



# Aircraft Cabin Air Sampling Study; Part 1 of the Final Report

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# Preface

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This report describes the methodology and results of a study of aircraft cabin air quality undertaken by Cranfield University and two contracted analytical laboratories on behalf of the Department for Transport (DfT). The project began in 2007 and was carried out under the leadership of the late Helen Muir OBE (Professor of Aerospace Psychology, Cranfield University) until her illness and untimely death in the first quarter of 2010. The authors and project team are indebted to Helen for her inspiring contribution that made this project and our report possible. She is sadly missed.

Derrick Crump

## *Authors and acknowledgements*

Dr Christopher Walton (Cranfield University) has played a key role in the project since inception having worked alongside Professor Helen Muir to set up the project. He subsequently co-ordinated the air monitoring measurements and collated the results, and then worked alongside Dr Derrick Crump (Director of IEH, Cranfield University) and Professor Paul Harrison (Visiting Professor, Cranfield University) to prepare this report of the study. Derrick Crump and Paul Harrison joined the study to aid its completion following the death of Professor Helen Muir.

BRE (Watford, Herts. WD25 9XX) and AES (Analytical and Environmental Services, Tyne and Wear NE28 0QD) were contracted after an open competition to undertake air sampling and subsequent laboratory chemical analyses. They also contributed their expertise to the operational planning. We acknowledge the work of the following individuals within these companies:

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We also gratefully acknowledge the participating airlines, airports and their staff for their co-operation during the study.



# Summary

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This study was set up in light of concerns about possible adverse impacts on the health and well-being of air crew resulting from exposure to substances in cabin air.

The principal objectives were to analyse cabin air for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), particles and carbon monoxide (CO) in normal operations during all phases of flight (e.g. climb, cruise, descent), and to detect and characterise any anomalous elevations of VOC, SVOC and particle concentrations during any 'fume events' or 'air quality events' where unusual smells or similar occurrences were reported. A total of 100 flights in 5 different aircraft types were monitored in this way.

Monitoring of the total VOC (TVOC) concentration was carried out using a photo-ionisation detector (PID). Samples were also collected onto sorbent tubes using a portable pump for subsequent laboratory analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) to determine specific VOCs and SVOCs. The PID was additionally used as a real-time detector of possible fume events. Carbon monoxide concentration and ultrafine particle count were determined using a gas monitor (electrochemical sensor) and P-Trak ultrafine particle counter, respectively.

The sampling strategy allowed for a series of samples to be taken at defined points on all flights, with additional provision for samples of any 'fume events' to be obtained immediately should they occur. These additional 'air quality event' samples were initiated by the researcher conducting the measurements whenever any change in air quality was detected by the PID or ultrafine instruments, or reported by anyone on the aircraft. The protocol was designed to yield samples of these events that were directly comparable to the routine samples taken.

The first part of the study involved monitoring on Boeing 757 cargo aircraft and included all necessary preparatory work for these operations, including equipment purchase, questionnaire design and protocol development. Subsequently Parts 2 to 5 of the study utilised the equipment and methods of Part 1 to carry out monitoring on Boeing 757, Airbus A320/1, BAe 146 and Airbus A319 passenger aircraft respectively.

Flight crew and cabin crew (if any) were requested to complete a post-flight questionnaire for all flights. This included questions concerning any fumes or smells that occurred during the flight. It was also completed by the scientist conducting the air quality measurements. The flight staff were informed that the questionnaire was to be used in addition to normal fume event reporting procedures and that it did not replace them. No fume event occurred during this study which triggered the airline's formal reporting procedures.

Sorbent tube samples were analysed for the following target compounds:

- Tri-*ortho* cresyl phosphate (TOCP); one of a number of TCP isomers,
- Other tri-cresyl phosphate (TCP) isomers; applications include a minor component of engine oil,
- Tri-butyl phosphate (TBP); applications include a component of hydraulic fluid,
- Toluene,
- m+p- xylenes,
- Limonene,
- Tetrachloroethylene (TCE),
- Undecane.

Mean values (and percentiles) for VOC/SVOC concentrations are presented for all data (all samples for all flights and all flight phases), for each flight, for each flight phase, and for each part of the study (aircraft type). For ultrafine particles, TVOCs and CO, the number of flights (flight sectors) with levels within specified ranges are presented. More detailed data are provided in Part 2 of this report.

Mean ultrafine particle numbers (all flight sectors) were always in the range 1,000-100,000 particles  $\text{cm}^{-3}$ . On five flight sectors peak concentrations exceeded the maximum range of the instrument (500,000 particles  $\text{cm}^{-3}$ ). Mean total VOC concentrations were mostly below 2 ppm and a number of the short duration peak concentrations above 10 ppm were probably due to exposure to isopropyl alcohol vapour generated by the p-Trak instrument. Maximum CO concentrations were mostly below 2 ppm.

The most abundant VOC/SVOCs were generally limonene and toluene. Highest concentrations of TBP, limonene, m+p-xylene and undecane occurred during first engine start, while TCE concentrations were highest during the 'immediate' sampling period. Highest levels of TOCP, other TCPs and toluene occurred during climb, pre-landing and take-off respectively.

A total of 30 air quality event sorbent tube samples were collected during the study. Numbers of events were similar in Parts 1, 2, 3 and 5 of the study, and highest in Part 4. Events were largely concentrated at engine start and take-off, with few occurring at top of climb or during cruise. Concentrations of target analytes during these events were not elevated compared with the routine samples collected in each respective phase of flight.

A total of 38 flights had fumes or smells reported by at least one crew member or researcher in a post flight questionnaire. The dominant smell descriptor was 'oil' or 'oily', reported by 26 persons. Other descriptors were 'sweet', 'toilet smell', 'exhaust', 'chlorine', 'de-icing fluid', 'fuel', 'heated dust' and 'human waste'. Four persons reported that the fumes/smells caused a health effect (headache or slight headache in all cases). Some flights had up to 3 persons reporting a smell/fume and others had only one person; a total of 60 (of 552) questionnaires reported a smell/fume. Some flights had reports of smells in more than one phase, and in two instances the smell of human waste was reported throughout the flight. On other flights, fumes/smells were reported during only one phase.

The European standard 'Aircraft internal air quality standards, criteria and determination methods' (BS EN 4618: 2009) sets safety limits, health limits and comfort limits for a number of substances, including two that were measured in this study – carbon monoxide and toluene. The monitoring results indicate that concentrations of carbon monoxide did not exceed safety or health limits. Concentrations of carbon monoxide recorded during nine flights were equivalent to the 8h TWA (time weighted average) health limit, but this is believed to have been due to instrument malfunction rather than actual elevated levels of carbon monoxide. All measurements of toluene undertaken using sorbent tubes were well below the BS standard comfort limit of 153  $\text{mg m}^{-3}$ , the maximum concentration of toluene measured during flight being 0.17  $\text{mg m}^{-3}$ .

In the absence of specific cabin air standards for the other pollutants measured in this study, reference is made to other standards and guidelines established, for example, for domestic (home) or occupational environments. Such standards/guidelines are available for TCE, TBP, TOCP, xylenes and limonene (as well as for toluene and CO). None of these standards/guidelines was exceeded. One short term (5 minute) concentration of limonene occurred (during Part 3 of the study) that exceeded a recommended long term exposure limit; however, this short duration peak would have a small impact on longer term average exposure.

It is informative also to compare measured cabin air concentrations with levels typically seen in domestic indoor environments. Based on the reasonably extensive database for VOCs in indoor air in buildings, it can be concluded that the concentrations of toluene, limonene, xylenes, undecane and TCE in the aircraft cabin air are of similar magnitude to those occurring in homes in developed countries. Concentrations of CO generated by combustion sources, notably gas cookers, are often higher than those occurring in the aircraft cabins. For TBP and TCPs, there are few data to allow comparison of the measured levels in aircraft cabin air with the indoor air in buildings. There are more extensive data available on levels of organophosphates in household dust, including studies reporting levels of TBP, but these are of limited relevance to the present study. It is notable that in over 95% of the cabin air samples, no detectable amounts of TOCP or other TCPs were found. TBP was detected more routinely, but not in the majority of samples. The highest level of TBP recorded was  $21.8 \mu\text{g m}^{-3}$  (overall mean  $1.07 \mu\text{g m}^{-3}$ ) which exceeds any reported domestic indoor air level. TBP levels were highest during first engine start.

Mean concentrations of most VOCs showed a trend, with minimum values occurring during the main phases of flight (climb to descent) and higher values when on the ground and during take-off. This trend was not found for limonene or the TOCP and other TCP measurements. Regarding the possible influence of aircraft type, no TCPs were detected during Part 3 (A320/1 aircraft), whereas limonene concentrations were relatively high on these flights. Other identified differences included highest concentrations of m+p-xylene occurring in Part 5 and lowest concentrations of toluene in Part 2.

In conclusion, this study successfully completed a range of air quality measurements during the course of 100 flights. No fume events occurred during these flights that triggered the airline's protocols for formal reporting of incidents. Flight and cabin crew, as well as the investigating scientists reported a number of fume /smell events in a post-flight questionnaire. Samples specifically taken during recorded air quality events did not have notably elevated concentrations of any of the individually measured pollutants. Therefore, with respect to the conditions of flight that were experienced during this study, there was no evidence for target pollutants occurring in the cabin air at levels exceeding available health and safety standards and guidelines.



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# 1 Introduction

The Department for Transport (DfT), on behalf of the Government's Aviation Health Working Group (AHWG), commissioned Cranfield University to organise, manage and deliver a major monitoring study of the cabin air environment of commercial aircraft. The project flowed from the House of Lords Select Committee on Science and Technology report on "Air Travel and Health" in 2000 (HoL 2000). Whilst the Committee did not find evidence of harmful contaminants in cabin air they nonetheless remarked:

"We have seen no evidence that cabin air is monitored or sampled either routinely or even under abnormal or unusual conditions when passengers or crew feel that conditions are not right. We recommend airlines to carry out simple and inexpensive cabin air sampling programmes from time to time, and to make provision for spot-sample collection programmes from time to time, and to make provision for spot-sample collection in the case of unusual circumstances. This would be helpful for passengers and staff, and also benefit airlines themselves. We also suggest that this might form part of Government-sponsored research."

Concerns continued to be expressed, for example by the British Airline Pilots Association (BALPA), that the intermittent "fume events" on aircraft – in particular on two types of aircraft – may have long-term health impacts. Hence the Government asked the independent Committee on Toxicity (COT) to review the available evidence and advise on further research required. In this report (COT 2007) the Committee concluded that "It was not possible on the basis of the available evidence in the BALPA submission or that sourced by the Secretariat and DH Toxicology Unit to conclude that there is a causal association between cabin air exposures (either general or following incidents) and ill-health in commercial aircraft crews. However, we noted a number of oil/hydraulic fluid smoke/fume contamination incidents where the temporal relationship between reports of exposure and acute health symptoms provided evidence that an association was plausible" (paragraph 86). With regard to the need for exposure monitoring research, COT advised that an initial stage involves the determination of the identity and concentration of chemical compounds and any particulates that might be present in cabin air under normal conditions and during an oil/hydraulic fluid smoke/fume incident (paragraph 65).

The COT also agreed that: "there was considerable uncertainty regarding the identity of any VOCs, SVOCs and other pyrolysis products released into the cabin air during an oil or hydraulic fluid smoke/fume incident (paragraph 43 above and TOX/2007/10 Annex 1). Members considered that approaches to exposure measurement should cover the widest possible range of potential contaminants from oil/hydraulic fluid that could be analysed and should not focus on only a single chemical group. Also, the investigation should be undertaken on appropriate aircraft (e.g. B757s fitted with the RR535C engine) during flight." They also recommended study of the BAe 146 aircraft.

The overall objectives for the programme of work undertaken by Cranfield University for the DfT were:

1. The analysis of the cabin air for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), particles and carbon monoxide (CO) in normal operations (and during any fume incidents) during all phases of flight (e.g. climb, cruise, descent).
2. The detection and characterisation of anomalous elevations of VOC, SVOC, particle and CO concentrations.

The preparatory phase of the work identified the sampling methods most suitable for the determination of background levels of VOC and SVOC and for the detection and analysis of fume events. A method was required that was highly sensitive and able to determine analytes of interest during a short duration event. The recommendation of this study by Muir et al., (2008) was that monitoring of general levels of VOCs and SVOCs should be carried out using a photo-ionisation detector (PID), with samples also being collected onto sorbent tubes using a portable pump, for subsequent laboratory analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). In a trial involving the release of a test solvent, the PID was found to be a useful real time detector which could be used to trigger sorbent tube sampling so that the VOC and SVOC compounds present in the air during a possible fume event could be determined. The sampling undertaken on aircraft demonstrated that the pumped sorbent tube method could measure low level airborne concentrations of engine oil and hydraulic fluid and their components (including tri-cresyl phosphates and tri-butyl phosphate).

In the main part of the study, reported here, the recommended equipment was used to obtain air samples from the flight decks of commercial aircraft in scheduled operation. The study plan was to undertake air sampling on one hundred flight sectors (i.e. whole flight or period of flight involving one take off and one landing) distributed equally amongst five commercial carriers and referred to as Parts 1 – 5 of this study. In addition to VOCs/SVOCs, the carbon monoxide concentration and ultrafine particle count were to be determined. The sampling strategy adopted allowed for a series of samples to be taken at defined points on all flights, with additional provision for samples of any ‘fume events’ to be obtained immediately should they occur. These additional ‘air quality event’ samples were initiated by the researcher conducting the measurements whenever any change in air quality was detected by the PID or ultrafine instruments, or reported by anyone on the aircraft. This protocol was designed to yield samples of these events that were directly comparable to the routine samples, whether or not the event triggered the airline’s formal reporting procedure.

Part 1 of the study involved monitoring on the Boeing 757 cargo aircraft. In addition to the collection and analysis of air samples, Part 1 included all necessary pre-work to these operations, including equipment purchase, questionnaire design and protocol development, including detailed analytical protocols. Subsequent Parts utilised the equipment and methods of Part 1 to carry out monitoring on Boeing 757, BAe 146 and Airbus (A319, A320 and A321) passenger aircraft.

The results of the study are being made available as a report comprising two main sections. This first part describes the sampling strategy, methodology and presents a summary of the air quality measurements and an overview of findings. The second part contains the detailed measurement data for each flight sector.

## 2 Sampling strategy

### *Outline*

An important consideration in the design of the sampling strategy was the avoidance of bias. This was achieved by maintaining independence of the sampling and analytical activities so that laboratory analysis could be carried out with staff having only minimal information as to the nature of each sample. In practice this entailed the involvement of two independent organisations; Analytical and Environmental Services (AES) and the Building Research Establishment (BRE). For any given flight one organisation was responsible for sampling and the other for analysis. Independence was further reinforced by transporting all samples via Cranfield University. For a full discussion of sample handling, refer to section 3.

A researcher travelled on each flight sector by prior arrangement with the airline. Samples were taken exclusively in the flight deck. The samples were taken onto sorbent tubes using a portable air sampling pump for subsequent analysis by TD/GC/MS. A second pump of the same type and configuration was also carried to allow rapid sampling of possible air quality events should they occur and was reserved exclusively for this purpose. The shortest practicable sample duration was adopted in order to maximise the ability to capture transient air quality events. Measurement methods requiring high volume sampling over extended periods that may, for example, be appropriate for measuring 8 hour time weighted average (TWA) concentrations were therefore not suitable for the study.

Other equipment carried comprised a PID/gas analyser and a particle counter to monitor levels of vapour and aerosol respectively. Both instruments logged data continuously throughout the flights and provided potential warning of elevations in air contaminant concentrations that may not necessarily have been detectable by the flight deck occupants through perceived odour or other symptoms. All instruments carried were capable of logging their data against a real-time clock. Instrument data logs were transmitted to Cranfield University by email and/or CD.

A stock of sampling tubes containing the appropriate sorbent material was purchased through Cranfield University specifically for this project. Both laboratories maintained their own subset of these tubes, each identified by a unique serial number. Tubes were conditioned (i.e. pre-cleaned by heating) at the analysing laboratory prior to each use and then sent to the other ('sampling') laboratory to await use in airborne sampling. Once sampling was completed, the tubes were sent to Cranfield University together with the written sampling records. At Cranfield, an analytical schedule was drawn up specifying which tubes required analysis (those used for air sampling and a minimum of one travel blank, and often an additional 'second travel blank'). The tubes and schedule were then passed to the analysing laboratory; the written sampling records were retained at Cranfield University so that the chemical analysis was carried out blind. Tubes were transferred in security-tagged bags.

Following analysis, the results were passed to Cranfield University, identified only by a serial number to be collated against the original written records. The whole process was controlled using chain-of-custody documents designed for the purpose.

### *Sampling Plan*

The plan defined at the outset of the study was to carry out air sampling on 100 flights over the course of the 5 parts of the study. Table 1 shows the aircraft types and number of flight sectors undertaken and the tasks allocated to the different parties for each part of the study.

More than one flight sector was monitored on some aircraft; for example in Part 1 of the study the 20 flight sectors involved 10 different aircraft (all Boeing 757-236 with Rolls Royce RB211-535C engines) and Part 4 involved five different aircraft (146-200, 146-300 and 146-300A all with engines manufactured by Honeywell). Details about each flight were recorded by the researcher undertaking the air sampling using the form shown in Appendix A. A further two flights, additional to Part 2, were monitored as pilot studies to finalise procedures for monitoring on passenger aircraft. The results from these flights are included in the second part of the report.

Table 1. Number of flight sectors, aircraft types and tasks of different parties during the five parts of the main study.

Aircraft	Part 1 Boeing 757 cargo	Part 2 Boeing 757 pax	Part 3 Airbus A320/1 pax	Part 4 BAe 146 pax	Part 5 Airbus A319 pax	Total
Sampling AES Analysis BRE	10	10	10	10	10	50
Sampling BRE Analysis AES	10	10	10	10	10	50
Data collation Cranfield University	20	20	20	20	20	100

pax = passenger aircraft

Ten sampling points were defined for each sector at various phases of flight; Table 2 defines each phase and the cues used by the researcher to initiate sampling. The duration of each sample was an important consideration since a longer sampling time improves analytical sensitivity (because a larger volume of air can be passed through the sorbent tube) but on the other hand might be less representative of a phase of flight that lasts only a few minutes (e.g. Take off). In order to maintain strict comparability between samples it was decided that all should have the same duration, and this extended to include air quality event samples.

A sample duration of 5 minutes was selected as it provided good analytical sensitivity while still retaining the ability to characterise air quality events which might prove to be transient in nature. The concentration measured was therefore the mean for each period of sampling and concentrations may have fluctuated during that time. However, inclusion of the PID and ultrafine instruments (recording data with a logging interval of 1 second) was designed to establish the detailed timecourse of the total VOC concentration and particle count (as well as CO) throughout each sector and allow the duration of any air quality events to be established. Air quality event samples were initiated if the researcher noticed any significant rise in VOC or ultrafine particle count readings or became aware of any odour or odour was reported by any member of the crew.

A minority of samples were of shorter duration, usually because of insufficient time within a given phase of flight. The use of pumps with a data logging capability meant that these samples could be positively identified, their actual duration calculated and the concentrations of the target analytes in air correctly determined. These samples were therefore suitable for

analysis but have a proportionally elevated limit of detection. Some flight phases were of too short a duration (particularly cruise phase of short flights) to allow a sample to be taken and so were omitted.

Table 2. Summary of flight phases and sampling cues.

Sample No.	Flight phase	Cues	Comments
1	Immediate	As soon as kit is set up	
2	First engine start	Pilot says "Starting right/left engine"	Usually during push-back
3	Taxi	As aircraft begins to move under own power	
4	Take off	Throttle up	
5	Climb	As aircraft climbs above 20,000 ft	In some cases (e.g. short sectors) the altitude for this sampling cue was reduced to 13,000 ft after consultation with the flight crew
6	Top of climb	Throttle back	
7	Cruise	10 minutes after top of climb	
8	Start of descent	Throttle back, aircraft pitches down	
9	Pre-landing	2,500 feet ("Radio altimeter" heard -757 only)	Will include landing and into Taxi
10	Taxi-back	End of previous sample	
F	Air quality event	Smell reported or warning from PID or ultrafine particle monitoring instruments	Second pump started immediately

A detailed schedule for sampling during each flight sector (see Appendix B) was provided to the researcher. Measurements were undertaken over the period September 2008 to February 2010. Table 3 shows the periods during which the monitoring took place.

Table 3. Periods when sampling was carried out for each part of the study.

Study part	Period
1	8/9/08 to 17/3/09
2	27/10/08 to 14/11/08
3	14/10/09 to 30/10/09
4	7/12/09 to 17/12/09
5	10/2/10 to 18/2/10

## 3 Methodology

### *Sampling equipment*

The principal instruments carried are listed below together with a résumé of their important characteristics. These instruments were procured by Cranfield University for Part 1 of the study and issued to the participating laboratories. In addition to the instruments themselves, each laboratory also received appropriate ancillary items and consumables (not described here). As a contingency, Cranfield University retained a spare example of each instrument which could be issued in the event of breakdown.

1. Ion Science FirstCheck+5000. This instrument combines a highly-sensitive (parts per billion, ppb) PID with a four-channel gas monitor. The PID responds to VOCs in air but is not able to identify any specific compound present. It is calibrated according to the detector response to isobutylene and its relative response to a wide range of other VOCs is known. Therefore it provides a measure of the total VOC concentration equivalent to the concentration of isobutylene that would produce the same detector response. The manufacturer reports a measuring range of 1ppb to 10,000 ppm with an accuracy of +/- 5%.

The analyte of primary interest determined by the gas monitor is carbon monoxide (CO); detection is by an electrochemical cell. The working range for CO is given as 0.1 – 1,000 ppm. Battery life and memory were sufficient to allow continuous monitoring throughout each sector at a sampling interval of one second.

2. TSI Model 8525 P-Trak ultrafine particle counter. This instrument is a condensation particle counter which can detect and record particles down to a diameter of 0.02  $\mu\text{m}$  (range 0.02 to 1  $\mu\text{m}$ ). This size range includes particles that are classified as both fine and ultrafine particles (ultrafines being those less than 0.1  $\mu\text{m}$  diameter) but particle number is generally considered to be dominated by the ultrafine fraction and so that term is used in this report with regard to the data determined by the P-Trak. At the time of planning the study, available instruments capable of detecting particles smaller than 0.02  $\mu\text{m}$  were too large to be readily portable and had unacceptable power supply requirements. One disadvantage of the P-Trak is the requirement for analytical grade alcohol which must be periodically replenished, although the unit will run for 8 hours between refills. Replenishment was undertaken on the ground outside the aircraft. Particle count was logged throughout each sector at a sampling interval of one second.
3. TSI Model SP730 air sampling pump and passivated stainless steel sorbent tubes. One pump was used to take a series of nominal air samples at each phase of flight. Up to ten samples were taken per sector (see Table 1) onto stainless steel sorbent tubes packed with quartz wool and Tenax TA. These sorbents were selected to retain a wide range of compounds including, but not limited to, those on the target analyte list. Air was sampled at a flow rate of approximately 500 ml  $\text{min}^{-1}$  and normally for 5 minutes, giving a total sample volume of 2.5 litres. On some occasions the operator reduced the sampling time in order to link samples to a particular phase of flight.

