2009. Urban Dust/Organics. National Institute of Standards and Technology. U.S. Department of Commerce, Gaithersburg, MD. https://www-s.nist.gov/srmors/view_detail.cfm?srm=1649B.
- Valavanidis, A., Fiotakis, K., Vlahogianni, T., Papadimitriou, V., Pantikaki, V., 2006. Determination of selective quinones and quinoid radicals in airborne particulate matter and vehicular exhaust particles. *Environmental Chemistry* 3, 118–123.
- Vasconcellos, P.C., Zacarias, D., Pires, M.A.F., Pool, C.S., Carvalho, L.R.F., 2003. Measurements of polycyclic aromatic hydrocarbons in airborne particles from the metropolitan area of São Paulo City, Brazil. *Atmospheric Environment* 37, 3009.
- Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., Van Langenhove, H., 2010. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: molecular characterization and occurrence. *Atmospheric Environment* 44, 1831–1846.
- Wang, W., Jariyasopit, N., Schrlau, J., Jia, Y., Tao, S., Yu, T.-W., Dashwood, R.H., Zhang, W., Wang, X., Simonich, S.L.M., 2011. Concentration and Photochemistry of PAHs, NPAHs, and OPAHs and Toxicity of PM(2.5) during the Beijing Olympic Games. *Environmental Science & Technology* 45, 6887–6895.
- Wilson, N.K., McCurdy, T.R., Chuang, J.C., 1995. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmospheric Environment* 29, 2575–2584.
- Wingfors, H., Hagglund, L., Magnusson, R., 2011. Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and n-alkanes in urban environments in Afghanistan. *Atmospheric Environment* 45, 4360–4369.
- Yassaa, N., Meklati, B.Y., Cecinato, A., Marino, F., 2001. Organic aerosols in urban and waste landfill of Algiers metropolitan area: occurrence and sources. *Environmental Science & Technology* 35, 306–311.
- Zhu, L., Lu, H., Chen, S., Amagai, T., 2009. Pollution level, phase distribution and source analysis of polycyclic aromatic hydrocarbons in residential air in Hangzhou, China. *Journal of Hazardous Materials* 162, 1165.