The SP730 allows sample flow rate and duration to be pre-programmed, minimising operator workload. Once configured, sampling is rapidly initiated by the press of a button. The instrument has a built-in flow rate sensor and the flow rate actually achieved is logged to onboard memory at intervals of one minute. This information is used subsequently to determine true sample volume and

improve the ultimate accuracy of reported concentrations. These units simultaneously log ambient temperature and pressure. A second TSI Model SP730 air sampling pump with an identical configuration to the first was used exclusively to sample any 'air quality events' indicated by the sampling equipment or noticed on the flight deck.

All instruments logged data against a real-time clock which was set against a PC clock prior to leaving the laboratory. An important consideration with regard to the type and number of instruments carried was that of operator workload as airline operational considerations dictated that only one scientist could be carried on any one sector. Trials in flight simulators and in the air demonstrated that the configuration applied maximised the amount of high-quality data that could be obtained.

Care was taken with respect to the physical placement of the instruments during flight. However it was not possible to adopt an absolutely consistent approach because of the different aircraft types involved with differing flight deck layouts. Instruments were always placed so that their intakes were not obstructed. Typically the PID would be placed in a cup holder or in the webbing behind the Captain's or First Officer's seat and secured as necessary with elastic cords or string carried for the purpose. The pumps were kept in an open flight bag on the floor, being held in place by their integral clips, while the P-trak instrument was placed on the floor itself. One characteristic of the P-trak instrument is that it gives off a small amount of isopropyl alcohol (IPA) vapour, used as part of the measurement process. Placing it at floor level ensured that the ceiling-to-floor airflow in the flight deck flushed this away from the other instruments.

### ***Post-flight questionnaire***

Flight crew and cabin crew (if any) were requested to complete a post-flight questionnaire for all flights (Appendix C). This included questions concerning any fumes or smells they may have noticed during the flight. It was also completed by the researcher conducting the air quality measurements. The flight staff were informed that the questionnaire was to be used in addition to normal fume event reporting procedures and that it did not replace them.

### ***Sample handling and laboratory analysis***

At the end of each flight sector or series of sectors the sorbent tube air samplers were placed in a security-tagged transport bag for transport to Cranfield University. Samples were accompanied by a record form (Appendix D) completed by the researcher together with any post-flight questionnaires. This process was controlled using chain-of-custody documentation shown in Appendix E, held by Cranfield University.

At Cranfield University, tubes were separated from the sector record form, which links the unique tube identification number to the flight and phase on which it was used, prior to transfer to the analysing laboratory. It was impracticable for the laboratory analyses to be undertaken completely blinded. Therefore the chain-of-custody documentation was also used to provide minimal sample information to the analysing laboratory. Air quality event samples were identified because during study design it was anticipated that these samples might contain relatively high concentrations of the target analytes. If the calibration range of the method were exceeded this would produce inaccurate results. These samples were therefore identified so that re-analysis could be undertaken if necessary (by re-collection of the split flow during the thermal desorption analysis process; see Appendix F). In practice however, re-analysis was never required. Tubes which had not been used for sampling or as blank (control) samples were also identified to save the time and expense of analysing them.

Laboratories reported their results as analyte concentrations against tube number only; Cranfield University re-collated these with sector record forms and instrument data-logs.

Sorbent tube samples were analysed reciprocally using the harmonised TD/GC/MS protocol developed in Part 1 of the study. All tubes, including samples, blanks and replicates were analysed quantitatively against a common Target Analyte List. The list agreed at the outset included compounds indicating sources of hydraulic fluid and aviation fuel as well as sources such as consumer products known to occur widely in indoor environments:

1. Tri-*ortho* cresyl phosphate (TOCP); one of a number of TCP isomers.
2. Other tri-cresyl phosphate (TCP) isomers; applications include as a minor component of engine oil.
3. Tri-butyl phosphate (TBP); applications include a component of hydraulic fluid.
4. Toluene; widely occurring VOC e.g. in inks, adhesives, component of solvent cleaners and petroleum based fuels.
5. m+p-xylene; often occur with toluene.
6. Limonene; present in natural products such as wood and citrus fruits and widely applied as fragrance in a range of cosmetic and cleaning products.
7. Tetrachloroethylene (TCE); a solvent used in cleaning products.
8. Undecane; present in petroleum mixtures such as fuels and solvents e.g. white spirits used in construction products and cleaning liquids.

A major advantage of TD/GC/MS as an analytical technique is that it allows identification of a very wide range of compounds present in a sample. This is particularly useful in situations where the compounds likely to be encountered are poorly defined in advance. A typical air sample from a domestic or workplace setting may contain potentially hundreds of VOCs/SVOCs, though these will mostly be at very low concentrations. Quantification of an individual compound (as opposed to merely identifying it) by TD/GC/MS requires calibration against a high-purity standard of that compound. While this is clearly impracticable for every compound which might be present, retrospective quantification of archived data is feasible for selected compounds if required. For any such compound of interest, the mass spectrometer response factor for that compound relative to the internal standard could be determined to enable quantification of the amount on the tube and thereby the airborne concentration.

During the course of the study both laboratories determined some other components that can be found in hydraulic fluid and engine oil in a qualitative manner. Further details of the TD/GC/MS method are provided in Appendix F. Essentially the method for sampling and analysis is based on the guidance in the international standards ISO 16000-6 and BS EN ISO 16017-1 that describe safe sampling volumes, calibration methods and other method parameters such as quality control procedures.

### ***Thermal desorption tubes***

The use of stainless steel sorbent tubes containing Tenax sorbent for pumped sampling and analysis by TD/GC/MS is a well established method for measuring a wide range of VOCs as well as some very volatile and semi-volatile compounds. An important consideration is the ability of the selected sorbent, Tenax TA, to retain the compounds on our target analyte list. The principal means of assessing this is by determination of the breakthrough volume, which is the volume of air required to elute a given compound from a known mass of sorbent. This value is strongly temperature-dependent and is normally quoted in terms of litres of air per gram of sorbent at 20°C. The breakthrough volumes of Tenax for the majority of our target

analytes are well characterised and published (see for example <http://www.sisweb.com/index/referenc/tenaxta.htm> and ISO 16000-6). Table 3a shows breakthrough volumes calculated for the average mass of Tenax in the TD tubes used for this study (0.2g). These are greatly in excess of the sampling volume of 2.5 litres, indicating that these compounds are very well retained.

Table 3a. Breakthrough volumes for sorbent tubes containing Tenax TA.

Target analyte	Breakthrough volume (litres)
Toluene	80
m+p-Xylene	310
Limonene	2,400
Tetrachloroethylene	42
Undecane	2,520

The retention of organophosphates on Tenax TA has not been investigated to the same extent, particularly at the high flow rates required in this study. However, the UK Health and Safety Laboratory methods for measuring VOCs in occupational environments using sorbent sampling and TD/GC analysis were first published in the 1980s and included a method for the relatively involatile dioctylphthalate that specified the use of Tenax TA sorbent in a stainless steel tube with a flow rate of 500 ml min<sup>-1</sup> (HSL, 1983). Significant improvements to instrumentation since that time have allowed the development of more sensitive methods for environmental monitoring and their application to a wider range of substances (Woolfenden, 2010). The suitability of the sampling and analytical method used in the present study for the determination of components of oil vapour (including TCPs) generated by heating Jet II oil has been demonstrated (Appendix F). The use of sorbent tubes packed with quartz wool and Tenax TA has also been demonstrated for determination of a range of semi-volatile organophosphate pesticides (Markes, 2009).

Sorbent tube sampling and TD/GC/MS analysis is currently described in international standard methods for measuring organic compounds in indoor air (ISO 16000-6, BS EN ISO 16017-1). As well as vapour phase organics, sorbent tubes containing Tenax TA have been shown to effectively trap particles in the size range of 0.020 – 0.700 µm (Jamriska and Uhde, 2003). The authors are not aware of any study that has examined the collection of larger particles. ISO 16000-6 is currently undergoing revision and the addition of quartz wool at the front of the tube is described in the current draft (DIS) to enhance collection and recovery of SVOCs, particularly those above n-C<sub>22</sub>. The method provides high sensitivity relative to methods that require solvent desorption of the analytes from the air samplers.

### ***Comparability of results***

Analysis was undertaken by two independent laboratories and it is important therefore to understand the comparability of the two sets of data. Both laboratories used very similar analytical methods, although there were some differences in the instrumentation, most notably the mass spectrometers applied. They are both accredited by the United Kingdom Accreditation Service (UKAS) for determination of VOCs but the specific procedures

developed to meet the objectives of the current study were not accredited. To investigate comparability the participating laboratories (BRE and AES) were required to undertake an initial method harmonisation exercise in advance of the main part of the study. This entailed the exchange, in September 2008, of 7 sorbent tubes spiked with known masses of lubricating oil and hydraulic fluid. These tubes were analysed by the two laboratories according to the agreed method and the results compared. A further comparison exercise was undertaken in September 2009 during the main sampling programme, and involved the exchange of tubes spiked with known masses of the individual target analytes. Further details are provided in Appendix G.

### ***Data handling***

TD/GC/MS results were reported blind (i.e. against tube identifier only) to Cranfield University by the participating laboratories in an agreed common format. AES and BRE also provided raw data files from their laboratory analytical instruments. Instrument data-logs were transmitted to Cranfield University electronically in both proprietary format and as character-delimited text files where this option was available. Cranfield University maintains an archive of all data on a password-protected computer.

## 4 Results

Detailed results for each flight for the measurements of air quality are provided in Part 2 of this report. This section provides a summary of those results.

### *Chemicals determined by TD/GC/MS*

#### *All data (i.e. all flight phases for all flights)*

Mean values and percentiles for VOCs/SVOC concentrations in air for all data (all samples for all 100 flights and all flight phases) are shown in Table 4. A total of 981 samples were collected and successfully analysed. The results for each target analyte are presented in terms of the mean, standard deviation, minimum and maximum values as well as the percentile values from the distribution of data points e.g. 50% is the median value and therefore half of all readings were less than this value and the other half were greater than this value. The data are also presented as cumulative frequency diagrams in Appendix H and the geometric means and geometric standard deviations are tabulated. The most abundant chemicals were toluene and limonene. Concentrations of TCPs were below the limit of quantification for over 95% of samples.

Table 4. Mean and percentile concentration values for target chemicals measured in all flight phases (including additional samples taken during ‘air quality events’).

Compound (n)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM**	SD	min	max
TOCP (981)	ND*	ND	ND	ND	0.07	0.88	ND	22.8
Other TCPs (981)	ND	ND	ND	ND	0.14	1.36	ND	28.5
Sum of TOCP and other TCPs	ND	ND	ND	ND	0.22	2.08	ND	37.7
TBP (981)	ND	0.4	1.3	5.0	1.07	1.96	ND	21.8
Toluene (981)	ND	6.3	16.6	50.1	13.93	21.23	ND	170.2
m+p xylene (981)	ND	0.4	1.8	9.1	1.78	3.63	ND	52.3
Limonene (981)	ND	1.4	6.5	37.8	11.85	45.77	ND	540.3
TCE (981)	ND	ND	0.6	1.8	0.43	1.04	ND	20.1
C <sub>11</sub> (981)	ND	ND	2.0	13.8	2.74	7.60	ND	87.3

\*ND = not detected i.e. below limit of quantification (Note: precise limit depends upon air volume sampled and thereby duration of air sampling, and also relates to method sensitivity as determined by appropriate calibration).

\*\*arithmetic mean (all non-detects were given a value of zero).

n = number of samples, SD = standard deviation

The protocols developed for the study aimed to minimize contamination at all stages; the effective conditioning of tubes, precautions during transit and laboratory analysis, and analytical conditions to prevent residual contamination in the TD/GC/MS. 185 sorbent tube travel blanks (including second blanks) were analysed during the study (for 100 flights). The results of the blank analysis are summarized in Appendix I and show that levels were low; for example, detectable amounts of TOCP, other TCPs and sum of TOCP and TCPs were detectable on only two blanks and TCE on none. The air sampling results summarized here have not been corrected for any amount of background contamination found on the blank tubes.

### *Each flight (based on mean of measured values during each flight)*

The mean VOC/SVOC air concentration for each flight was calculated from the measured concentration in each phase of flight. There are therefore 100 values for each target analyte; the properties of each of these data sets are summarized by statistical parameters shown in Table 5. Non-detects have been given a value of zero in the calculation of the mean values. As the sampling strategy involved more intense sampling during the early and late stages of flight than during cruise, this calculated mean may not be a true representation of the mean concentration particularly for a flight involving an extended cruise phase. It does, however, give an indication of the longer term mean concentration and therefore the exposure of crew through the duration of the flight.

Table 5. Mean and percentile concentrations of target chemicals based on mean concentration during each flight.

Compound (n=100)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	max
TOCP	ND	ND	ND	0.29	0.08	0.38	ND	2.5
Other TCPs	ND	ND	ND	0.44	0.15	0.74	ND	6.6
All TCPs	ND	ND	0.005	0.73	0.23	1.06	ND	8.0
TBP	ND	0.7	1.2	5.7	1.11	1.72	ND	8.2
Toluene	1.7	8.4	21.2	39.8	13.95	14.28	ND	70.1
m+p xylene	0.3	0.8	1.3	8.5	1.75	2.55	ND	11.3
Limonene	ND	2.2	6.1	37.0	11.68	42.88	ND	342.7
TCE	ND	0.1	0.6	1.5	0.43	0.67	ND	3.7
C <sub>11</sub>	ND	0.9	2.2	11.7	2.68	6.35	ND	47.1

***Each phase of flight (based on percentile, mean, minimum and maximum of each flight phase)***

As far as possible samples were collected in distinct phases of flight although the short duration of some phases during some flights meant that there was some overlap of phases. Where this occurred the data has been allotted to the phase during which sampling was initiated.

Tables 6a to 6i summarise the data for each analyte, broken down by phase of flight. All samples taken during an air quality event were summarised as one group of samples. Table 7 provides further information about these event samples. Arithmetic mean concentrations for each analyte during each phase of flight are presented graphically in Appendix J.

Highest concentrations of TBP, limonene, m+p-xylene and undecane occurred during first engine start, while TCE concentrations were highest during the ‘immediate’ sampling period. Highest levels of TOCP, other TCPs and toluene occurred during climb, pre-landing and take-off respectively. Concentrations of analytes determined during air quality events were broadly similar to values found during the sampling of flight phases and it is notable that all TCP measurements were non-detects.

Table 6a. Mean and percentile concentrations of TOCP for each flight phase.

Phase of flight	TOCPs Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	Max
Immediate (n=97)	ND	ND	ND	0.3	0.11	0.56	ND	4
First engine start (n=95)	ND	ND	ND	ND	0.09	0.51	ND	3.5
Taxi (n=94)	ND	ND	ND	ND	0.08	0.66	ND	6.4
Take off (n=97)	ND	ND	ND	ND	0.03	0.28	ND	2.8
Climb (n=94)	ND	ND	ND	ND	0.24	2.35	ND	22.8
Top of climb (n=95)	ND	ND	ND	ND	0.03	0.28	ND	2.7
Cruise (n=90)	ND	ND	ND	ND	0.08	0.82	ND	7.8
Start of descent (n=98)	ND	ND	ND	ND	0.03	0.32	ND	3.2
Pre-landing (n=98)	ND	ND	ND	ND	0.08	0.75	ND	7.4
Taxi-back (n=97)	ND	ND	ND	ND	0.03	0.24	ND	2.4
AQ event (n=25)	ND	ND	ND	ND	ND	-	ND	ND

Table 6b. Mean and percentile concentrations of Other TCPs for each flight phase.

Phase of flight	Other TCPs Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	max
Immediate	ND	ND	ND	0.6	0.14	0.90	ND	8.4
First engine start	ND	ND	ND	0.2	0.21	1.48	ND	14.0
Taxi	ND	ND	ND	ND	0.2	1.14	ND	10.4
Take off	ND	ND	ND	0.4	0.07	0.47	ND	4.6
Climb	ND	ND	ND	0.2	0.18	1.54	ND	14.9
Top of climb	ND	ND	ND	ND	0.07	0.50	ND	4.5
Cruise	ND	ND	ND	ND	0.20	1.86	ND	17.7
Start of descent	ND	ND	ND	ND	0.05	0.37	ND	3.4
Pre-landing	ND	ND	ND	0.4	0.32	2.87	ND	28.5
Taxi-back	ND	ND	ND	0.5	0.07	0.36	ND	2.5
AQ event	ND	ND	ND	ND	ND	ND	ND	ND

Table 6c. Mean and percentile concentrations of sum of TOCP and Other TCPs for each flight phase.

Phase of flight	Sum of TOCP and other TCPs concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	max
Immediate	ND	ND	ND	1.0	0.25	1.42	ND	12.5
First engine start	ND	ND	ND	1.0	0.30	1.92	ND	17.5
Taxi	ND	ND	ND	ND	0.25	1.47	ND	10.4
Take off	ND	ND	ND	0.5	0.10	0.75	ND	7.4
Climb	ND	ND	ND	0.2	0.42	3.89	ND	37.7
Top of climb	ND	ND	ND	ND	0.11	0.77	ND	7.3
Cruise	ND	ND	ND	ND	0.28	2.68	ND	25.5
Start of descent	ND	ND	ND	ND	0.09	0.67	ND	6.5
Pre-landing	ND	ND	ND	0.4	0.39	3.62	ND	36.0
Taxi-back	ND	ND	ND	0.6	0.09	0.43	ND	2.5
AQ event	ND	ND	ND	ND	ND	-	ND	ND

Table 6d. Mean and percentile concentrations of TBP for each flight phase.

Phase of flight	TBP Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	max
Immediate	ND	0.4	1.7	5.4	1.26	2.02	ND	11.7
First engine start	ND	1.0	2.2	9.1	2.06	3.57	ND	21.8
Taxi	ND	0.3	1.7	3.7	1.06	1.85	ND	12.0
Take off	ND	0.6	1.6	4.9	1.01	1.49	ND	7.1
Climb	ND	ND	1.0	5.0	0.80	1.42	ND	7.0
Top of climb	ND	ND	0.8	4.5	0.79	1.54	ND	9.1
Cruise	ND	ND	0.8	3.0	0.65	1.13	ND	6.6
Start of descent	ND	0.4	1.0	4.6	0.86	1.41	ND	6.6
Pre-landing	ND	0.5	1.2	6.1	1.08	1.82	ND	9.5
Taxi-back	ND	0.5	1.5	6.6	1.21	2.04	ND	10.3
AQ event	ND	ND	0.7	4.2	0.67	1.44	ND	5.8

Table 6e. Mean and percentile concentrations of toluene for each flight phase.

Phase of flight	Toluene concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	min	max
Immediate	2.6	7.1	13.8	31.1	11.62	15.03	ND	127.5
First engine start	4.2	15.2	35.0	82.9	26.00	29.47	ND	152.2
Taxi	ND	9.6	38.1	78.7	22.95	29.94	ND	159.0
Take off	ND	6.2	24.7	53.7	16.76	26.34	ND	170.2
Climb	ND	4.3	14.9	41.1	10.10	12.62	ND	57.6
Top of climb	ND	3.1	10.3	36.5	7.57	10.74	ND	45.7
Cruise	ND	3.4	11.5	40.9	8.00	11.74	ND	49.8
Start of descent	ND	3.6	12.4	41.2	9.38	14.89	ND	94.0
Pre-landing	ND	4.0	11.8	49.6	12.12	22.92	ND	150.8
Taxi-back	ND	7.1	16.5	59.4	13.80	17.32	ND	73.3
AQ event	0.4	10.1	19.1	82.4	17.69	25.03	ND	107.6

Table 6f. Mean and percentile concentrations of m+p-xylene for each flight phase.

Phase of flight	M+p-xylene concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
Immediate	ND	1.6	2.8	12.8	3.12	4.75	ND	29.6
First engine start	0.3	1.9	3.7	16.3	3.77	6.59	ND	52.3
Taxi	ND	1.3	2.3	13.2	2.72	3.95	ND	18.4
Take off	ND	0.6	1.5	11.2	1.77	3.11	ND	12.8
Climb	ND	ND	0.4	5.4	0.88	2.15	ND	10.7
Top of climb	ND	ND	0.3	4.6	0.73	1.88	ND	9.1
Cruise	ND	ND	0.3	4.5	0.71	1.68	ND	8.2
Start of descent	ND	ND	0.3	4.2	0.61	1.37	ND	6.7
Pre-landing	ND	ND	0.9	5.7	0.90	1.73	ND	7.1
Taxi-back	ND	1.0	2.9	13.3	2.37	3.46	ND	16.3
AQ event	ND	1.0	1.9	14.1	2.51	4.61	ND	16.8

Table 6g. Mean and percentile concentrations of limonene for each flight phase.

Phase of flight	Limonene concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
Immediate	ND	1.9	7.0	49.7	13.77	51.64	ND	414.4
First engine start	ND	2.7	6.7	54.2	16.46	64.78	ND	540.3
Taxi	ND	2.2	9.7	50.4	16.94	65.33	ND	487.3
Take off	ND	1.0	2.9	53.3	11.88	40.76	ND	330.3
Climb	ND	1.3	5.3	36.5	12.25	48.66	ND	405.2
Top of climb	ND	1.0	5.8	27.8	9.97	39.30	ND	328.2
Cruise	ND	1.3	7.2	36.3	12.16	40.68	ND	300.0
Start of descent	ND	1.0	5.3	25.1	7.64	27.67	ND	230.9
Pre-landing	ND	1.2	6.6	33.2	8.80	32.72	ND	276.8
Taxi-back	ND	1.5	6.5	37.8	10.31	38.53	ND	324.3
AQ event	ND	0.5	8.3	35.0	6.78	11.20	ND	36.4

Table 6h. Mean and percentile concentrations of TCE for each flight phase.

Phase of flight	TCE concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
Immediate	ND	ND	0.6	2.2	0.65	2.12	ND	20.1
First engine start	ND	0.5	1.3	3.1	0.89	1.45	ND	10.2
Taxi	ND	ND	0.8	2.2	0.51	0.84	ND	4.2
Take off	ND	ND	0.5	2.2	0.39	0.71	ND	3.2
Climb	ND	ND	0.3	1.7	0.35	1.03	ND	8.4
Top of climb	ND	ND	0.2	1.2	0.23	0.54	ND	3.5
Cruise	ND	ND	0.4	1.2	0.25	0.50	ND	3.02
Start of descent	ND	ND	0.2	1.3	0.22	0.45	ND	1.8
Pre-landing	ND	ND	0.4	1.5	0.31	0.61	ND	3.5
Taxi-back	ND	ND	0.7	1.9	0.54	0.87	ND	4.9
AQ event	ND	ND	0.8	1.0	0.36	0.45	ND	1.3

Table 6i. Mean and percentile concentrations of undecane for each flight phase.

Phase of flight	Undecane concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
Immediate	ND	1.0	3.2	18.0	4.02	8.88	ND	49.7
First engine start	ND	2.2	4.5	17.4	4.49	10.68	ND	87.3
Taxi	ND	1.2	3.0	18.7	3.71	8.87	ND	55.1
Take off	ND	0.6	2.5	19.6	3.13	9.30	ND	70.1
Climb	ND	ND	1.4	11.6	1.92	6.18	ND	45.0
Top of climb	ND	ND	0.7	8.6	1.39	4.61	ND	32.4
Cruise	ND	ND	0.9	8.3	1.46	4.52	ND	30.4
Start of descent	ND	ND	0.8	6.6	1.21	3.46	ND	23.1
Pre-landing	ND	ND	0.9	10.0	1.61	4.93	ND	34.2
Taxi-back	ND	0.8	3.0	32.4	4.33	9.51	ND	49.2
AQ event	ND	ND	2.6	24.3	3.30	8.39	ND	35.2

Table 7 lists all the air quality events recorded on the sample record form by the researcher. Those appearing under “Taxi-back” were taken at various times after landing, often when the aircraft was parked and doors open. They may therefore represent entrainment of ambient air and odours from, for example, refuelling. Of these thirty events, five are omitted from the tabulated concentration data for the following reasons: no TD/GC/MS data available due to instrument failure in the laboratory (3); experimental error – sample taken using incorrect tube (1)<sup>1</sup>; apparent air quality event was the result of IPA from incorrectly positioned particle counter (1)<sup>2</sup>.

These thirty events were distributed over twenty-five flights. Twenty-one flights experienced a single air quality event; three flights experienced two; and a single flight had three events recorded. Numbers of events were similar in Parts 1, 2, 3 and 5 and highest in Part 4. Leaving aside the events listed under Taxi in (see above) the highest numbers occurred during Engine start and Take-off. Notes by the researcher on the sampling record form reported the presence of odour (or smell), such as ‘oily’ and ‘fuel smell’ (none reported smoke), associated with 19 of the air quality events; others reported changes in the TVOC or ultrafine particle number as reasons for initiating the sample (one event has no associated comment).

<sup>1</sup> It remains unclear exactly how this came about. The rogue tube became associated with the correct tubes while they were being prepared for sampling. The restricted conditions, including poor light, on the flight deck meant that this error was not detected by the researcher.

<sup>2</sup> The Sampling Record form for this flight shows that the researcher moved the PID to the other side of the cabin immediately following the apparent event: this caused the VOC reading to fall suggesting that IPA from the particle counter was being sampled by the PID. The relevant TD tube was nonetheless analysed and the data incorporated into Part 2 of this report.

Table 7. Number of air quality events sampled during the study.

Part	Phase of flight										
	Immediate	Engine start	Taxi	Take off	Climb	Top of climb	Cruise	Start descent	Pre-landing	Taxi back	Total
1						1		1	1	1	4
2		3		2							5
3		2		1				2			5
4	1	1		2	2		2		2	1	11
5			2							3	5
Total	1	6	2	5	2	1	2	3	3	5	30

***Each Part of study (i.e. aircraft type) based on all measurements in flight***

Tables 8a-e provide a breakdown of the VOC/SVOC data for each Part of the study. Part 3 is notable for the relatively high levels of limonene and for being the only Part with all TCP measurements being non-detects. Toluene concentrations were relatively low in Part 2. The maximum TOCP and ‘sum of TOCP and other TCPs’ values occurred in Part 2, whilst the highest ‘Other TCPs’ occurred in Part 1. The maximum toluene and TBP concentrations were also in Part 1. The maximum undecane and TCE concentrations occurred in Part 3 and the maximum m+p-xylene in Part 5. Figure 1 illustrates the arithmetic mean concentrations for TBP. Appendix K-1 presents graphs of this type for all analytes.

Table 8a. Part 1 (Boeing 757 cargo; 20 Flights).

Compound (n = 190)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
TOCP	ND	ND	ND	2.6	0.24	1.01	ND	7.8
Other TCPs	ND	ND	ND	2.8	0.57	2.85	ND	28.5
Sum of TOCP and other TCPs	ND	ND	ND	5.7	0.81	3.74	ND	36.0
TBP	ND	2.4	4.9	9.1	3.18	3.34	ND	21.8
toluene	ND	1.2	5.2	20.2	6.21	19.00	ND	170.2
m+p xylene	ND	0.	1.5	3.6	0.93	1.40	ND	9.2
limonene	ND	ND	1.0	1.8	0.65	1.83	ND	20.5
TCE	ND	ND	ND	1.4	0.21	0.61	ND	4.7
C <sub>11</sub>	ND	ND	0.6	2.7	0.53	1.37	ND	12.6

Table 8b. Part 2 (Boeing 757 passenger; 20 Flights).

Compound (n=202)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
TOCP	ND	ND	ND	ND	0.14	1.66	ND	22.8
Other TCPs	ND	ND	ND	ND	0.09	1.07	ND	14.9
Sum of TOCP and other TCPs	ND	ND	ND	ND	0.24	2.73	ND	37.7
TBP	ND	ND	ND	1.1	0.14	0.38	ND	1.9
toluene	ND	1.2	3.7	9.9	2.51	3.37	ND	18.4
m+p xylene	ND	0.2	1.1	4.3	0.88	1.60	ND	8.4
limonene	ND	0.4	1.5	6.2	2.01	10.77	ND	150.7
TCE	ND	ND	0.4	1.9	0.36	0.86	ND	6.1
C <sub>11</sub>	ND	ND	0.6	3.1	0.57	1.38	ND	14.7

Table 8c. Part 3 (Airbus A320/1; 20 Flights).

Compound (n=191)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
TOCP	ND	ND	ND	ND	ND	ND	ND	ND
Other TCPs	ND	ND	ND	ND	ND	ND	ND	ND
Sum of TOCP and other TCPs	ND	ND	ND	ND	ND	ND	ND	ND
TBP	ND	0.7	1.0	1.7	0.63	0.65	ND	2.9
toluene	2.2	6.5	12.5	27.8	10.15	12.33	ND	82.8
m+p xylene	ND	0.3	1.1	2.3	0.64	0.81	ND	3.4
limonene	7.3	19.5	37.8	300.0	51.49	92.96	ND	540.3
TCE	ND	ND	ND	1.1	0.34	1.78	ND	20.1
C <sub>11</sub>	ND	3.1	9.0	40.1	8.42	13.66	ND	87.3

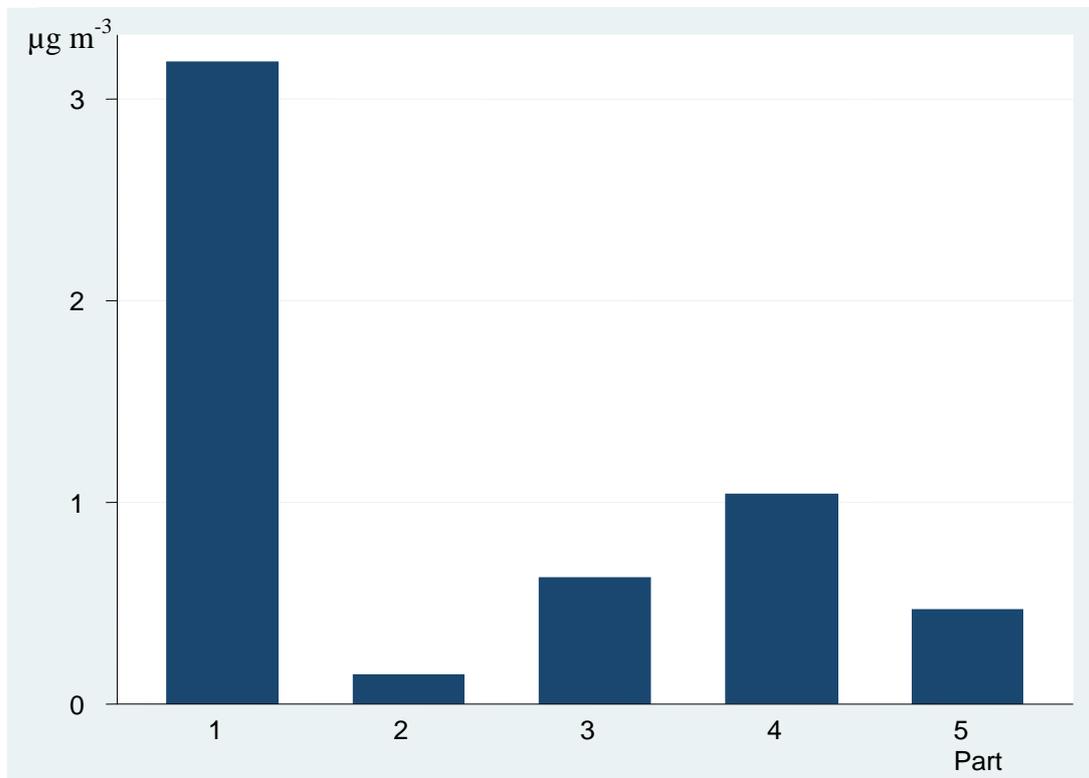
Table 8d. Part 4 (BAe 146 Passenger; 20 Flights).

Compound (n=194)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
TOCP	ND	ND	ND	ND	0.002	0.02	ND	0.2
Other TCPs	ND	ND	ND	ND	0.02	0.13	ND	1.37
Sum of TOCP and other TCPs	ND	ND	ND	ND	0.02	0.14	ND	1.4
TBP	ND	0.7	1.8	3.3	1.04	1.28	ND	9.1
toluene	6.0	22.4	42.4	82.5	30.42	27.7	ND	159.0
m+p xylene	ND	ND	0.9	2.9	0.77	2.32	ND	29.6
limonene	ND	3.6	6.5	15.0	4.99	7.66	ND	83.5
TCE	ND	ND	0.7	2.1	0.49	0.81	ND	4.9
C <sub>11</sub>	ND	ND	0.9	3.2	0.81	1.91	ND	18.3

Table 8e. Part 5 (Airbus A319; 20 Flights).

Compound (n=203)	Concentration $\mu\text{g m}^{-3}$							
	10%	50%	75%	95%	AM	SD	Min	max
TOCP	ND	ND	ND	ND	0.007	0.06	ND	0.7
Other TCPs	ND	ND	ND	0.5	0.04	0.22	ND	2.5
Sum of TOCP and other TCPs	ND	ND	ND	0.5	0.05	0.27	ND	3.2
TBP	ND	0.4	0.7	1.7	0.47	0.63	ND	5.6
Toluene	3.1	14.4	23.5	55.4	20.19	21.50	ND	152.2
m+p xylene	ND	4.2	8.6	15.6	5.46	6.02	ND	52.3
limonene	ND	0.2	2.2	4.6	1.44	2.38	ND	22.0
TCE	ND	0.5	1.1	1.9	0.74	0.67	ND	3.5
C <sub>11</sub>	ND	1.2	3.2	16.1	3.48	7.26	ND	49.2

Figure 1. Arithmetic mean TBP concentration ( $\mu\text{g m}^{-3}$ ) during each Part of the study.



### *Ultrafine particle count*

Numbers of ultrafine particles in air were monitored continually during the flight with a value logged each second. Table 9 summarises the data with respect to the mean, minimum and maximum values recorded for each flight sector. The maximum count of the instrument is 500,000 particles  $\text{cm}^{-3}$  and this value was recorded as the maximum reading at some timepoint during five flights. Three of these highest readings occurred during Part 1 and two during Part 4.

Figure 2 shows the ultrafine particle count for one flight during which the maximum count recorded exceeded 500,000 particles  $\text{cm}^{-3}$ . This occurred during the ‘immediate phase’. ‘Engine on’ was at 10:02 h. During ‘take off’, at 10:18 h, there was a smaller peak in particle number. Particle numbers remained low during cruise, with a small increase after ‘taxi-back’ which occurred at 11:41 h. No air quality event was recorded during this flight. It can be seen that the main peak in concentration occurred for only a few minutes.

Table 9. Summary of ultrafine particle counts expressed as number of flight sectors with counts in defined ranges of particle number (data for 100 sectors).

Number of Particles $\text{cm}^{-3}$	0-100	101-1,000	1,001-10,000	10,001-50,000	50,001-100,000	100,001- >500,000
Minimum	95	5	0	0	0	0
Mean (for duration of flight)	0	0	63	34	3	0
maximum	0	0	0	13	22	65*

\*5 of the 65 were >500,000 particles  $\text{cm}^{-3}$

Figure 2. Ultrafine particle concentration (particle  $\text{cm}^{-3}$ ) during a Part 4 flight on 9/12/09.

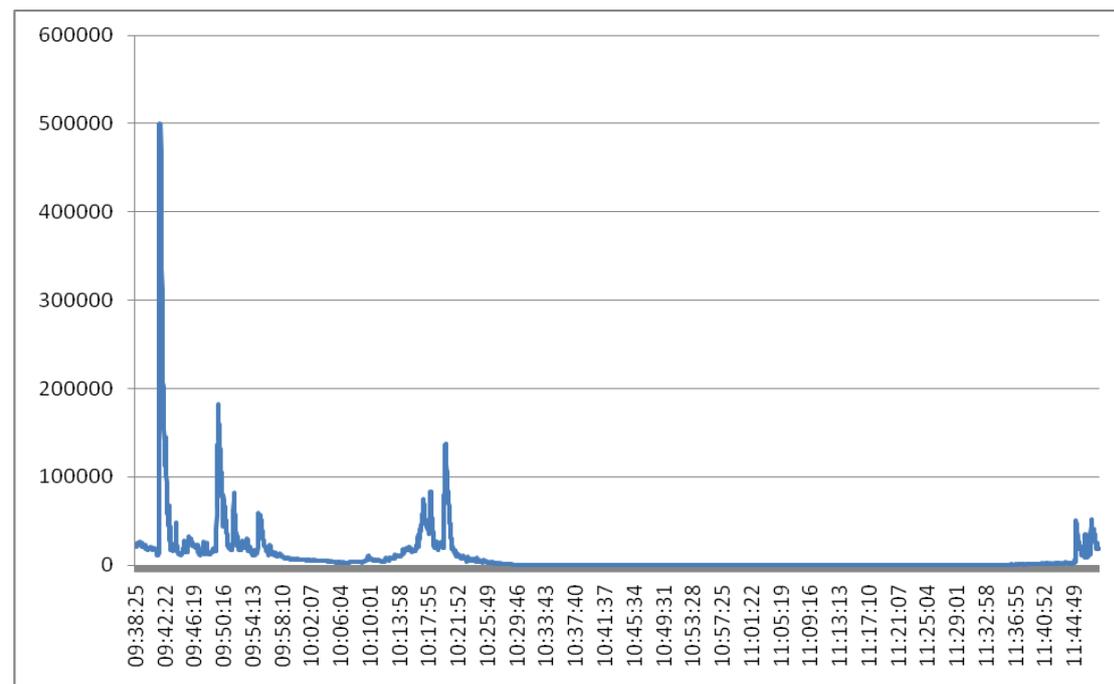


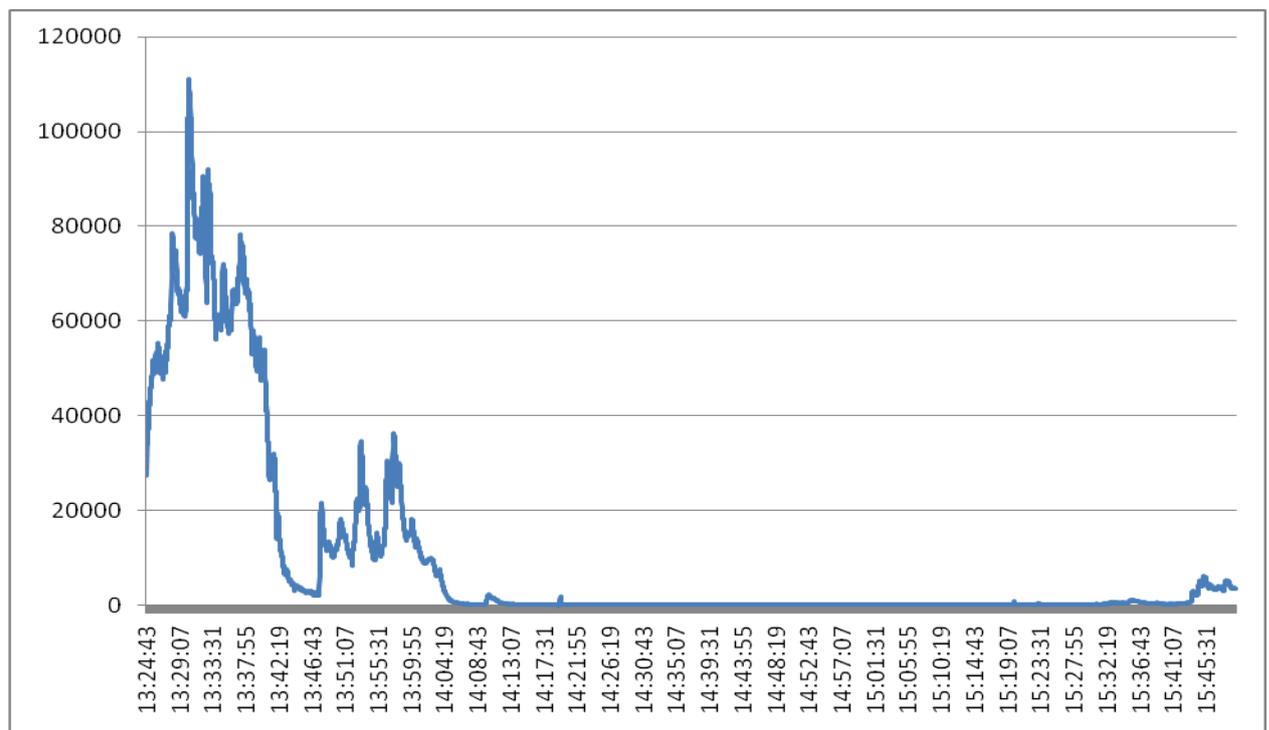
Table 9A shows the particle count data for the 25 flights during which air quality events were reported by the researcher. These indicate that ultrafine concentrations during these flights were not exceptional and none had maximum levels exceeding 500,000.

Table 9A. Summary of ultrafine particle counts for flights with an air quality event.

Number of Particles $\text{cm}^{-3}$	0-100	101-1,000	1,001-10,000	10,001-50,000	50,001-100,000	100,001- >500,000
minimum	24	1	0	0	0	0
mean	0	0	12	12	1	0
maximum	0	0	0	1	5	19

Figure 3 is an example of a flight with a reported air quality event, described in this instance as an oily odour during engine start. In this case the highest particle count occurred in the immediate phase and before engine start which was at 13:48 h. There are smaller peaks associated with engine start which decline at about the time of 'take off' at 14:01 h. Particle counts remain low during cruise, with a small increase at 15:43 which was after the 'taxi-back' tube sampling.

Figure 3. Ultrafine particle number during a Part 2 flight on 29/10/08.



### ***Total VOC by PID***

Total VOC readings were logged continuously (each second) during the flights using the PID. Table 10 summarises the maximum values found during each flight sector. Instrument failure prevented collection of data during 10 flights.

Table 10. Maximum values of total VOC.

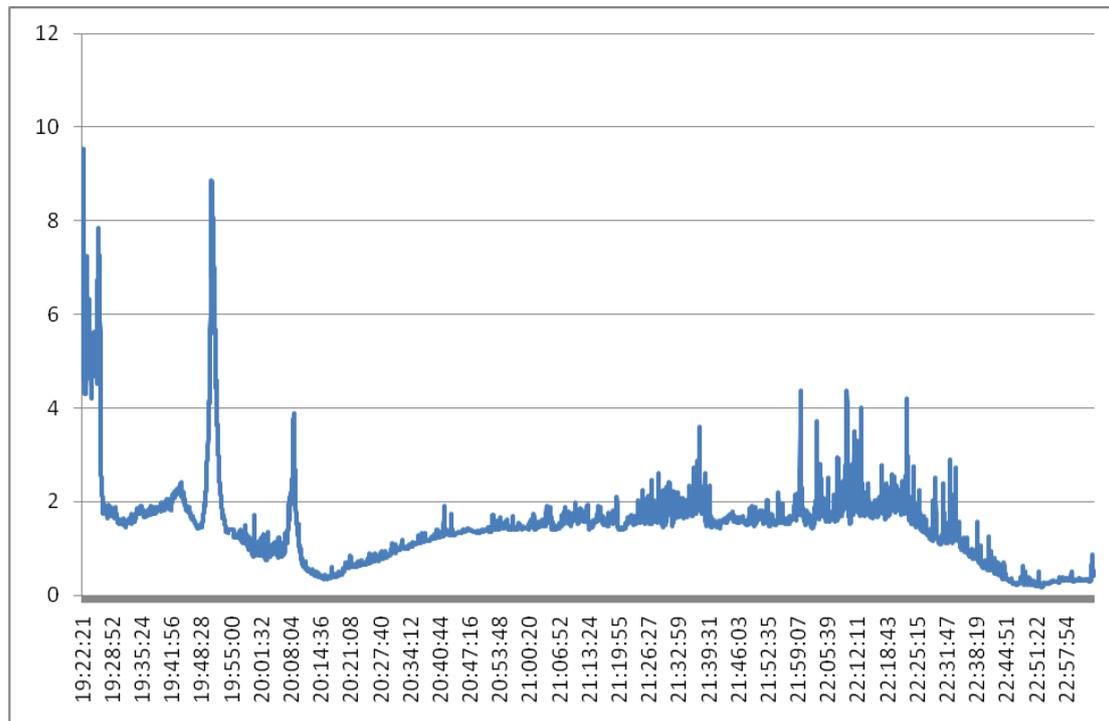
Total VOC ppm	0-2	2-4	4-6	6-10	>10
Number of sectors (n)	34	27	5	5	19

Peak concentrations of more than 10 ppm were recorded during 19 flights. The only air quality event recorded on these 19 flights occurred during taxi out. The associated sorbent tube was analysed but the data are not included in the statistical analysis but will be presented in Part 2 of the report: See Footnote 2 on page 22.

The peaks were short term events (lasting a few minutes or less) and mean concentrations were mostly less than 2 ppm, with the highest mean value being 3.5 ppm for the 19 flights with the highest peak concentrations. Thirteen of these peak (>10 ppm) concentrations occurred during the 'immediate / taxi out' phase of the flight. The researcher noted on the sampling record forms for the flights with two of the four highest readings (539 and 39.1 ppm) that the air outlet of the p-Trak containing IPA vapour may have influenced the PID. The third highest peak (55.6 ppm) was coincident with the reported switching on of the p-Trak. While the researchers tried to avoid close proximity of the p-Trak and PID, the confines of the available space in the cockpit made this difficult, particularly during instrument placement at the start of the flight sector. The second highest reading (123 ppm) occurred during the taxi back phase and was not associated with any recorded AQ event. The reading was recorded just as the PID was switched off following a rise in concentration during the previous 2 minutes.

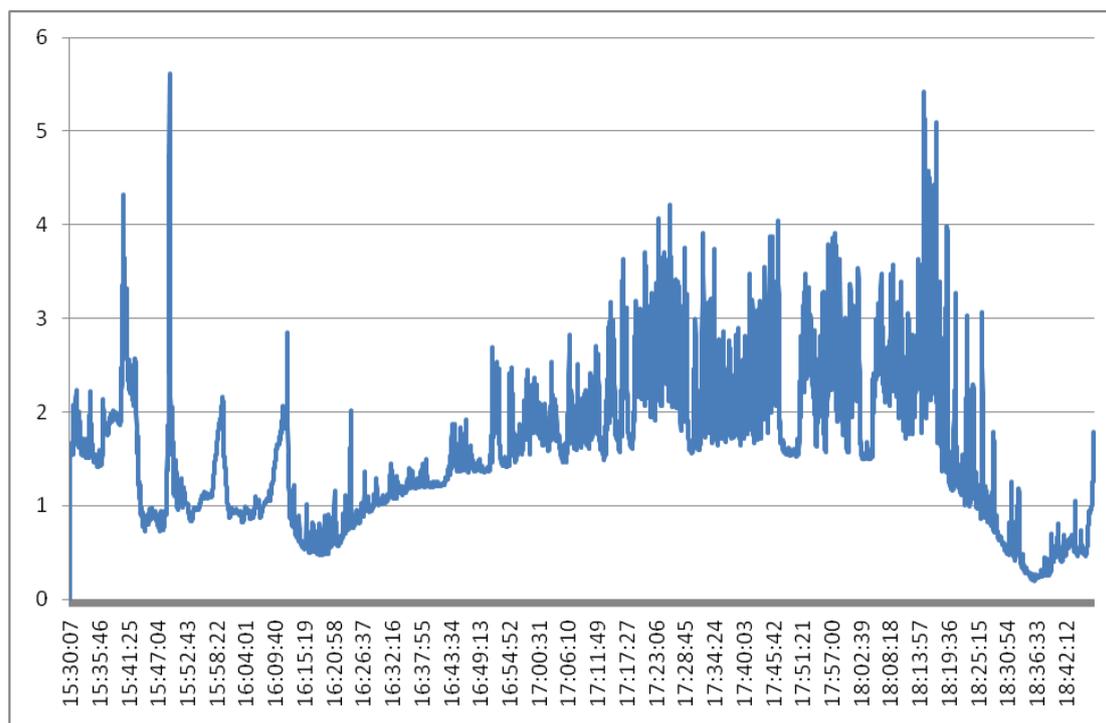
The possibility that exposure to IPA vapour may explain some of the peaks in total VOC concentration is a confounder in the interpretation of the data. While the results show that the VOC PID data is not a clear indicator of the air quality events, there is some evidence for an association between the PID value and some types of air quality event. Figure 4 shows the trace for a Part 3 flight where the researcher collected an event sample and reported an oily smell. The event sample collection began at 19:48h (at engine start) and this coincides with a peak in the PID VOC trace (although this was not the maximum concentration recorded, which occurred when the instrument was switched on).

Figure 4. Total VOC concentration (ppm) during a Part 3 flight on 25/10/09 determined by the PID.



A further example is another report of an oily odour, also during engine start of a Part 3 flight, and the researcher duly collected an air quality event air sample, at 15.59. This coincides with a total VOC peak, but clearly a number of other peaks occurred during the flight that were not associated with an air quality event (Figure 5). Also data could be illustrated for other flights where there is no evidence of an increase in the total VOC concentration coincident with a reported air quality event.

Figure 5. Total VOC concentration (ppm) during a (another) Part 3 flight on 25/10/09 determined by the PID.



### *CO by electrochemical sensor*

CO readings were logged continuously (value recorded every second) during the flights. Table 11 summarises the maximum values found during each flight sector. Instrument failure (memory fault requiring repair by manufacturer) prevented collection of data during 10 flights. In a further 9 flights there was some form of instrument malfunction (see table 11 footnote).

Table 11. Maximum values of CO (ppm).

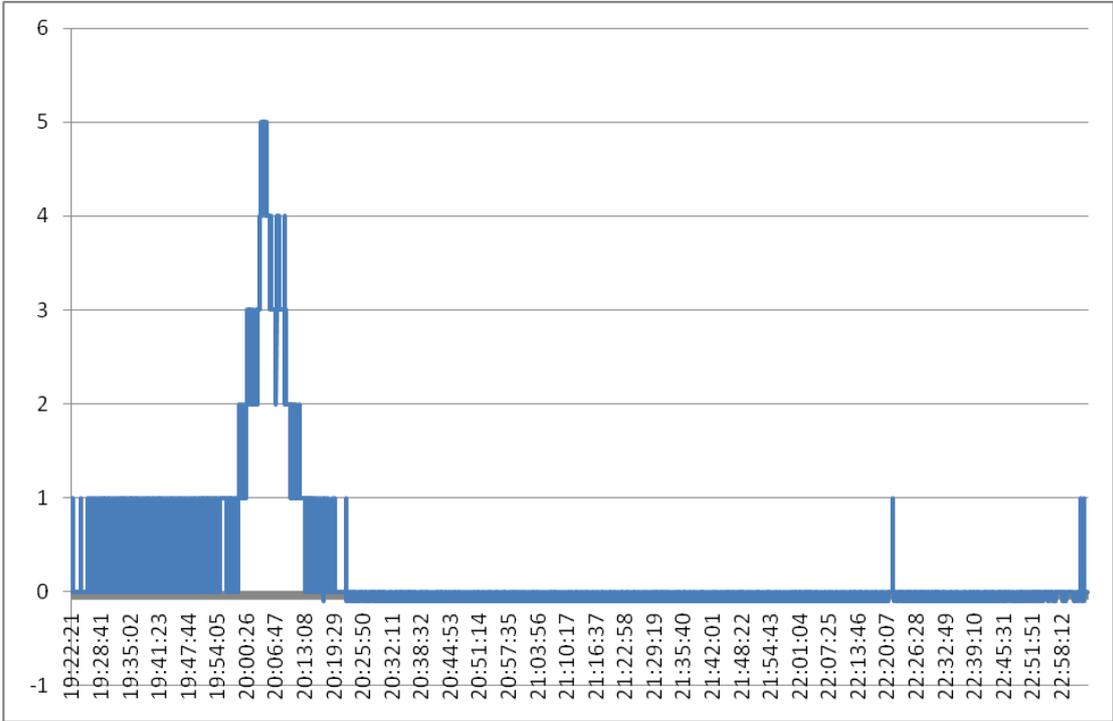
CO ppm	<1	1	2	3-5	>5
Number of sectors (n)	6	45	23	6	1*

\*A further 9 sectors had values >5 ppm, but equipment malfunction is strongly suspected. All occurred as a sequential block in Part 4, and in each case the instrument recorded a constant level of 9-10 ppm throughout almost the entire flight. Since this deviation of  $\pm 1$  ppm is within the analogue-to-digital conversion “jitter” of the instrument, the likelihood of this being a correct estimate of flight deck CO concentration is extremely small.

Of the 7 flights with maximum concentrations of >3 ppm, an air quality event was reported by the researcher on two flights. On one of these (the same flight as illustrated in Figure 4) the peak (5 ppm) occurred during taxi out/take off and not during engine start (Figure 6). In the other case, a peak of 7 ppm occurred during taxi back; this was of about 5 minutes duration (i.e. period when readings were >3ppm) and was immediately before an air event sample was

collected in response to a reported fuel odour when doors were opened. There does not, therefore, seem to be a direct link between the CO peak and the air quality event.

Figure 6. CO concentration (ppm) during a Part 3 flight on 25/10/09.



### ***Questionnaire reports of fume/smell events***

At least one questionnaire was completed for 96 of the 100 flights and the total number completed was 552. It should be noted that these questionnaires were completed at the end of the flight and were completed by all crew, not only those present on the flight deck where air sampling was conducted.

A total of 38 flights had fumes/smells reported on the post flight questionnaires by at least one crew (flight and cabin) member or researcher. This is greater than the number of air quality events listed in Table 7 which addresses only those identified by the researcher in the cockpit at the time of sampling. It is quite plausible that fumes/smells may be experienced by crew in parts of the aircraft that are not experienced on the flight deck because the air supply to the flight deck is normally separate from the supply to other areas of the aircraft, and there may be local sources of fume/smell such as toilets and ingress of air through open doors when on the ground. Also people have different sensitivities to smell and therefore a larger number of people may be expected to detect more events.

None of the fume/smell events reported in the questionnaires triggered the formal airline reporting mechanism. Table 12 shows the number of flights with at least one questionnaire completed, the total number of questionnaires completed and the number with reports of a smell/fume for each Part of the study. It should be noted that numbers of crew differ between Parts and flights and that the number of returns was dependent upon the co-operation of the crew (in some cases there were practical difficulties because of tight time schedules between flights).

Some flights had more than one person (up to three) reporting a smell/fume and others had only one person; a total of 60 questionnaires contained a report of the occurrence of a smell/fume during the flight. Some flights had reports of smells in more than one phase, there being two reports of the smell of human waste throughout the flight. Others reported fumes/smells during only one phase. Four of the fumes/smells were reported by the respondents to have a 'health effect', in all cases this was headache/slight headache. The highest percentage of questionnaires reporting a smell/fume was 16% for Part 2; the lowest was 4% for Part 5.

The dominant smell descriptor was oil/oily; this was used to describe the fume/smell in 26 questionnaires. Other descriptors were sweet, toilet smell, exhaust, chlorine, de-icing fluid, fuel, heated dust and human waste.

Table 12A represents the number of smell/fume events occurring during each phase of flight (reported by at least one crew member or researcher; two or more persons reporting an event at the same location and phase is counted as only one report), broken down by aircraft type (i.e. Part of study). This shows that the greatest number of reported smells/fumes occurred during engine start, taxi out and take off.

Table 12. Questionnaires completed by crew members (including the researcher) during each Part of the study.

Part	Flights with questionnaire returned	Total no. of questionnaires	No. with smell / fume reported	% with report of smell/fume
1	20	62	7	11%
2	20	154	25	16%
3	20	172	20	12%
4	17	69	4	6%
5	19	95	4	4%
Total	96	552	60	11%

Table 12A. Fume/smell events reported in each phase of flight.

Part	Phase of flight										Total
	Immediate	Engine start	Taxi out	Take off	Climb	Top of climb	Cruise	Start descent	Pre-landing	Taxi in	
1	0	0	0	2	1	0	0	2	2	2	9
2	0	6	8	7	3	0	0	0	0	0	24*
3	0	5	6	0	1	0	1	1	2	0	16*
4	0	0	1	0	0	0	0	2	1	0	4
5	0	0	1	1	0	0	0	0	0	2	4
Total	0	11	16	10	5	0	1	5	5	4	57

\*Plus one report of smell of human waste throughout flight

## 5 Discussion

Measurements were successfully undertaken during 100 flight sectors that included both cargo and passenger aircraft and five main different aircraft types. The study was conducted according to the intended sampling strategy. Data capture was very high, with failure of the CO and PID instrument on nine and ten flights respectively (and uncertainty about reliability of the CO data on a further 9) being the most notable data losses. The following discussion compares the measured concentrations with available health, safety and comfort guidelines as well as with concentrations in other indoor environments that have been reported in some peer reviewed publications.

### *All data*

The European standard 'Aircraft internal air quality standards, criteria and determination methods' (BS EN 4618: 2009) was prepared by the Aerospace and Defence Industries Association of Europe - Standardization (ASD-STAN) in order to specify requirements and methods for determination of air quality in newly certificated commercial passenger aircraft. It may also be applied to current production aircraft, should it be shown to be technically feasible and economically justifiable. The standard distinguishes between safety, health and comfort conditions for passengers and crew under a variety of phases of flight, including embarkation and disembarkation. The standard is intended for use in the design, manufacturing, maintenance and normal operation of commercial aircraft; the persons under consideration include both passengers and crew but exclude individuals with pre-existing infirmity or ill-health. Two of the substances determined in the present study are included in the standard (Table 13). Three types of limits for these substances are provided;

- safety limits - limits for cabin environment parameters that if exceeded would prevent the safe operation of the aircraft,
- health limits - limits for cabin environment parameters that if exceeded would lead to temporary or permanent pathological effects to the occupants,
- comfort limits - limits for cabin environment parameters that if exceeded would not achieve an acceptable cabin environment.

Table 13. Substances with limits in air specified in BS EN 4618.

substance	concentration		
	safety limits	health limits	comfort limits
Carbon monoxide	58.1 mg m <sup>-3</sup> (50 ppmv) peak value	29.1 mg m <sup>-3</sup> (25 ppmv) TWA 1 h; 11.6 mg m <sup>-3</sup> (10 ppmv) TWA 8 h.	-
Toluene	760 mg m <sup>-3</sup> (200 ppmv) (15 min exposure)	190 mg m <sup>-3</sup> (50 ppmv) (8 h exposure)	153 mg m <sup>-3</sup> (40 ppmv)

Two further substances monitored and quantified are referred to in the standard but no limit values are provided; these are ultrafine particles and tricresyl phosphate (TCP). The standard states that typical values for ultrafines found in the cabin of a taxiing aircraft are 100,000-300,000 particles cm<sup>-3</sup> and that in general, levels less than 500 particles cm<sup>-3</sup> have been measured during cruise; peaks in concentration have been associated with taxiing, galley usage and food preparation. TCP is described as a substance that if present is a marker of oils, lubricants and hydraulics.

The total VOC concentration measured by the PID comprises a mixture of a wide range of VOC compounds. There are no health and safety limits for concentrations of mixtures of unknown composition. If the PID response was due to a single compound, a relative response factor could be applied to determine the concentration of that compound. As with the measurement of ultrafine particle count, the PID was used to inform the identification of ‘air quality events’ rather than providing data that could be compared with health based standards or guidelines for air quality. As highlighted in the results section, there is the possibility of some peak PID readings arising through close proximity to the outlet of the p-Trak ultrafine counter, although precautions were taken to minimise this occurrence as far as possible.

The results of monitoring in the present study show that levels of carbon monoxide did not exceed safety or health limits. Concentrations recorded during nine flights were equivalent to the 8 h TWA health limit but instrument malfunction is strongly suspected (the minimum concentration was 9-10 ppm for the whole period that data was logged; it is considered likely that actual concentrations were in the range 0-3 ppm).

All measurements of toluene undertaken using sorbent tubes were well below the comfort limit of 153 mg m<sup>-3</sup> in the BS standard, the maximum concentration of toluene measured during flight being 0.17 mg m<sup>-3</sup>.

For compounds without defined limit values in BS EN 4618, other limits and guidelines can be considered in order to assess the significance of any risk to health of exposure to the concentrations measured in the cabin air. Table 14 lists the UK workplace exposure limits (WEL) for an 8 hour exposure period set by the UK Health and Safety Executive for occupational environments (HSE 2005) for several of the substances monitored. These are appropriate for the protection of the health of a working adult exposed in a workplace and are not applicable to other groups such as children or elderly persons or to other environments that are not workplaces. It is of note that for substances detected in the aircraft, the measured concentrations were lower than these exposure occupational limits and standards. The nearest concentration to any of the WELs was for TOCP where the maximum 5 minute mean concentration recorded by sorbent tube sampling was 0.02 mg m<sup>-3</sup> and the 8 hour TWA is 0.1 mg m<sup>-3</sup>. This concentration was measured during the climb phase of a flight in Part 2 of the study. There was no air quality event sample taken and no report of smell/fume by the flight crew or researcher recorded in the questionnaires. TOCP concentrations during all other phases of this flight were below the quantification limit (as was the travel blank).

The highest concentration of other TCPs occurred during the pre-landing phase of a flight in Part 1 of the study. Other TCPs were present in 5 other phases of this flight at a lower level and the travel blank was below the quantification limit. There was no air quality event sample taken and no report of smell/fume by the flight crew or researcher recorded in the questionnaires.

Table 14. Summary of WEL for substances monitored and quantified without a limit value in BS EN 4618.

Compound	UK 8h WEL mg m <sup>-3</sup>	UK 15 min WEL mg m <sup>-3</sup>
o-m-p isomers of xylene or mixture	220 (50 ppm)	441 (100 ppm)
tetrachloroethylene	345 (50 ppm)	689 (100 ppm)
TBP	5	5
TOCP	0.1	0.3

There are no UK air quality standards for individual VOCs or CO for non-occupational indoor environments. There are however a number of guidelines that have been recommended by different groups in the UK, EU and WHO and those for substances monitored and quantified in the present study are shown in Table 15.

Table 15. Indoor air quality guidelines recommended by the WHO, EU and in the UK.

Pollutant	Recommended exposure limit
Limonene	Kotzias et al., (2005); 450 $\mu\text{g m}^{-3}$ long term exposure.
Tetrachloroethylene	WHO (2000); 8,000 $\mu\text{g m}^{-3}$ with an averaging time of 30 minutes based on sensory effects or annoyance reactions.
Toluene	Kotzias et al. (2005); 300 $\mu\text{g m}^{-3}$ weekly average, acute 15,000 $\mu\text{g m}^{-3}$ . WHO (2000); 260 $\mu\text{g m}^{-3}$ with an averaging time of 1 week based on effects other than cancer or odour/annoyance, 1,000 $\mu\text{g m}^{-3}$ with an averaging time of 30 minutes based on sensory effects or annoyance reactions.
Xylenes (C <sub>8</sub> H <sub>10</sub> ) meta (m-), para (p-) and ortho (o-)	Kotzias et al., (2005); chronic exposure limit 200 $\mu\text{g m}^{-3}$ , Short-term limit 20 $\text{mg m}^{-3}$ .
Carbon monoxide	WHO (2000); 100 $\text{mg m}^{-3}$ (87 ppm) for 15 minutes averaging time, 60 $\text{mg m}^{-3}$ (52 ppm) for 30 minutes averaging time, 30 $\text{mg m}^{-3}$ (26 ppm) for 1 hour averaging time, 10 $\text{mg m}^{-3}$ (9 ppm) for 8 hours averaging time. WHO (2010) retained 15 min and 8 h values. Modified 1 h value to 35 $\text{mg m}^{-3}$ (31 ppm) and introduced new 24 h guideline of 7 $\text{mg m}^{-3}$ (6 ppm). DCLG (2006); same values as WHO (2000). COMEAP (2004); same values as WHO (2000).

The 30 minute WHO guideline value for toluene was not exceeded. Concentrations of TCE, xylenes and toluene did not exceed any guideline values. One measurement of limonene (during Part 3 of the study) exceeded the long term exposure limit recommended by Kotzias et al., (2005); however, this short term concentration would have a small impact on the longer term average exposure. The WHO 8 hour TWA guideline for CO is effectively equivalent to the BS health limit and therefore the earlier discussion applies with regard to this WHO guideline. The 2010 WHO 24 hour guideline value was attained for a period of a few minutes during one flight.

It is informative to compare the substances monitored with available data for concentrations in normally occupied homes to consider how exposure during flight compares with the home, where most people spend the majority of their time. There is an extensive worldwide literature on the occurrence of some airborne contaminants in buildings, particularly VOCs, formaldehyde and inorganic gases formed by combustion. As examples of studies of indoor pollutants in developed countries, a number of major UK studies are summarized below. With respect to absolute concentrations of pollutants and implications for health the situation in the UK is similar to many developed countries particularly those having a temperate climate.

The first major study of indoor air pollutants in the UK determined concentrations of a range of substances in 174 homes over a 12 month period in Avon, South West England (Berry et al., 1996). All participants were expectant mothers when they joined the study which was conducted between 1990 and 1993. Measurements of chemicals and gases were by diffusive samplers providing data for average concentrations over periods ranging from 3 days to 4 weeks. Table 16 summarises the concentrations in main bedrooms of the substances that were measured in the current study of aircraft cabins.

Table 16. Air pollutants in homes in the ALSPAC study (Berry et al., 1996).

Compound	Annual mean concentration $\mu\text{g m}^{-3}$			
	Indoors			Outdoors
	mean	10th percentile	95 th percentile	mean
toluene	40	14	73	12
undecane	14	10	69	6

### *National survey of indoor pollutants in homes*

In the late 1990s a nationally representative survey was undertaken to determine concentrations of a number of indoor pollutants in homes in England. This involved the measurement of  $\text{NO}_2$ , CO, formaldehyde and VOC concentrations using diffusive samplers in over 800 homes (Raw et al., 2004). CO was monitored for two weeks in the kitchen. VOCs were determined by diffusive sampling tubes with an exposure period of four weeks. The concentration determined by the diffusive method is the mean concentration for the exposure period. TVOC (total VOCs determined by TD/GC/MS) concentrations were determined as well as the concentration of 22 individual VOCs.

Table 17 summarises results for some pollutants. CO levels were higher in autumn and winter than spring and summer and the highest levels in kitchens were associated with the presence of a gas oven for cooking.

Table 17. Air pollutants in bedrooms of English homes (Raw et al., 2004).

Compound	concentration $\mu\text{g m}^{-3}$		
	GM	10th percentile	95th percentile
CO	390 (0.34 ppm)	120 (0.10 ppm)	1680 (1.45 ppm)
Toluene	15.1	4.4	74.9
m/p xylene	3.8	0.9	30.3
undecane	2.6	0.5	33.6
limonene	6.2	1.3	51

GM = geometric mean

The national survey determined average concentrations of pollutants over periods of days to weeks and did not consider short term peak concentrations which are also a potential health concern. To address this issue, at least for CO and  $\text{NO}_2$ , a separate study of 73 gas cooking homes was undertaken using continuous monitoring methods (Ross and Wilde, 1999). This study found that 13% of the homes during summer and 18% of the homes during winter had CO levels that exceeded the WHO one-hour guideline value (WHO 2000). Croxford (2007) summarised two studies in the UK of CO levels in living rooms of homes selected as most at risk of having old and poorly maintained gas appliances. In the first study it was found that 13 or 23% of the 56 homes exceeded one or more WHO guideline. In the second project, a similar proportion, 18% (50) of the 270 dwellings had CO concentrations that exceeded the 8-

hour average guideline level, of these, 26 (9.4%) exceeded the 1 hour level of 26 ppm, and 10 (3.6%) of these exceeded the 30 minute guideline values of 52 ppm.

A further study of 37 newly built homes in England during 2002 involved simultaneous measurements of air quality and rates of ventilation (Dimitroulopoulou et al., 2005). Table 18 summarises the results of measurements of selected air pollutants (2 week mean values).

Table 18. Summary of results of IAQ measurements in living rooms of 37 homes in England.

Compound	location	GM (weighted average) concentration ppm or $\mu\text{g m}^{-3}$	Maximum ppm or $\mu\text{g m}^{-3}$
CO winter	out	0.04 ppm	0.21 ppm
	Living room	0.12 ppm	0.46 ppm
	kitchen	0.14 ppm	0.46 ppm
CO summer	out	0.01 ppm	0.16 ppm
	Living room	0.17 ppm	0.4 ppm
	kitchen	0.18 ppm	0.39 ppm
		$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$
Toluene winter	out	2.5	7.6
	Living room	12.9	53.1
	Main bedroom	15.4	49
Toluene summer	out	2.7	8.4
	Living room	13.8	184.1
	Main bedroom	11.5	86.5
m+p xylene winter	out	1.0	3.6
	Living room	2.1	30.5
	Main bedroom	2.2	16
m+p xylene summer	out	0.5	4.2
	Living room	1.0	13.5
	Main bedroom	1.2	17.3

### *Other studies*

Crump (2009) summarised major studies of VOC concentrations determined by diffusive samplers in homes in a number of countries and Table 19 summarises the data for the substances monitored and quantified in the current study. Exposure periods for the samplers ranged from 1 day to 4 weeks in the studies cited; the concentrations shown represent mean concentrations over those periods.

Table 19. VOC concentrations in major studies of air quality in homes.

Compound	Concentration $\mu\text{g m}^{-3}$					
	Germany		France	USA	USA	Canada
	AM	Max	GM	AM	AM	AM
Toluene	31.8	814	15.8	28	-	41
limonene	36.7	1278	12.9	17.6	-	20
m/p-xylene	9.6	2496	5.1	9.8	17.7	20
undecane	10.2	582	7.6	-	-	-

Brown (1994) reviewed data on concentrations of VOCs in indoor air reported world wide. They derived geometric mean concentrations for a range of VOCs by weighting values for individual studies according to the number of buildings investigated. Table 20 shows results for selected VOCs measured in established buildings.

Table 20. Summary of some published concentrations of predominant VOCs in buildings (Brown et al., 2004).

Compound	GM (weighted average) concentration $\mu\text{g m}^{-3}$
Toluene	37
limonene	21
m/p-xylene	18
undecane	<5
tetrachloroethylene	7

The data for concentrations of VOCs in indoor air in buildings are therefore quite extensive. Broadly the concentrations of toluene, limonene, xylenes, undecane and TCE in the aircraft cabin air are of similar magnitude to those reported to occur in homes in developed countries. Concentrations of CO generated by combustion sources, notably gas cookers can produce concentrations in rooms containing the source that are higher than those occurring in the aircraft cabins.

There is much less information on the occurrence of organophosphate levels in homes compared with levels of VOCs. This is in part because the compounds are relatively involatile (e.g. TBP boiling point of 289°C) and are in the range described by the WHO as a semi-volatile organic compound (SVOC) (WHO 1989). They therefore have low vapour pressure and are not expected to be at high concentration in air at normal ambient temperatures. The measurement methods widely used in the past for indoor air quality studies were often optimised for VOCs and were unable to quantify SVOCs. In recent years sampling and analytical methods appropriate for SVOC analysis in indoor air have become more widely available and there has been an increasing interest in the occurrence of SVOCs in household dust and the potential for human exposure arising from that source.

Butte (2009) reviewed published data on the occurrence of SVOCs in indoor environments. Regarding organophosphates (those compounds with application as plasticisers and flame retardants) they found there were no large datasets for concentrations in air. They refer to a German study that included determination of para-tricresyl phosphate in indoor air and none was detected. Also referenced are two small Swedish studies that determined TBP in indoor air and levels of between 0.0005 and 0.12  $\mu\text{g m}^{-3}$  are reported. Bergh et al. (2010) report concentrations of TBP in 30 buildings in Sweden; median concentrations for private homes, day care centres and workplaces were 9.1, 18, and 2.3  $\text{ng m}^{-3}$  respectively and the maximum value reported was 320  $\text{ng m}^{-3}$ . Their method involved sampling a relatively large volume (1.0 – 1.5  $\text{m}^3$ ) of air over an 8 hour period through a cartridge containing an aminopropyl silica phase that was subjected to solvent desorption prior to GC/MS analysis. There are more extensive data available in the scientific literature on levels of organophosphates in settled household dust, including studies reporting levels of TBP.

There are, therefore, few data for comparison of the measured levels of TBP and TCPs in the aircraft cabin air with the indoor air in buildings. It is notable that no detectable amount of TOCP or other TCPs were found in over 95% of the cabin air samples. TBP was detected more routinely, but not in the majority of samples.

There is an increasing interest in measurements of ultrafine particles in air and while there is no comprehensive study of indoor environments in the UK, there are some indoor studies that

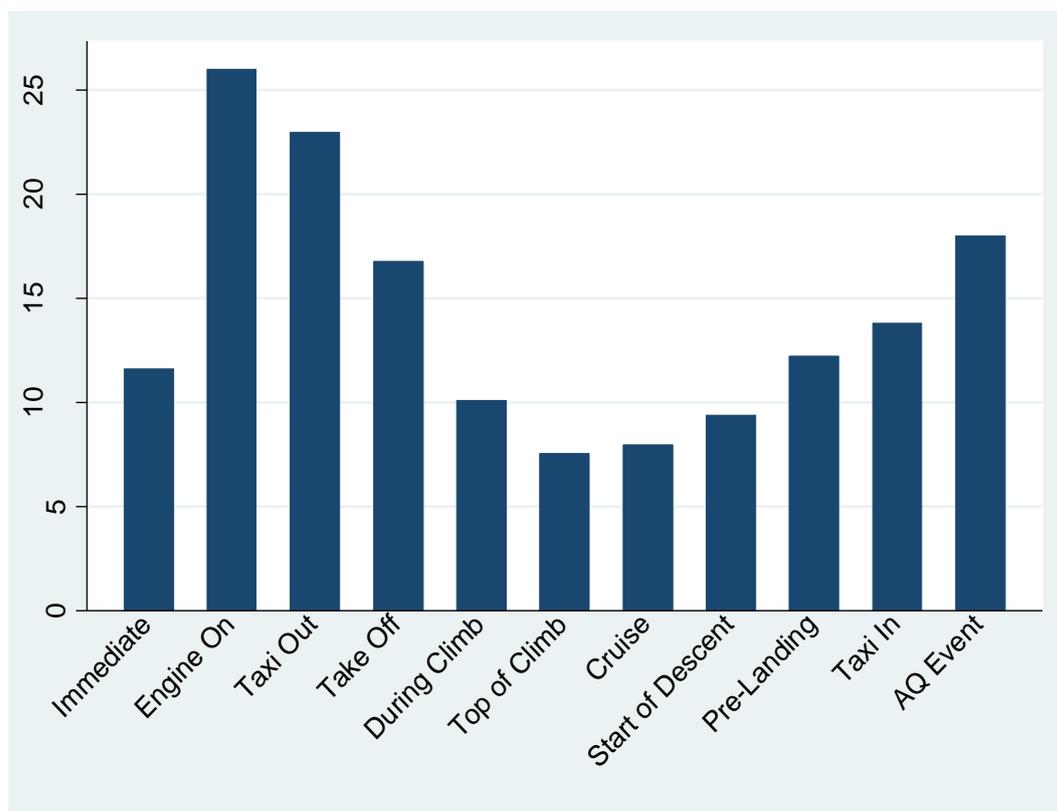
enable comparison with the concentrations measured on the aircraft. For example, Kaur and Nieuwenhuijsen (2009) measured ultrafine particles using a P-Trak in air in London streets and in vehicles during travel. The mean concentration of particles during transport was 100,018 particles  $\text{cm}^{-3}$  in buses, 101,770 in cars and 91,947 in taxis. Nazarof et al. (2010) measured ultrafines in seven occupied homes in California, USA, using newly developed water-based condensation particle counters, and reported average indoor concentrations ranging from 3,700 to 28,000 particles  $\text{cm}^{-3}$  with an overall mean of 14,500. In a review of the possible role of ultrafine particles in triggering asthma symptoms, Weichenthal et al. (2007) reviewed a number of studies that had characterised indoor sources of these particles, such as home cooking and heating systems, tobacco smoke, burning candles and vacuum cleaning. Wallace and Ott (2011) report an investigation of personal exposure to ultrafines involving 3 households in the USA and a range of activities. They used a condensation particle counter able to detect particles sized between about 0.01 and 1  $\mu\text{m}$ . Exposures during driving were about 30,000 particles  $\text{cm}^{-3}$  compared with an average outdoor background of 8,000 particles  $\text{cm}^{-3}$  and concentrations in restaurants were consistently 50,000 – 200,000 particles  $\text{cm}^{-3}$ . Cooking with gas or electric stoves and electric toasters were major sources in homes, with peak exposures often exceeding 100,000 particles  $\text{cm}^{-3}$ ; e.g. concentration of 400,000 particles  $\text{cm}^{-3}$  measured in a living room during cooking of tortillas. While some caution is required when comparing studies that have used different instrumentation, the findings suggest that the concentration of ultrafines measured on the aircraft may be routinely experienced by people in other indoor environments.

### ***Phase of flight***

The mean concentrations and percentile values for toluene, xylene, TBP, undecane and TCE during the different phases of flight show minimum values during the main phases of flight (climb to descent) and higher values when on the ground and at take off. This is illustrated in Figure 7 for toluene which shows a strong trend, possibly due to vapour from fuel and fumes from the combustion of fuel. This trend was not seen for limonene, TCPs or TOCP; indeed, for the latter two analytes relatively few measurements were above the limit of quantification (Appendix J).

In Table 7 'AQ events' represents a group of samples taken during any phase of flight according to the sampling protocol. It is notable that none of the concentrations of toluene in this group of samples are markedly higher than in the various flight phases. Neither TOCP nor other TCPs were detected during any of these events. It should be noted that reported AQ events cover a range of observations, from sweet smells, fuel smells and oily smells, as well as observed increases in PID and ultrafine readings, and therefore cover a range of situations with probably a number of different causes and associations. As stated previously, none of the AQ events or any other sample is associated with a cabin air sample taken during a reportable fume incident, as no such incident occurred during any of the flights.

Figure 7. Mean concentration ( $\mu\text{g m}^{-3}$ ) of toluene in cabin air during the different phases of flight.



### ***Aircraft type*** (study Part)

The study was in five parts and the type of aircraft was different in each part. Part 3 was undertaken on Airbus A320/321 passenger aircraft and is notable for the relatively high levels of limonene and for being the only Part with all TCP measurements being non-detects. Highest concentrations of m+p-xylene occurred in Part 5 (Airbus A319 passenger) and lowest concentrations of toluene in Part 2 (Boeing 757 passenger). Also maximum ‘Other TCPs’, toluene and TBP concentrations occurred in Part 1 (Boeing 757 cargo) while the maximum undecane and TCE concentrations occurred in Part 3. Appendix K further illustrates the breakdown of data by phase of flight for each Part of the study.

### ***Further work***

The authors plan to undertake additional analysis of the data to further investigate any relationships between changes in concentration of the different air quality parameters during different stages of flight. This may give further information about the nature of sources of gases, chemicals and particles in the cabin air during flight and when on the ground, but would not impact the interpretation of the data with regard to available safety, health and comfort standards and guidelines. It would also be possible to further process the chromatography data produced by the TD/GC/MS analysis of the sorbent tubes to investigate the occurrence of additional organic compounds, should a requirement be identified for data about a particular additional compound (see ‘Sample handling and laboratory analysis’ in section 3).

## 6 Conclusion

A range of air quality measurements were successfully conducted during the course of 100 flights. No fume events occurred during these flights that triggered the airline's protocols for formal reporting of incidents. The main findings of the monitoring programme were:

- The most abundant target VOC/SVOCs were generally limonene and toluene. Highest concentrations of TBP, limonene, m+p-xylene and undecane occurred during first engine start, while TCE concentrations were highest during the 'immediate' sampling period. Highest levels of TOCP, other TCPs and toluene occurred during climb, pre-landing and take-off respectively.
- Mean ultrafine particle numbers (all flight sectors) were always in the range 1,000-100,000 particles cm<sup>-3</sup>. On five flight sectors peak concentrations exceeded the maximum range of the instrument (500,000 particles cm<sup>-3</sup>).
- Mean Total VOC concentrations measured by PID were mostly below 2 ppm. A number of the short duration peak concentrations above 10 ppm were probably due to exposure to isopropyl alcohol vapour generated by the p-Trak instrument. There is evidence for a rise in total VOC concentration coincident with some reported air quality events.
- Maximum CO concentrations were mostly below 2 ppm. Peak concentrations of >3 ppm recorded on 7 flights were not associated with reported air quality events.
- A total of 30 air quality event sorbent tube samples for VOCs/SVOCs were collected during the study by the researcher when aware of an odour in the flight deck or noticing a change in readings of the continuous monitors. Concentrations of target analytes measured during these events were not elevated compared with the routine samples collected in each respective phase of flight. There was some evidence of an association between the occurrence of peaks in the Total VOC concentration and some events, but many such peaks occurred during flights without association with an event.
- A total of 38 flights had fumes or smells reported by at least one crew member or researcher in a post flight questionnaire. The dominant smell descriptor was 'oil' or 'oily', reported by 26 persons. Other descriptors were 'sweet', 'toilet smell', 'exhaust', 'chlorine', 'de-icing fluid', 'fuel', 'heated dust' and 'human waste'. Four persons reported that the fumes/smells caused a health effect (headache or slight headache in all cases).
- The monitoring results indicate that levels of carbon monoxide and toluene did not exceed safety, health or comfort limits described in the European standard 'Aircraft internal air quality standards, criteria and determination methods' (concentrations of carbon monoxide recorded during nine flights were equivalent to the 8h TWA health limit, but this is believed to be due to instrument malfunction rather than actual elevated levels of carbon monoxide).
- Concentrations of other pollutants measured were compared to available standards and guidelines for air quality established, for example, for domestic (home) or occupational environments. Such standards are available for TCE, TBP, TOCP,

xylenes and limonene (as well as for toluene and CO). No concentrations exceeded workplace exposure limits. Concentrations of TCE and xylenes did not exceed any guideline values. One short term concentration of limonene occurred (during Part 3 of the study) that exceeded a recommended long term exposure limit; however, this short duration peak would have a small impact on longer term average exposure.

- Based on the reasonably extensive database for VOCs in indoor air in buildings, it can be concluded that the concentrations of toluene, limonene, xylenes, undecane and TCE in the aircraft cabin air are of similar magnitude to those occurring in homes in developed countries. Concentrations of CO generated by combustion sources, notably gas cookers, are often higher than those occurring in the aircraft cabins. For TBP and TCPs, there are few data to allow comparison of the measured levels in aircraft cabin air with the indoor air in buildings. The highest level of TBP recorded was  $21.8 \mu\text{g m}^{-3}$  (overall mean  $1.07 \mu\text{g m}^{-3}$ ) which exceeds any reported domestic indoor air level.
- The mean concentrations of most VOCs measured during the different phases of flight did show a trend, with minimum values occurring during the main phases of flight (climb to descent) and higher values when on the ground and during take-off. This trend was not found for limonene or the TOCP and other TCP measurements.
- Regarding the possible influence of aircraft type, no TCPs were detected during Part 3 (A320/1 aircraft) whilst limonene concentrations were relatively high on the flights monitored in Part 3 compared with those in the other four Parts. Other identified differences included highest concentrations of m+p-xylene occurring in Part 5 and lowest concentrations of toluene in Part 2.
- Samples specifically taken during recorded air quality events did not have notably elevated concentrations of any of the individually measured pollutants.
- With respect to the conditions of flight that were experienced during this study, there was no evidence for target pollutants occurring in the cabin air at levels exceeding available health and safety standards and guidelines.

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## **Appendix A – Flight record form**

# CABIN AIR QUALITY RESEARCH PROGRAMME

## Sector Detail Record

Date:	
Flight number:	
Aircraft registration number:	
Sector route: (e.g. EMA - CDG)	
Time of departure:	
Weather conditions at time of departure:	
Expected cruise altitude: (You need this information as you will be taking a sample once the aircraft reaches it's cruise altitude)	
No. of flight crew onboard:	
No. of cabin crew onboard:	
Is this the aircraft's first flight of the day?  (Please tick the appropriate box.)	Yes <input type="checkbox"/>  No <input type="checkbox"/>  Don't Know <input type="checkbox"/>
Researcher Name:	
Company:	
Security Tag Number:	

## **Appendix B –Cabin air sampling schedule**

Sample No.	Description	Cue	Start Sample	Comments
1	Immediate	Kit set up – you have maximum, 20 minutes from boarding. Aim to board early.	Once kit set up.	If possible take this sample before APU is switched on.  Note whether aircraft is running on APU or ground connection.  Note whether the flight deck windows and door are open or shut.
2	First Engine On	During the pushback the Pilot says “starting right engine”. Engine takes approx 90 seconds to start. The right air conditioning pack is switched on you hear a rush of air noise.	When you hear the rush of air noise.	After the first (right) engine is started and the right pack switched on, the left engine will be started and the left air con pack switched on.  The engine starting is usually accomplished as the aircraft is being pushed back from the stand.
3	Taxi	Aircraft has been pushed back and goes onto taxiway.	Once aircraft moves under its own power.	
4	Take Off	“Clear for take off” heard in headset.	When throttle levers are moved forwards.	
5	During climb	Watch altimeter. Listen for one pilot saying “altimeter check” and the other responding “Flight level 200”	As the aircraft climbs above 20000ft (Flight Level 200)	
6	Top of climb	Cruise altitude should be available to you at start of the flight. Pilot will say “we are in cruise now”.	Thrust levers move back slightly.	Make a note of the time at this point.
7	Cruise		Take sample 10 minutes after top of climb.	
8	Start of descent	One Pilot will brief the other about	Throttles start coming back,	

		the planned descent approx ten minutes before descent commences. At the point of descent, the throttles will move back and you will feel the aircraft pitch down and see the altimeter “wind down”	altimeter starts winding down. You will feel the decent.	
9	Pre-landing	“Radio altimeter” heard. Height 2500 feet on radio altimeter.	On hearing the automatic call out “Radio Altimeter”. A white radio altitude height (2500) will also appear on the primary flight display.	A five minute sample, will take you through landing and into taxi.  For Info: The radio altimeter automatically appears as the aircraft descends below 2500 feet above the ground. The conventional altimeter will not necessarily be 2500 ft at this point as it is referenced against seal level.
10	Taxi back	End of previous sample	Start sample 10 straight away.	Aircraft taxi to stand.
F	Fume Event	Crew mention smell	Start 2 <sup>nd</sup> pump immediately	Note the time
		Instruments indicate fume event	Start 2 <sup>nd</sup> pump immediately	Note the time

The flight crew will endeavour to alert you to the commencement of each sampling phase period. However, you should not rely on their prompt.

## **Appendix C – Post flight questionnaire**

## **Cabin Air Quality Research Programme Questionnaire**

Your airline, along with a number of other airlines, has kindly agreed to participate in a cabin air quality research programme which is being managed by Cranfield University. The University have been commissioned by the Department for Transport (DfT) on behalf of the Government's Aviation Health Working Group (AHWG) to test a variety of air sampling devices capable of detecting a wide range of compounds in a cabin air environment. The aim of the programme is to collect samples of air at during certain phases of flight – both during normal flights and also in the event of a sudden 'fume event'.

We would be grateful if you would take some time at the end of the flight to complete this questionnaire. There are no right or wrong answers. Please do not discuss your answers with other crew members until after you have returned your completed questionnaire. By completing the questionnaire, you are giving consent for the information to be used by Cranfield University for research purposes. Please hand the completed questionnaire back to the researcher or post it directly back to Cranfield University - a FREEPOST envelope has been supplied for this purpose. (We would be grateful if you would complete the questionnaire within 24 hours of leaving the aircraft and if using the FREEPOST envelope, put it in the post within 7 days).

Please detach the Contact Information sheet at the end of this questionnaire for your future reference.

**PLEASE NOTE: If a fume event is experienced during this flight, you will still need to follow Company reporting procedures as you usually would do.**

Thank you for helping us with our research by completing this questionnaire. Please read each question carefully and provide as much detail as you can.

**Section One: Flight Details**

*This section asks for basic flight and aircraft information.*

1. Date: \_\_\_\_\_
2. Flight Number: \_\_\_\_\_

**Section Two: Your Details**

*This section asks for some basic information about yourself.*

4. Please give your age: \_\_\_\_\_
5. Are you:      Male                            Female
6. What is your role on this flight?  
Flight Crew                        
Cabin Crew                        
Researcher                        
Other                        
If other, please state your role: \_\_\_\_\_
7. Please state the number of years you have worked as professional crew:  
\_\_\_\_\_
8. Please give the number of years you have worked on the current aircraft type:  
\_\_\_\_\_

**Section Three**

*In this section, we would like you to tell us about any fumes or smells you may have experienced during the flight.*

10. Did you experience any aircraft fumes/smells during this flight?

Yes  No  (Please go straight to section 4)

If yes, what did it smell like on the first occasion it occurred?

---

If fumes/smells occurred on a second occasion, what did it smell like?

---

11. At what stage during the flight did you experience the fumes/smells? Please circle as appropriate.

Taxi Out	Take-Off	Climb	Cruise
Descent	Landing	Taxi In	

12. Whereabouts in the aircraft were you when you experienced the fumes/smells? For example, cockpit, galley, toilet, cabin etc.

On the first occasion? \_\_\_\_\_

and if there was a second occasion? \_\_\_\_\_

13. Did you experience any effects from the fumes/smell?

Yes  No

If yes, what were they on the first occasion? \_\_\_\_\_

---

and if there was a second occasion?

---

**Section Four**

In this section, we would like you to tell us if you have any other comments to make:

**Thank you for completing the questionnaire.**

Date completed questionnaire \_\_\_\_\_

Please hand it back to the researcher  
or use the attached FREEPOST envelope to post it back to:  
Professor Helen Muir, Department of Systems Engineering and Human Factors,  
Cranfield University, Wharley End, Bedfordshire, MK43 0AL, UK.

## **Cabin Air Quality Research Programme**

### **Contact Information**

If you have any concerns about this project or the way in which it was conducted, please contact the Cranfield Project Manager at the following address:

Professor Helen Muir  
Systems Engineering and Human Factors Department  
Cranfield University  
Wharley End  
Bedfordshire, MK43 0AL, UK  
Tel: 01234 750111

**Thank you for your participation.**

## Appendix D – Sampling Record Form

<b>CABIN AIR SAMPLING RECORD</b>		Date	Sector & route	Aircraft <small>tail no</small>
		Flight No.	Aircraft ID	Watch time
PID On Time:		P-Trak On Time:	Pumps On Time:	Pump ID
Clip	Description	Tube No. and Letter	Time	Comments
1	Immediate			
2	Engine On			
3	Taxi Out	A/C moves under own power		
4	Take Off	Throttles forward		
5	During climb	20,000 ft		
6	Top of climb	Altitude		
7	Cruise	10 minutes after TOC		
8	Start of descent	Throttle back; alt. decreases		
9	Pre-landing	2,500 ft Radio alt. starts		
10	Taxi In	Immediately after Pre-landing samp.		
<b>FUME EVENTS &amp; BLANKS</b>				Pump ID:
Clip	Description	Tube No. and Letter	Time	Comment
11				
12				
13				
14	Travel blank			

## **Appendix E – Chain of custody form**

<b>TUBE CUSTODY &amp; ACTION FORM</b>					
<b>Event</b>		<b>Date</b>	<b>Time</b>	<b>Location/notes</b>	<b>Signature</b>
Conditioned at <b>AES / BRE*</b>	Tag A No.				
Transport to sampling					
Received for sampling	Tag A Secure?				
Transfer to airline/ secure custody	Tag B No.				
Transfer to courier					
Receipt at CU	Tag B Secure?				
Analysis Request Completed					
Courier to <b>AES / BRE*</b>	Tag C No.				
Receipt at <b>AES / BRE*</b>	Tag C Secure?				
Tubes analysed & ready for reconditioning.					

ANALYTICAL SCHEDULE							Tag C No:
KEY: A = to be analysed      N/A = not to be analysed      F = Fume event							Airline:
	Tube Number	Action	Comments		Tube Number	Action	Comments
1				26			
2				27			
3				28			
4				29			
5				30			
6				31			
7				32			
8				33			
9				34			
10				35			
11				36			
12				37			
13				38			
14				39			
15				40			
16				41			
17				42			
18				43			
19				44			
20				45			
21				46			
22				47			
23				48			
24				49			
25				50			

## **Appendix F - TD/GC/MS analytical method**

This appendix provides details of the analytical procedures (information provided by the two laboratories).

## ***BRE method***

### ***Introduction***

BRE developed protocols for the conditioning of air sampling sorbent tubes prior to air sampling and for the methods of analysis by TD/GC/MS. These were finalised based on experience gained during the preparatory phase and Part 1 of the main study in collaboration with AES and Cranfield University. These protocols were also applied by AES although details of the analytical method were modified to be applicable to their mass spectrometer type. AES used a Varian quadrupole mass spectrometer whereas BRE used an instrument manufactured by Agilent.

### ***Protocol for conditioning of Q/Tenax tubes used to sample aircraft atmospheres***

Freshly packed tubes are subjected to a thorough conditioning procedure in a Markes TC20 tube-conditioning rig (2 hours at 320°C followed by 30 minutes at 335°C with a flow of high purity nitrogen of between 50 and 100 ml min<sup>-1</sup>). After this a representative sample of tubes are analysed to check for the significant presence of any target analytes before using for air sampling.

Following analysis and prior to further use, the tubes are conditioned for 45 minutes total time with the TC20 temperature set at 330°C. To ensure that the tube conditioner is functioning correctly, a sorption tube from every batch of conditioned tubes is analysed to ensure the target analytes have been removed. If concentrations of any of the target analytes detected on this tube are significantly above those found in typical conditioning checks, this is investigated.

### ***BRE Protocol for TD/GC/MS analysis of Q/Tenax tubes used to sample aircraft atmospheres***

This method describes the determination of a target list of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) which have been trapped onto adsorbent tubes containing quartz wool and Tenax TA during air sampling and are analysed by thermal desorption and gas chromatography/mass spectrometry/flame photometric detection. The method utilises the Agilent 5975 Mass Selective Detector (MSD) coupled to an Agilent 6890N Gas Chromatograph (GC) also fitted with a flame photometric detector (FPD), with sample input being achieved using a Markes Unity Thermal Desorber (TD) and Markes Ultra Autosampler.

### **Calibration**

Calibration solutions are prepared for target analytes. The relative response of each target analyte is determined relative to one of the two internal standards (1-bromo-4-fluorobenzene and Chlorfenvinphos). These internal standards were selected in agreement with AES.

### **TD parameters**

Cold trap packing = CW (Quartz/Tenax)  
Cold trap low temperature = -10°C  
Cold trap high = 320°C (max heating rate)

### **GC/MS parameters**

HP-5MS column, 30 m x 250 µm x 0.25 µm

Temperature programme = 40°C for 5 min then 5°C/min to 140°C then 10°C/min to 300°C, 9 min hold (run time 50 min)

Table F1. SIM parameters (for Skydrol LD4 and 500B4 and Jet II oil).

Group Name	Start Time (minutes)	m/z	Dwell (msec)
Toluene	4.0	91.05	100
Tetrachloroethylene	5.5	165.9	100
m-Xylene	7.5	91.05	100
Bromofluorobenzene	10	175.95	100
Limonene	13	136.1	100
Undecane	15	85.1	100
TBP	29.5	155.0	100
diBPhP*	33	175.1	100
Chlorfenvinphos	35	323.0	100
BdiPhP*	36.3	251.05	100
TCP	38.3	368.1	100
Esters*	43	299.1	100

TBP = tributylphosphate, diBPhP = dibutylphenylphosphate, BdiPhP = butyldiphenylphosphate TCP = tricresylphosphate

Note; \*The esters selected are components of Jet II oil and the diBPhP and BdiPhP are components of Skydrol LD4. Pure standards for these components were not available for calibration and quantification. However samples of lubricating oil and hydraulic fluid specific to the type of aircraft being sampled were provided by each airline participating in the study in new, unopened containers and these were analysed. A calibration was performed by spiking different amounts of the oil / hydraulic fluid onto standard sorbent tubes. This enabled a semi-quantitative value for the amount of engine oil and hydraulic fluid on an air sampling tube to be derived but on the assumption that no other sources of these compounds were present and that the relative concentration of the components in air is the same as that in the liquid oil. This would not be the case if all components of the oil are not fully volatilised and if some other process of discrimination, such as selective sorption of particular components to surfaces, or thermal degradation in the engine compressor occurs.

### Analytical activities

On receipt of sampled and travelling blank tubes these are checked against the attached chain of custody form, caps are tightened if they have become loose (and the numbers of those which had become loose are recorded) and they are stored at ambient temperature in sealed containers containing a charcoal scavenger until analysis.

Before each batch of samples is analysed the MSD air/water level is checked and recorded. If values outside the normal range for the instrument are obtained these are investigated before proceeding.

The sequence is begun with at least one empty tube and results for the target analytes are checked. This is followed by a QC standard containing pure chemicals (approximately 50 ng on the tube for toluene, 20 ng for tributylphosphate [TBP] and 0.5 ng for TOCP) and the internal standard mix. This standard is followed by an empty tube. Results are entered on the QC chart and response values and retention times are checked against those for recent runs (if necessary the method is re-locked).

All samples and blanks to be run are spiked with 1 µl of the internal standard mix and purged for approximately five minutes. The tubes to be run are then set out in the order for loading and the end caps are replaced with analytical end caps. A typical run of sorption tubes can consist of tubes expected to have small amounts of analytes (including blanks and tube conditioning check) followed by air samples, and with any samples described as a ‘fume incident’ being placed at the end of the sequence.

The sorption tube sequence is set up in the Unity and Chemstation software and analysis is undertaken. When the run is complete the tubes are removed from the Ultra trays and the letters associated with the tube number on the bag for the tube are incremented. After analysis the tubes are stored in the area designated ‘storage area for tubes requiring conditioning’.

The results are processed and amounts of each analyte found on each tube (ng) are copied to a results spreadsheet.

Reporting limits (for Part 1 oils) estimated during Part1 of the study taking into account blank levels are given in Table F2 below.

Table F2. Reporting Limits (for Part 1 oils).

Compound	Upper limit of calibration (ng)	Lower limit of quantification (ng)	Detection limit (ng)
Toluene	500	6	3.0
Tetrachloroethylene	50	1	0.1
m-Xylene	50	2	0.1
d-Limonene	1,000	12	2
Undecane	500	6	3
Tributyl phosphate	200	4	2
Skydrol 500B4 determined using dibutylphenyl phosphate peak from batch 0000079 QE-27302	100	5	2
Skydrol 500B4 determined using butyldiphenyl phosphate peak from batch 00000709 QE-27302	100	5	2
Triorthocresylphosphate (TOCP)	5	0.3	0.1
Other tricresylphosphates (TCPs) as trimetacresylphosphate (quantified using mass 368 ion) *	5 for any of the four TCP isomers/GC peaks found in Jet II	0.3 for any of the four TCP isomers/GC peaks found in Jet II	0.03 for any of the four TCP isomers/GC peaks found in Jet II
Jet II oil determined using ester peak R.T. 44.6 mins from batch E07K581 10 Oct 07	200	5	1
Jet II oil determined using ester peak R.T. 45.3 mins from batch E07K581 10 Oct 07	200	5	1

## Notes

Compounds present between the lower limit of quantification and the detection limit will be reported as 'TR = trace'.

ND = not detected (below detection limit).

\* For the TCPs with respect to each individual isomer/GC peak a value represents the sum of peaks above the quantification limit. 'Value + TR' denotes additional presence of other peaks at trace level.

## ***Application to determination of Jet II fumes in air***

A recovery experiment was carried out in a BRE room-sized chamber of approximate volume  $11\text{m}^3$  to investigate the performance of the sampling and analytical procedure for the detection of Jet II oil in air. The chamber is constructed of metal sheeting and for the purpose of this experiment was sealed with no ventilation. An internal mixing fan was used to assist mixing of air in the chamber. The air in the chamber was sampled using the pumped Q/Tenax sorbent tube method ( $500\text{ ml min}^{-1}$  for 5 minutes) and the tubes analysed by TD/GC/MS to check that no detectable amounts of Jet II oil or its components were present.

1  $\mu\text{l}$  of Jet II oil was volatilised in the chamber using a stream of hot air from a hot air gun. The temperature in the inlet of the volatilisation device was an indicated  $520^\circ\text{C}$ , and  $370^\circ\text{C}$  at the outlet.

At a sampling point in the centre of the test chamber duplicate samples were taken using pumped sorbent tubes. Two Q/Tenax tubes were connected in series to each pump with a flow rate of  $500\text{ ml min}^{-1}$  to check for breakthrough. On the first in line tubes the recoveries of total TCPs and esters were similar and averaged 132% and 106% respectively. The reason for the higher than 100% recovery is likely to be due to the difficulties of reproducibly introducing such small amounts of oil into the volatilisation device. On the second in line tubes the recoveries of total TCPs and esters averaged 23% and 20% respectively showing a trapping efficiency of about 80% by the first in line tube.

The first tubes in line during sampling were subject to repeat desorption and amounts of esters or TCPs were not found at above 3% of the amount detected on the initial desorption. This shows effective recovery of analytes by the thermal desorption procedure. Empty tubes analysed immediately after the heavily loaded first tubes showed zero carry-over into subsequent analyses on the TD/GC/MS system.

The ultrafine particle concentration in the chamber was monitored using the P-Trak. This showed a rapid rise in concentration from below  $1,000\text{ particles cm}^{-3}$  to a peak of about 270,000 followed by a more gradual decline to about  $200,000\text{ particles cm}^{-3}$  during the subsequent 10 minutes.

## AES Method Summary

(Method 091 Aircraft Cabin Air Analysis by Thermal Desorption GCMS)

### Principle

Volatile and semivolatile organic compounds in aircraft cabin air are collected by passing a known volume of air through a sorbent tube packed with quartz wool and Tenax TA. The tubes are then analysed by thermal desorption / gas chromatography/ mass spectrometry.

### Protocol for TD/GC/MS analysis

Tables F3 and F4 summarise the ions used for compound /oil quantitation and the calibration range.

Table F3. Compounds Analysed.

Compound	Retention Time (min)	Quantitation Ions	Upper limit of calibration <sup>1</sup> (ng)	Quantitation limit (ng) <sup>2</sup>	Detection limit (ng) <sup>2</sup>
Toluene	4.60	91	50	0.1	0.04
Tetrachloroethylene	5.79	94+131+164	50	0.5	0.2
m-Xylene	8.09	91+106	50	0.5	0.2
d-Limonene	13.68	67+91+93	50	0.5	0.2
Undecane	15.94	57+71	50	0.5	0.2
Tributylphosphate	28.87	99	50	0.03	0.01
Skydrol determined as dibutylphenylphosphate	31.84	94+174+175	250	1	0.4
Skydrol determined as butyldiphenylphosphate	34.56	94+171+249+251	250	3	1
Triorthocresylphosphate (TOCP)	39.10	368	50	0.4	0.2
Other tricresylphosphates as trimetacresylphosphate	39.22 to 40.0	368	50	0.2	0.1
Jet II oil determined as N-phenylnaphthylamine	34.92	217 to 219	250	15	5
Jet II oil determined as dioctyldiphenylamine	41.59	323+324	250	5	2

Note 1: If necessary the range can be extended by sample recollection and analysis at a higher split ratio.

Note 2: Quantitation limit is 10x signal to noise and detection limit 3x signal to noise. Concentrations between these two levels are reported as a trace quantity.

Table F4. Additional Lubricating and Hydraulic Fluids (These may replace Skydrol and/or Jet II for some carriers).

Compound	Retention Time (minutes)	Quantitation Ions	Upper limit of calibration <sup>1</sup> (ng)	Quantitation limit <sup>2</sup> (ng)	Detection limit <sup>2</sup> (ng)
Hyjet IV as tributylphosphate	28.87	99	250	0.03	0.01
Hyjet IV as triphenylphosphate	37.59	326	250	ND	ND

### Sample Tube Conditioning

Quartz wool/Tenax TA tubes are conditioned in the Markes TC-20 Tube Conditioner using high purity oxygen free nitrogen at 30psi. Freshly packed tubes are conditioned for 2 hours at 200°C followed by 30 minutes at 335°C. Reconditioning of used tubes is carried out at 335°C for 1 hour. Representative tubes from each batch are analysed before the sample tubes are used.

### Storage

Tubes are capped with 1/4 inch Swagelok fittings and one piece PTFE ferrules. The caps are tightened using a CapLok tool to ensure an adequate seal and to avoid overtightening. Sealed tubes are stored and transported inside clean, airtight containers.

### Equipment

Markes International Unity Thermal Desorption System.

Markes International Ultra 50:50 Autosampler with sample recollection.

Varian 4000 Ion Trap GCMS fitted with a Varian Factor Four VF-5ms 30m x 0.25mm x 0.25 µm capillary column.

Markes International TC-20 Tube Conditioner.

### Instrument Conditions

#### *Markes Thermal Desorption*

Standard 2 stage desorption

Trap Low: -10°C

Trap High: 320°C

Flow Path Temperature: 200°C

ColdTrap: Markes CW

#### *Varian 4000 GCMS*

Column Varian FactorFour VF5-MS 30m x 0.25mm x 0.25µm

Column Oven 5 minutes at 40°C

Ramp 1 - 5°C/minute to 140°C

Ramp 2 - 10°C/minute to 300°C

Report for DfT by the Institute of Environment and Health (Cranfield Ref No YE29016V)

Hold 9 minutes  
MS Configuration Internal EI  
Transfer line 280°C  
Mass Range 35-400

### **Procedure**

Performance checks are carried out on the thermal desorption GCMS system prior to analysis. 1 µl of an internal standard solution containing 100ng/µl of bromofluorobenzene and chlofenvinphos is added to all blanks, calibration and sample tubes prior to analysis.

A 5 point calibration is performed for each of the target compounds listed in table F3; an additional calibration is carried out using the appropriate oils for the aircraft being monitored. The samples are then analysed and the concentrations of the target compounds calculated from the calibration curves. Blanks and AQC samples are analysed with each batch of samples. The split from the thermal desorption cycle is recollected on the sample tube (or a separate tube) to allow the sample to be reanalysed if required. The results of the analysis are then transferred to a spreadsheet and reported for each analyte as ng/tube.

### Limits of Quantification in air

Tables F2 and F3 provide limits of quantification reported by each laboratory for the amount of particular analytes on the sorbent tube. As the normal sampling volume for determining amounts of analytes in air applied in the study is 2.5 L the value for the amount on the tube can be used to derive an equivalent concentration in air and this is shown in Table F5.

Table F5. Limit of quantification in 2.5 L air sample based on BRE and AES reporting limits.

Compound	AES $\mu\text{g m}^{-3}$	BRE $\mu\text{g m}^{-3}$
Toluene	0.04	2.4
TCE	0.2	0.2
M-xylene	0.2	0.8
D limonene	0.2	4.8
Undecane	0.2	2.4
TBP	0.01	1.6
TOCP	0.16	0.12
Other TCPs (for any of the isomers)	0.08	0.12

During the course of the study BRE reported limits of quantification appropriate for each Part of the study. There was little change as shown by the values in Table F6.

Table F6. Limit of quantification in air ( $\mu\text{g m}^{-3}$ ) reported by BRE for each Part of the study.

Compound	Part 1	Part 2	Part 3	Part 4	Part 5
Toluene	2.4	2.4	2.4	2.4	2.4
TCE	0.4	0.4	0.4	0.4	0.4
M-xylene	0.8	0.8	0.8	0.8	0.8
D limonene	4.8	4.8	4.8	4.8	4.0
Undecane	2.4	2.4	2.4	2.4	2.4
TBP	1.6	1.6	1.6	1.6	1.6
TOCP	0.12	0.12	0.12	0.12	0.12
Other TCPs (for any of the isomers)	0.12	0.12	0.12	0.12	0.12

## **Appendix G – Interlaboratory comparison of TD/GC/MS analysis**

## ***Introduction***

It was important to demonstrate comparability of the two analytical laboratories. While they were using common methods of sample tube preparation and analysis, including QA/QC procedures the protocols were being carried out by different scientists and there were some differences between the analytical equipment applied (although equipment differences should not be a source of inter-laboratory variation given the common calibration procedures). A first check of agreement between laboratories involved the exchange of solutions containing amounts of oil and hydraulic fluid. This was undertaken in September 2008. A further interlaboratory test involving the exchange of solutions containing measured amounts of pure compounds was carried out in September 2009.

## ***2008 Exercise***

### ***Set up***

A mass range of 50-200 ng Jet II (E07K581 10 Oct 07) and Skydrol 500B4 (00000709 QE-27302) was agreed upon for spiking onto sorbent tubes to be exchanged between BRE and AES.

Eight tubes were conditioned at BRE on 4 September 2008, one of which was labelled as a travel blank, and these were sent to AES on 12 September 2008 for spiking at their laboratories. The seven unlabelled tubes were each spiked at AES on 16 September 2008 with 2.5 µl of an acetone solution of the oils. This should have resulted in 63 ng of Skydrol and 126 ng of Jet II being loaded on to each tube.

AES sent eight tubes to BRE on 16 September, seven for BRE to spike with the oils, and one travel blank. The tube numbers were as follows:-

Mi118108b  
Mi118109b  
Mi118111b  
Mi118112b  
Mi118113b  
Mi118114b  
Mi118115b  
Mi118105-Blank

On 18 September 2008 these seven tubes were each spiked with the same solution containing 139.8 ng of Jet II and 79.0 ng Skydrol in 5 µl. These solutions had been made up using ethyl acetate then diluted in methanol and were each purged for five minutes following spiking according to the BRE protocol. The eight tubes were sent to AES for analysis on 18 September 2008.

### ***Analysis of Tubes spiked by AES***

The tubes spiked at AES were received at BRE on 17 September 2008, spiked with the internal standard mix, and analysed on 19 September 2008. Amounts found by BRE for each of the target analytes present in the oils are given in Table G1 and the results of analysis by AES are in Table G2. A comparison is made of the key analytes (TBP, TOCP and other TCPs) for which pure standards were available to enable calibration by comparing the amount determined as ng of analyte per ng of oil spiked. Also examined was the use of other Skydrol/Jet II components such as dibutylphenylphosphate for which standards were not available. A range of dilutions of Skydrol/Jet II were analysed to produce a plot of amount of

Skydrol/Jet II spiked versus area of chromatographic peak of the component. This plot could be used to determine the amount of Skydrol/Jet II on a tube spiked with (an unknown amount) of the same type of fluid/s.

Table G1. Results of tubes spiked by AES and analysed by BRE.

Tube No.	Mass spiked by AES	Mean ng determined by BRE	RSD %	Comment
Tributyl phosphate	Not known	9.4 (= 0.15 ng TBP/ ng Skydrol)	18.0	-
Skydrol 500B4 determined using dibutylphenyl phosphate peak	63	62.5	10.6	0.80% error of determined value compared to reported mass of Skydrol spiked
Skydrol 500B4 determined using butyldiphenyl phosphate peak	63	62.8	10.8	0.26% error of determined value compared to reported mass of Skydrol spiked
triorthocresylphosphate		ND	-	-
Other tricresylphosphates as trimetacresylphosphate quantified using mass 368 ion		2.6 (= 0.02 ng other TCPs/ ng Jet II)	11.0	-
Jet II oil determined using ester peak R.T. 44.6 mins	126	113	12.95	10.2% error of determined value compared to reported mass of Jet II spiked
Jet II oil determined using ester peak R.T. 45.3 mins	126	118	13.1	6.3% error of determined value compared to reported mass of Jet II spiked

ND = Not detected (<0.3 ng for TOCP)

Table G2. Results of tubes spiked by BRE and analysed by AES.

Tube No.	Mass spiked by BRE	Mean ng determined by AES	RSD %	Comment
Tributyl phosphate	-	11.6 (= 0.15 ng TBP/ ng Skydrol)	18.8	-
Skydrol 500B4 determined using dibutylphenyl phosphate peak	79.0	63.4	2.9	19.7% error of determined value compared to reported mass of Skydrol spiked
Skydrol 500B4 determined using butyldiphenyl phosphate peak	79.0	59.9	4.5	20.9% error of determined value compared to reported mass of Skydrol spiked
triorthocresylphosphate		ND	-	-
Other tricresylphosphates as trimetacresylphosphate quantified using mass 368 ion		4.2 (= 0.03 ng other TCPs/ ng Jet II)	23.5	-
Jet II oil determined using N-Phenyl-1-naphthylamine	139.8	70.6	1.8	49.5% error of determined value compared to reported mass of Jet II spiked
Jet II oil determined using Dioctyldiphenylamine	139.8	75.9	19.5	45.7% error of determined value compared to reported mass of Jet II spiked

ND = not detected (<0.4 ng for TOCP)

Table G3 summarises the comparison for the target analytes determined by BRE and AES.

Table G3. Comparison of amounts of target analytes determined by BRE and AES

Laboratory analysing	TBP (ng/ng Skydrol)	TOCP (ng/ng jet II)	Other TCPs (ng/ng Jet II)
BRE	0.15	ND	0.02
AES	0.15	ND	0.03

### ***Conclusion***

The two laboratories were in good agreement for the target analytes present in Skydrol and Jet II. With regards to the use of other components to determine the mass of Skydrol/Jet II, there was good agreement between the mass determined by BRE and amount loaded by AES. However for the converse the calculated amounts of Skydrol and particularly Jet II were low. Further work would be needed to understand the differences observed. It would appear to be due to the analysis rather than the spiking procedure and possibly the recovery of the amines used by AES was low with the method applied.

## 2009 Comparison

### Method

Standard solutions were each prepared by BRE and AES containing eight compounds; TOCP, TMCP, toluene, TCE, m-xylene, d-limonene, n-undecane, tributylphosphate. Each laboratory spiked seven tubes and these together with at least one travel blank were sent to the other laboratory for analysis.

It was agreed that tubes should be spiked with masses of analytes within the ranges shown in table G4. Each laboratory reported the amounts spiked to Cranfield University as well as the results of the analysis of the tubes they received.

Table G4. Compounds and amounts for spiking on tubes.

compound	Amount to be spiked
toluene	10-50 ng
tetrachloroethylene	10-50 ng
m-xylene	10-50 ng
d-limonene	10-50 ng
n-undecane	10-50 ng
tributylphosphate	10-50 ng
triorthocresyl phosphate	1-3 ng
trimetacresyl phosphate	1-3 ng

**Results**

Table G5. Amounts of analytes measured by BRE on tubes spiked at AES.

Compound	Amount on tube (ng)								
	Mi117230g	Mi117225g	Mi121280b	Mi117267i	Mi117279h	Mi121271c	Mi118151j*	Mi121281b Blank	Mi121294b Blank
toluene	19.78	24.63	20.08	19.64	22.52	22.70	39.94	ND	ND
trichloroethylene	35.59	41.27	35.32	35.84	41.73	40.22	36.60	ND	ND
m_xylene	19.65	24.62	20.28	20.07	21.52	21.48	31.34	TR	TR
limonene	14.36	15.76	14.77	14.63	14.76	14.97	26.61	ND	ND
undecane	14.50	15.10	14.50	14.76	15.14	15.23	50.97	ND	ND
tributyl phosphate	21.13	20.29	20.27	21.58	21.83	20.70	23.79	ND	ND
triorthocresylphosphate	1.89	1.84	1.88	1.92	1.88	1.85	1.88	TR	TR
trimetacresylphosphate	2.23	2.35	2.39	2.25	2.35	2.15	1.68	TR	ND

TR = trace (below LOQ) ND=not detected.

\*apparent outlier for some analytes

Table G6. Summary of BRE data and percentage found by BRE of amounts spiked by AES.

compound	Amount spiked by AES	Amount measured by BRE*			% (measured/spiked)
		Mean	RSD (%)	SD	
toluene	21.6	21.56	2.03	9.44	100
TCE	41.5	38.33	3.05	7.96	92
m_xylene	21.7	21.27	1.81	8.51	98
limonene	21.1	14.88	0.48	3.21	71
undecane	18.5	14.87	0.33	2.21	80
TBP	25.8	20.97	0.66	3.14	81
TOCP	2.058	1.88	0.03	1.53	91
TMCP	2.007	2.29	0.09	4.00	114

\*Data not including outlier (tube Mi118151j)

Table G7. Amounts of analytes measured by AES on tubes spiked at BRE.

Compound	Amount on tube (ng)							
	Mi118121	Mi118122*	Mi118123	Mi118124	Mi118125	Mi118126	Mi118128	Mi118127 Blank
toluene	28.91	39.83	29.95	25.92	26.86	29.56	28.35	4.12
trichloroethylene	36.09	38.87	35.48	34.19	34.76	36.92	35.47	ND
m_xylene	19.39	58.99	18.43	18.216	18.98	19.23	19.31	0.38
limonene	23.15	25.01	26.28	22.44	23.60	23.84	23.57	0.31
undecane	23.9	36.31	23.36	22.28	23.37	23.75	23.72	0.61
tributyl phosphate	24.78	21.27	21.23	21.90	25.51	23.76	23.18	0.23
triorthocresylphosphate	1.49	7.14	1.58	1.51	1.56	1.49	1.69	ND
trimetacresylphosphate	1.46	8.38	1.69	1.93	1.58	1.69	1.54	0.31

\*apparent outlier for some analytes

Table G8. Summary of AES data and percentage found by AES of amounts spiked by BRE.

compound	Amount spiked by BRE	Amount measured by AES*			% (measured/spiked)
		Mean	RSD (%)	SD	
toluene	24.3	28.26	1.58	5.58	116
TCE	33.8	35.48	0.96	2.71	105
m_xylene	17.7	18.92	0.49	2.59	107
limonene	16.6	23.81	1.31	5.49	143
undecane	18.6	23.40	0.59	2.52	126
TBP	24.5	23.39	1.64	7.02	95
TOCP	2.06	1.55	0.08	4.97	75
TMCP	1.98	1.65	0.16	9.96	83

\*Data not including outlier (tube Mi118122)

### ***Conclusion***

Both the BRE and AES data sets contained one tube (of seven) that had outlier values for several but not all of the analytes. There is no clear explanation for this but possible reasons include contamination during transport / storage and also contamination of the tube before spiking. These tube results have been removed before the calculation of the mean and standard deviation of replicates and the percentage measured relative to the amount spiked.

The repeatability is good as indicated by the relative standard deviation (RSD) which is below 10% for all analytes and both laboratories and below 5% for some analytes. The amount measured is within +/-20% of that spiked for both laboratories except for limonene (for BRE and AES) and undecane and TOCP (for AES only). All are within 30% except limonene for AES.

## **Appendix H – Cumulative frequency diagrams and geometric means and standard deviations of concentrations of VOCs/SVOCs measured in all phases over 100 flights**

Figure H1. Cumulative frequency distribution of all TOCP in air measurements.

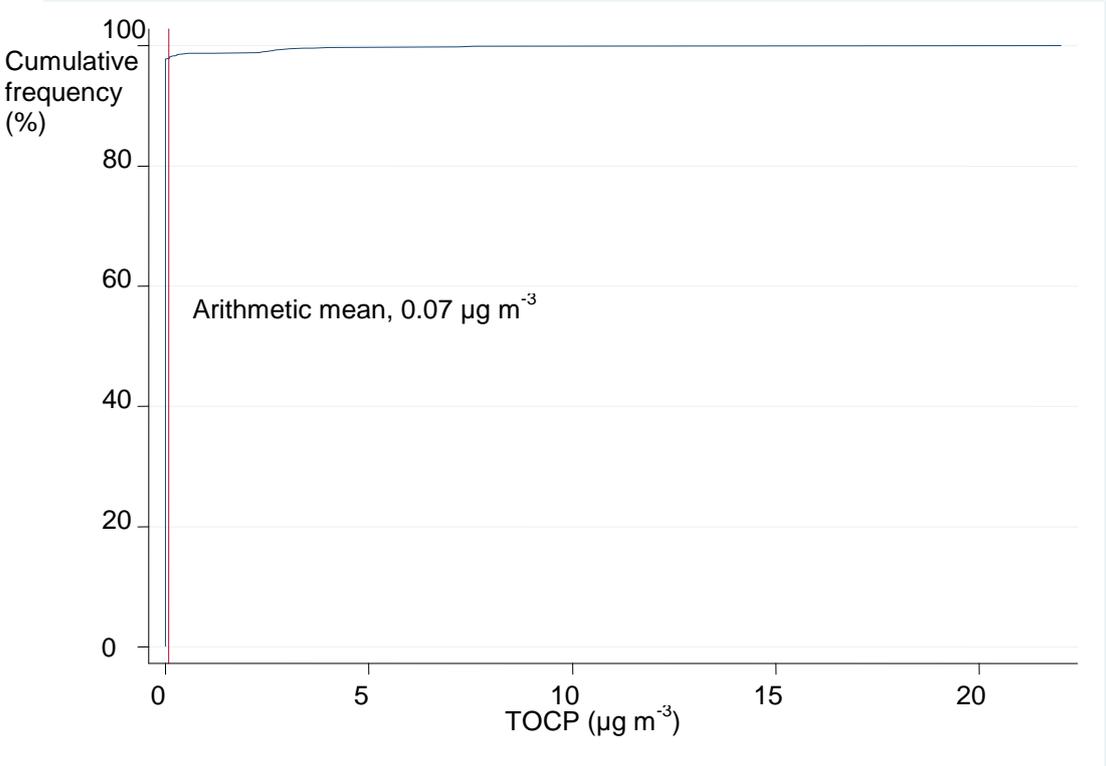


Figure H2. Cumulative frequency distribution of all other TCP in air measurements.

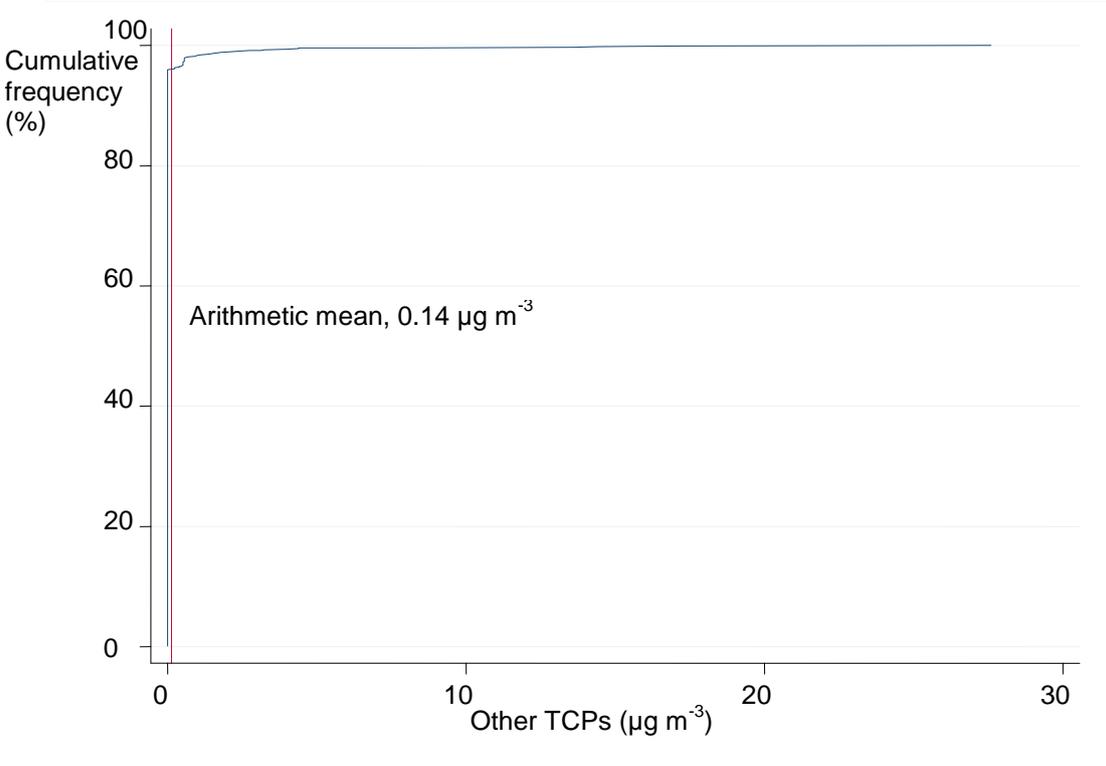


Figure H3. Cumulative frequency distribution of sum of all TOCP and other TCPs in air measurements.

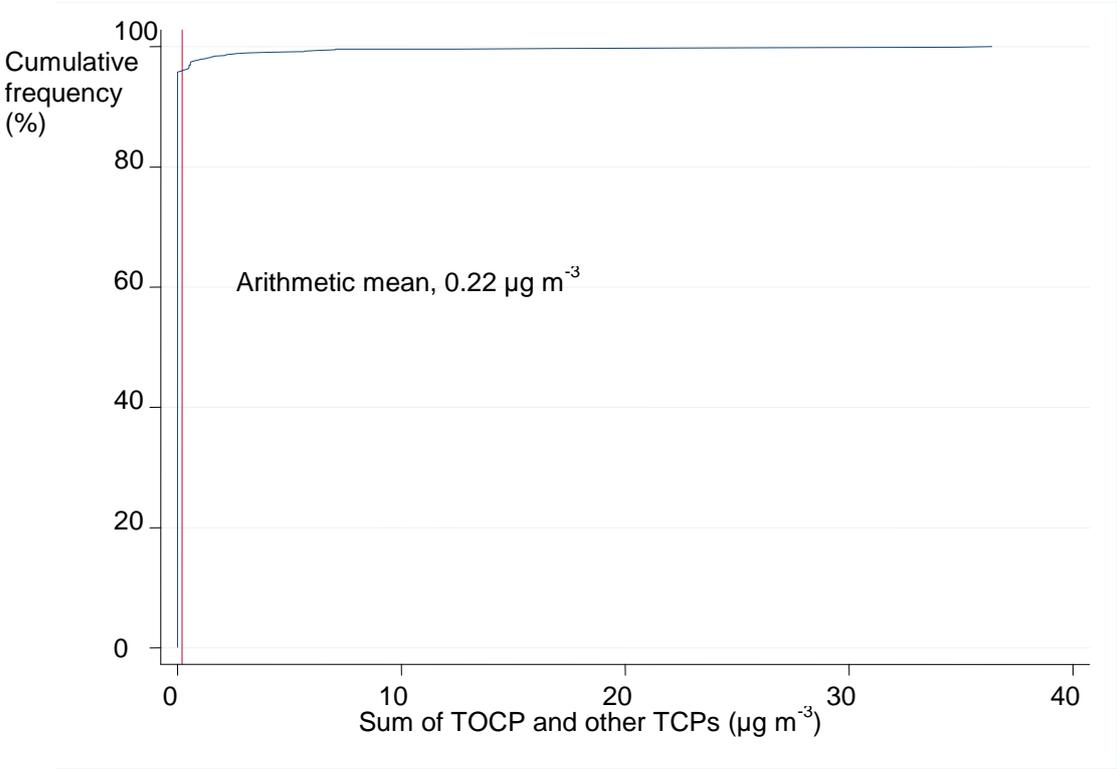


Figure H4. Cumulative frequency distribution TBP in air measurements.

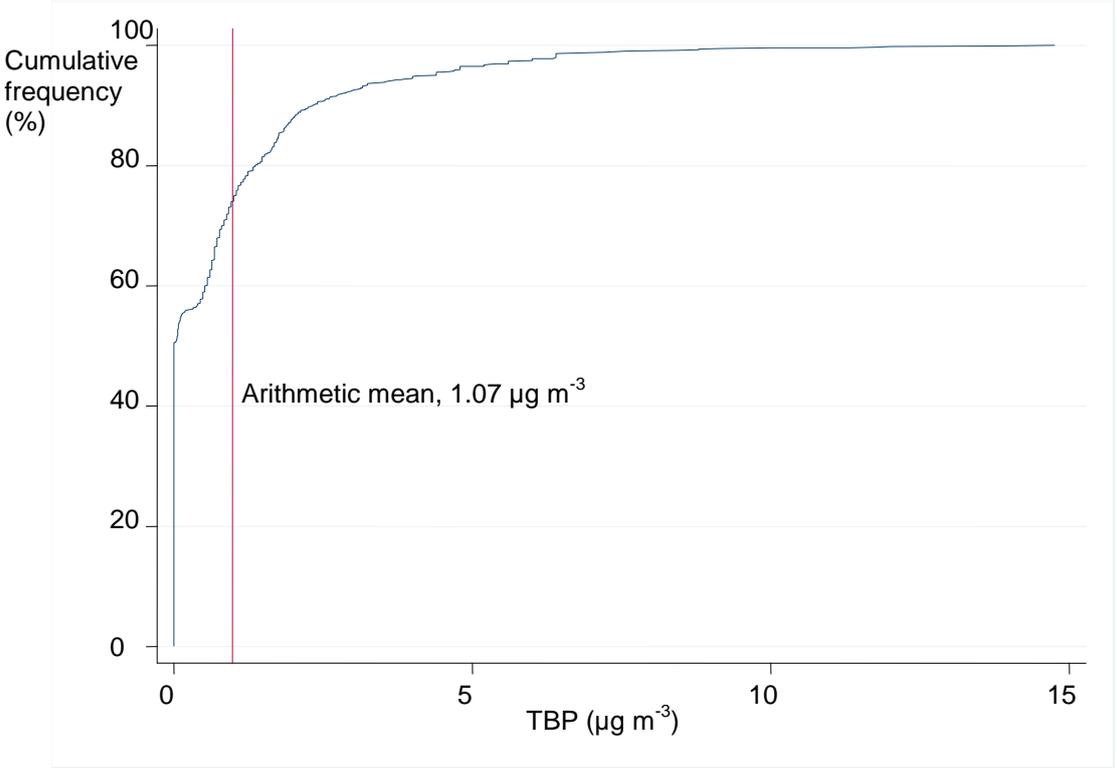


Figure H5. Cumulative frequency distribution of toluene in air measurements.

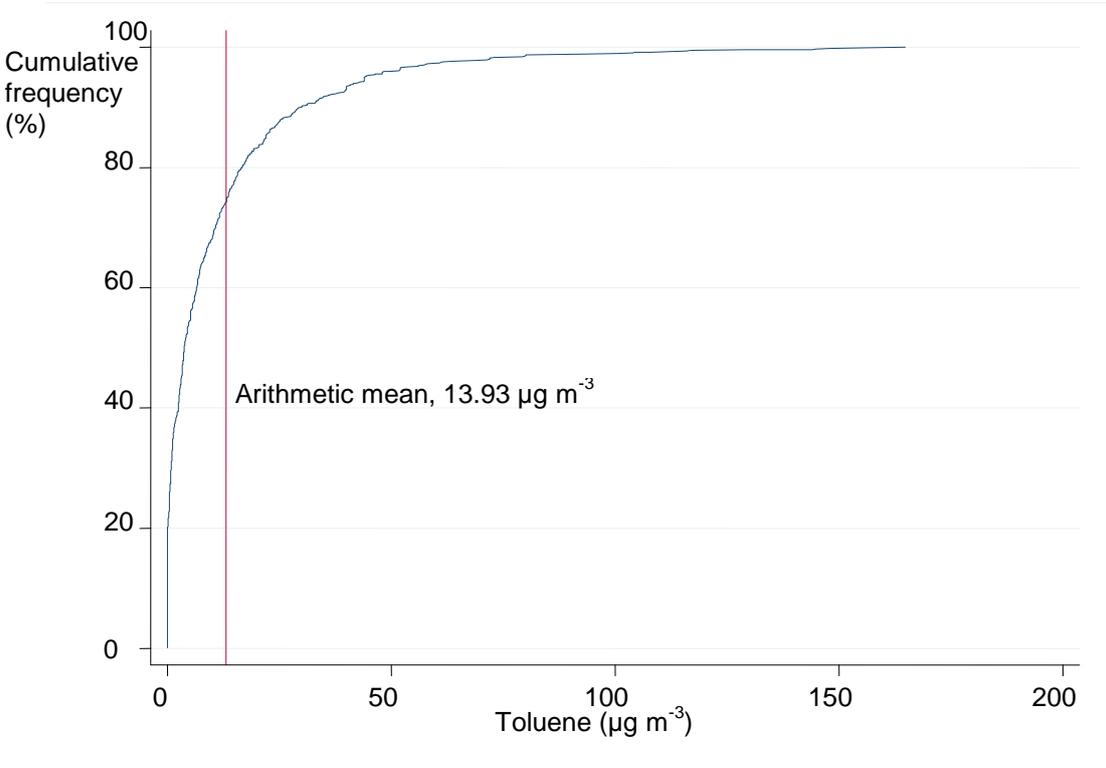


Figure H6. Cumulative frequency distribution of m+p xylene in air measurements.

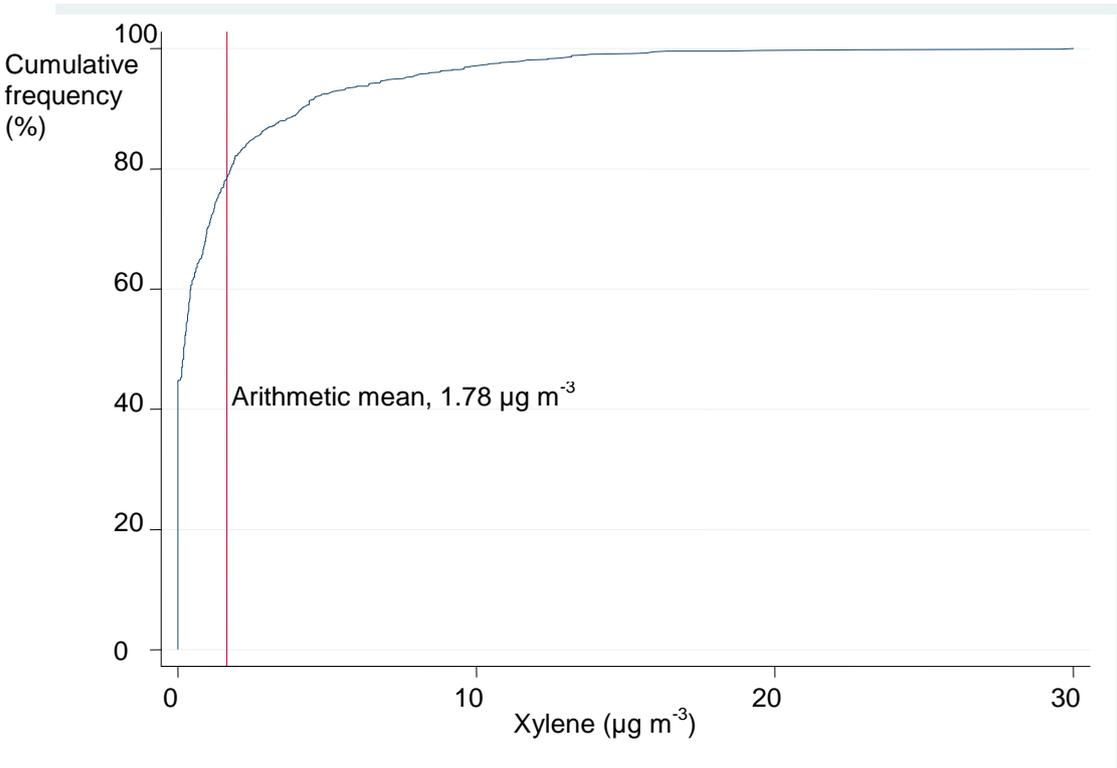


Figure H7. Cumulative frequency distribution of limonene in air measurements.

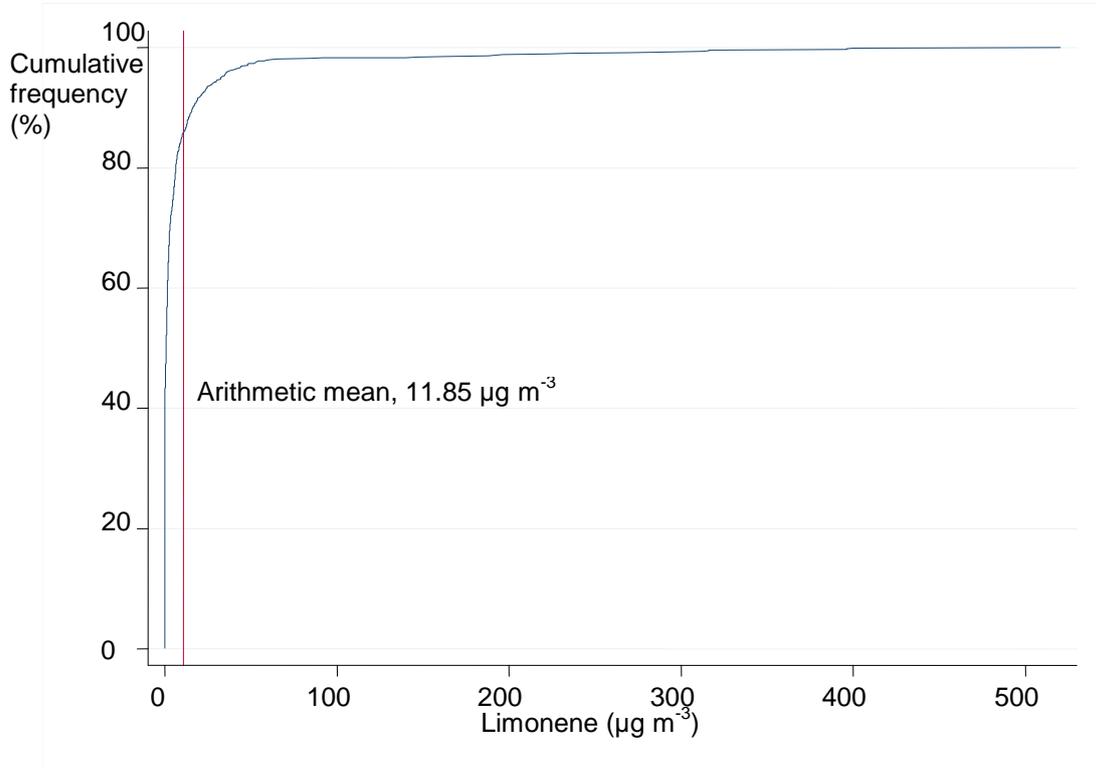


Figure H8. Cumulative frequency distribution of TCE in air measurements.

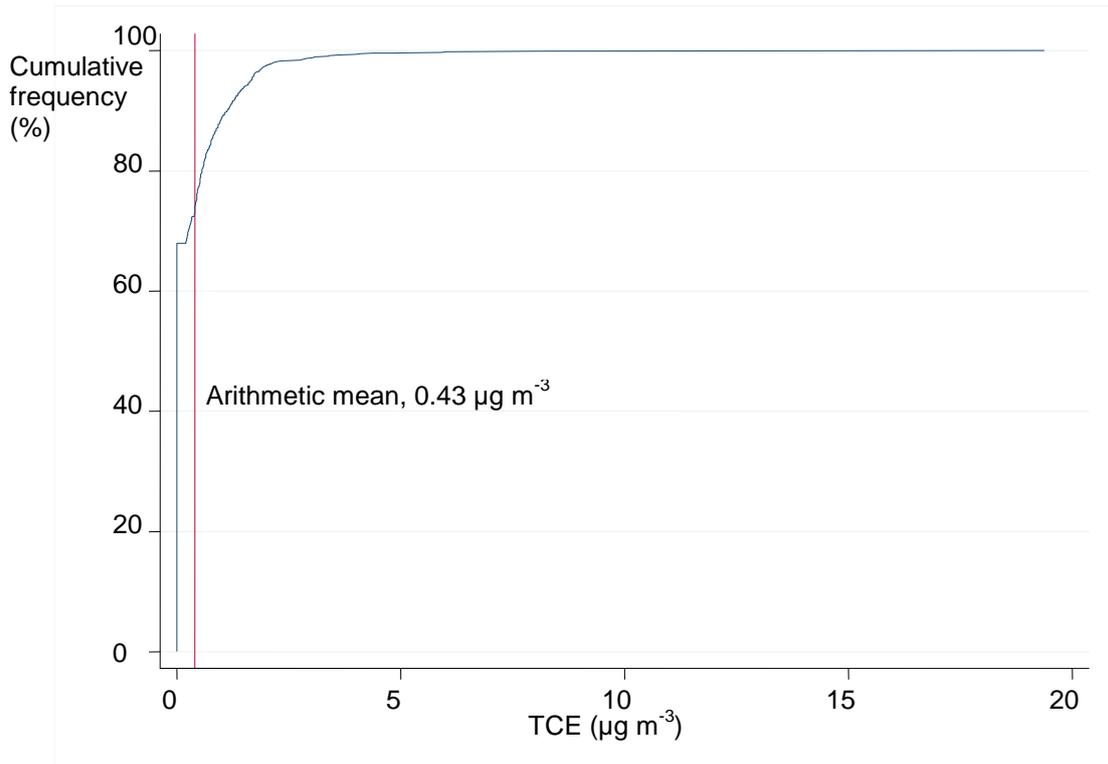


Figure H9. Cumulative frequency distribution of undecane in air measurements.

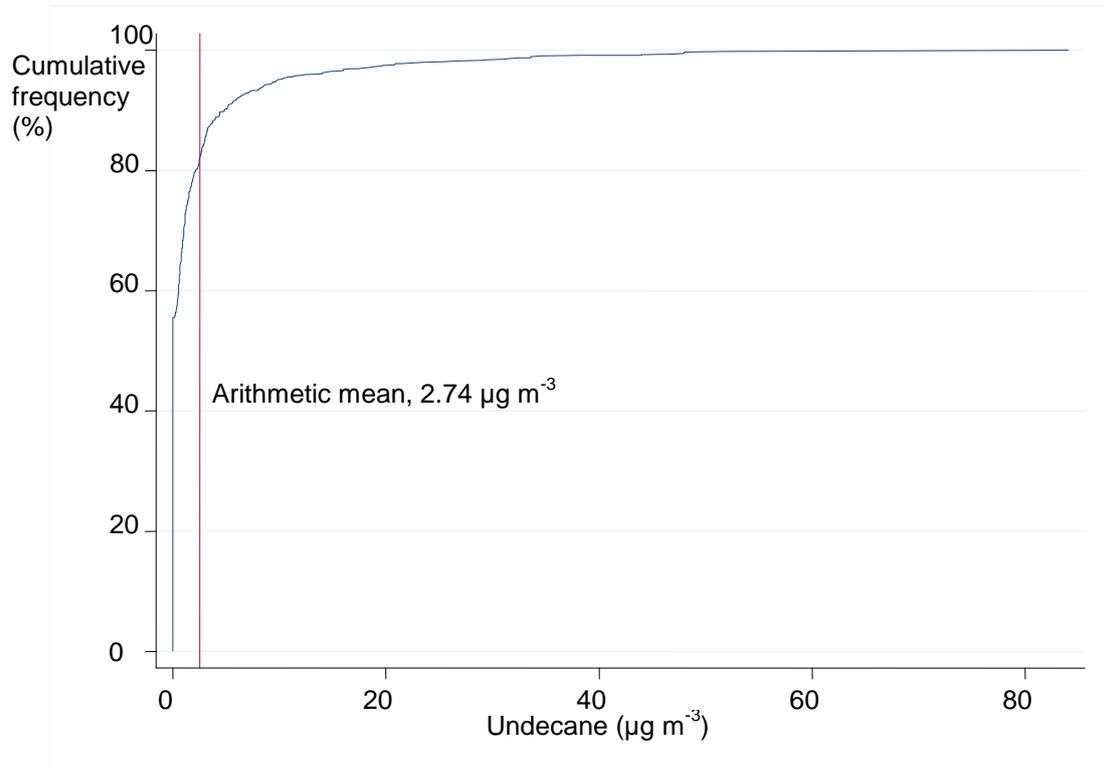


Table H1. Geometric mean and standard deviation for target chemicals measured in all flight phases (including additional samples taken during ‘air quality events’).

Compound (n)	Concentration $\mu\text{g m}^{-3}$	
	GM	GSD
TOCP (981)	ND	3.03
Other TCPs (981)	ND	4.41
Sum of TOCP and other TCPs (981)	ND	4.86
TBP (981)	0.04	40.20
Toluene (981)	2.20	28.59
m+p xylene (981)	0.09	37.26
Limonene (981)	0.20	72.71
TCE (981)	0.01	27.02
C <sub>11</sub> (981)	0.05	53.77

ND = none detected

Note; for calculation purposes all ND values given a nominal above zero value

## **Appendix I – Summary of results of analysis of blank sorbent tube samples**

During each flight at least one sorbent tube was identified as a travel blank. Also a further 'second blank' tube was normally analysed. A total of 185 blank tubes were analysed along with the tubes used for air sampling during 100 flights. The results of the TD/GC/MS analysis of target analytes is summarised in Table I1. Results are expressed in terms of the amount that the blank value would represent if it were collected from 2.5 L air.

Table I1. Results for all blanks (n=185).

Compound	Equivalent concentration ( $\mu\text{g m}^{-3}$ ) if collected from 2.5 L of air							
	10%	50%	75%	95%	AM*	SD	min	max
TOCP	ND	ND	ND	ND	0.01	0.094	ND	1.2
Other TCPs	ND	ND	ND	ND	0.02	0.114	ND	1.1
Sum of TOCP and other TCPs	ND	ND	ND	ND	0.03	0.2	ND	2.2
TBP	ND	ND	0.08	1.1	0.17	0.568	ND	5.2
Toluene	ND	ND	0.44	1.1	0.34	0.768	ND	6
m+p xylenes	ND	ND	ND	0.2	0.05	0.189	ND	1.4
Limonene	ND	ND	0.2	1.0	0.29	1.216	ND	14.4
TCE	ND	ND	ND	ND	ND	-	ND	ND
C <sub>11</sub>	ND	ND	ND	1.1	0.161	0.569	ND	5.0

It is notable that for all but two of the blanks, the TOCP, TCP and sum of TOCP and TCPs values were not detectable. Both of these tubes were second blanks and the travel blanks for the same flight were both non-detects. The maximum reading for xylene, limonene and undecane was for a travel blank on a flight where no second blank was determined. For TBP the highest value (5.2) was for a second blank and the travel blank for the same flight was lower (2.8). The blank tubes for the flight during which the highest TBP concentration ( $21.8 \mu\text{g m}^{-3}$ ) was recorded were  $0.6$  and  $2.0 \mu\text{g m}^{-3}$  equivalent concentration. For toluene the highest value (6) was for a travel blank and the second blank gave a very similar value (5.6). It was decided not to adjust the measured values during flights by blank deduction because of the generally low blank levels and to ensure a conservative comparison of the data with available air quality guidelines and standards.

## **Appendix J – Mean concentration of VOCs/SVOCs during different phases of flight**

Figure J1. Mean concentration (and 95% confidence interval) of TOCP ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

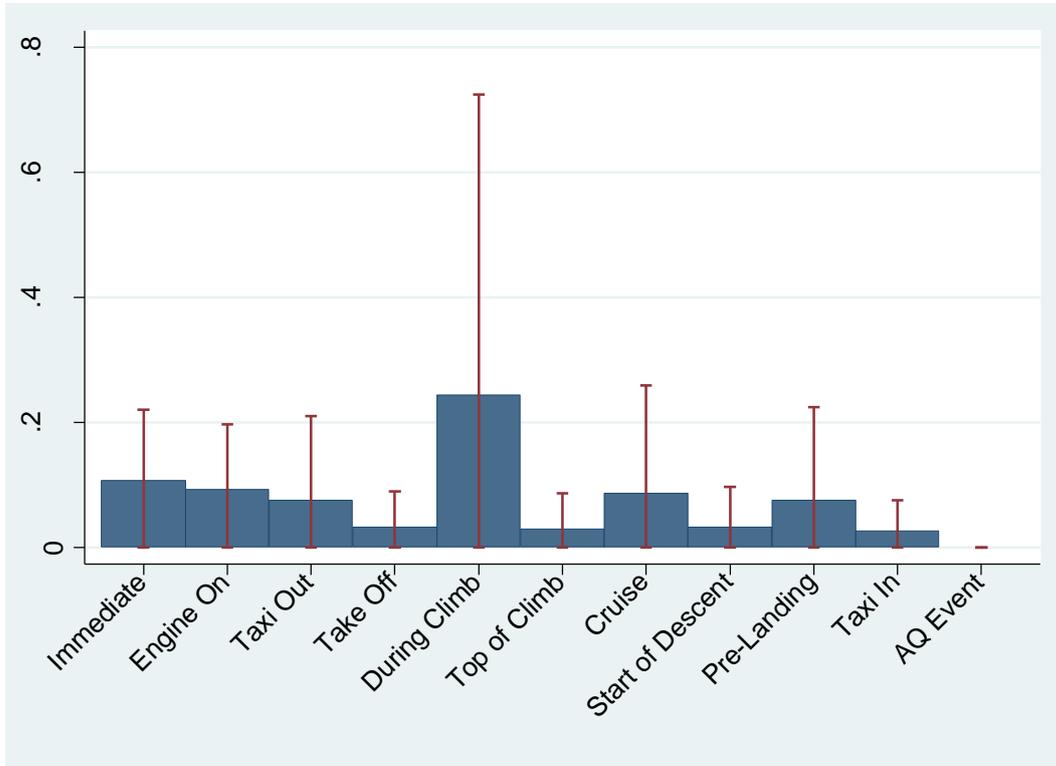


Figure J2. Mean concentration (and 95% confidence interval) of other TCPs ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

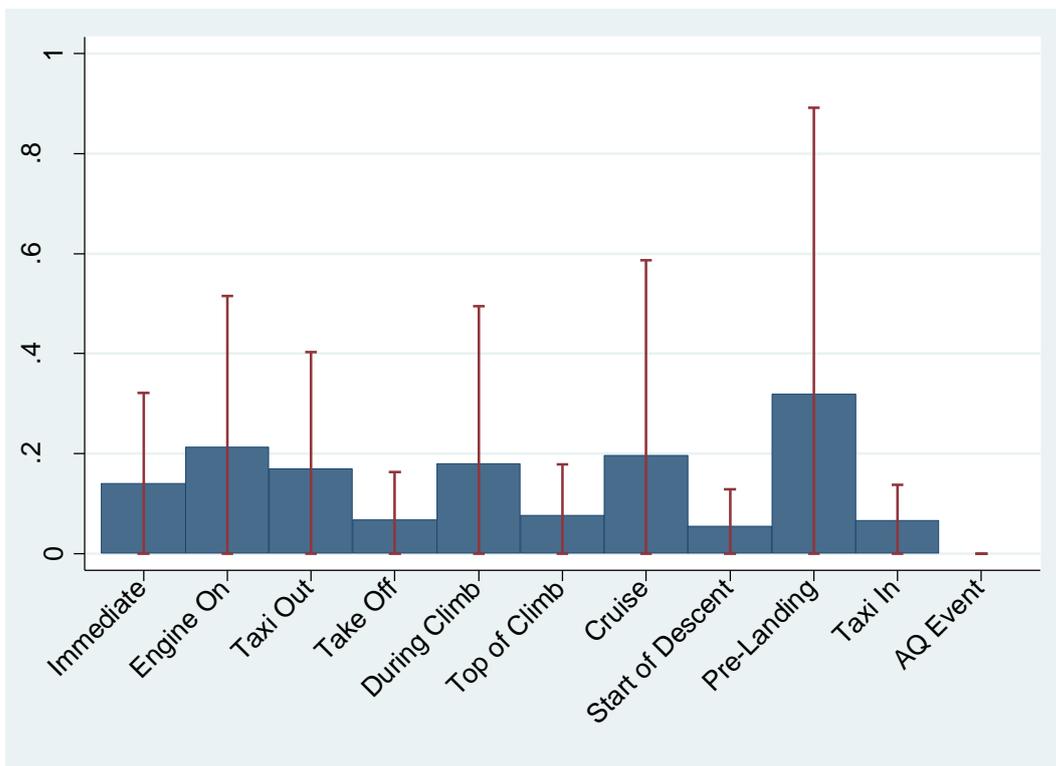


Figure J3. Mean concentration (and 95% confidence interval) of sum of other TCPs and TOCP ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

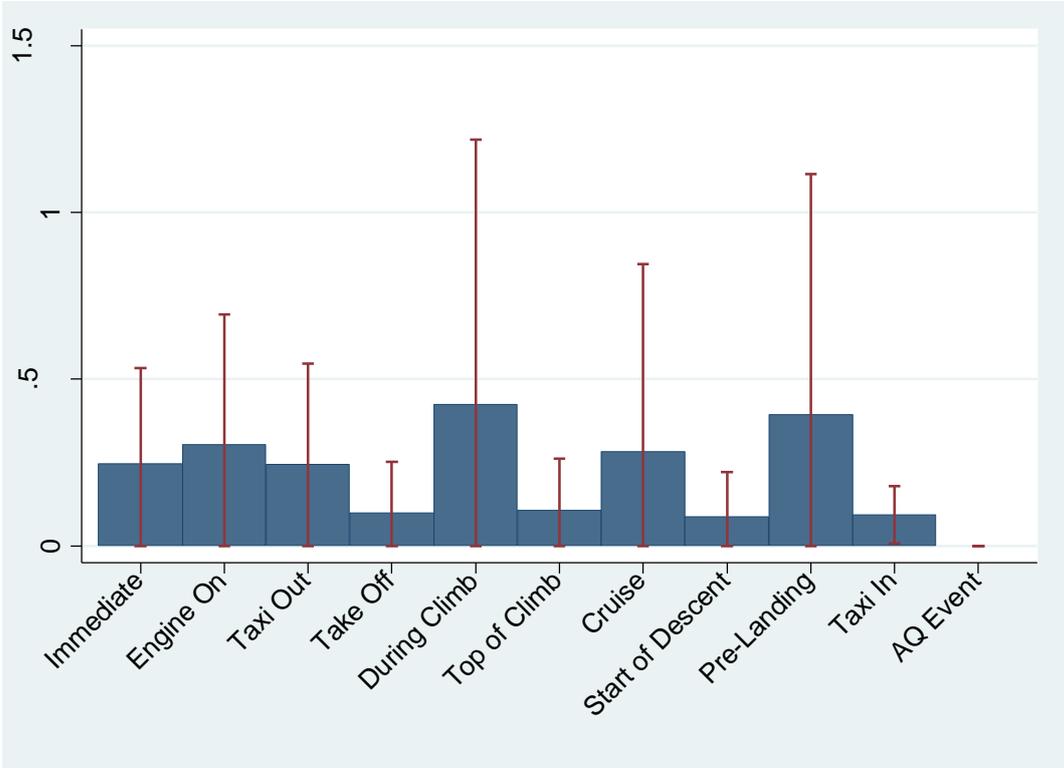


Figure J4. Mean concentration (and 95% confidence interval) of TBP ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

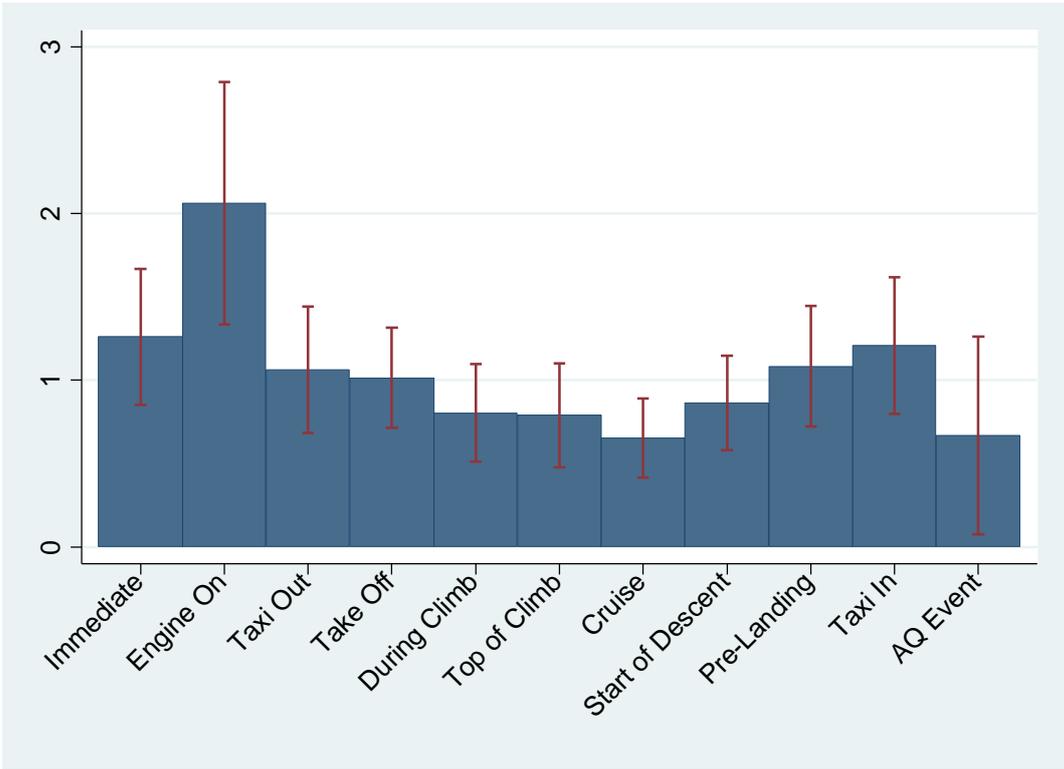


Figure J5. Mean concentration (and 95% confidence interval) of toluene ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

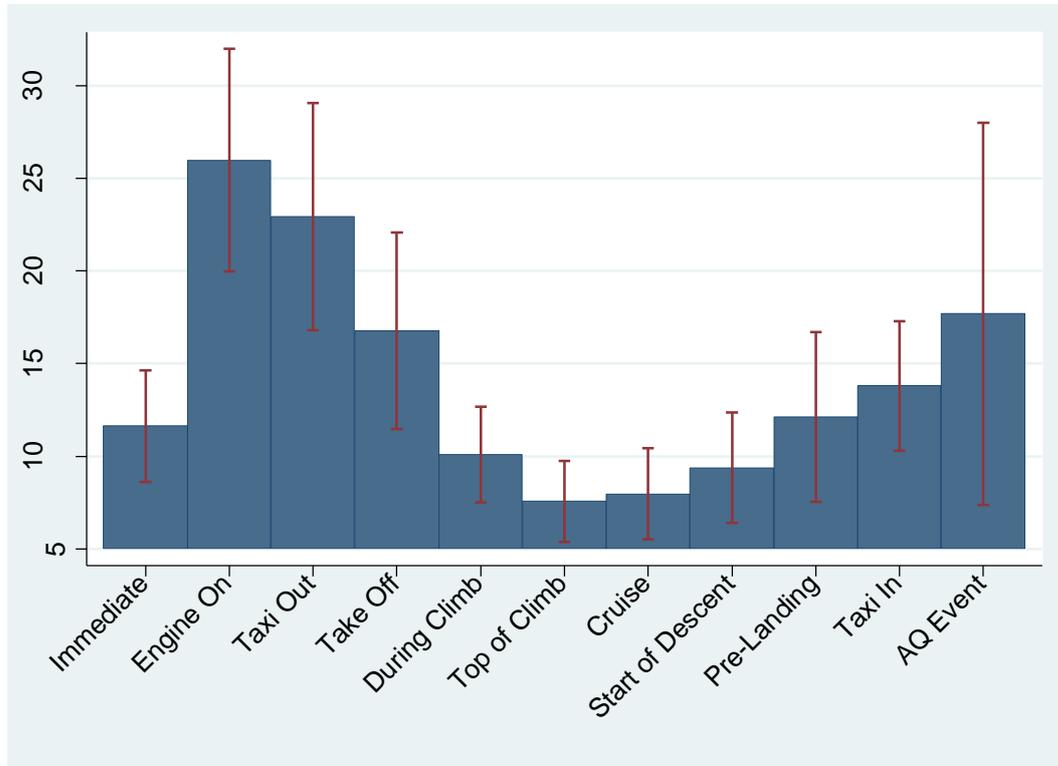
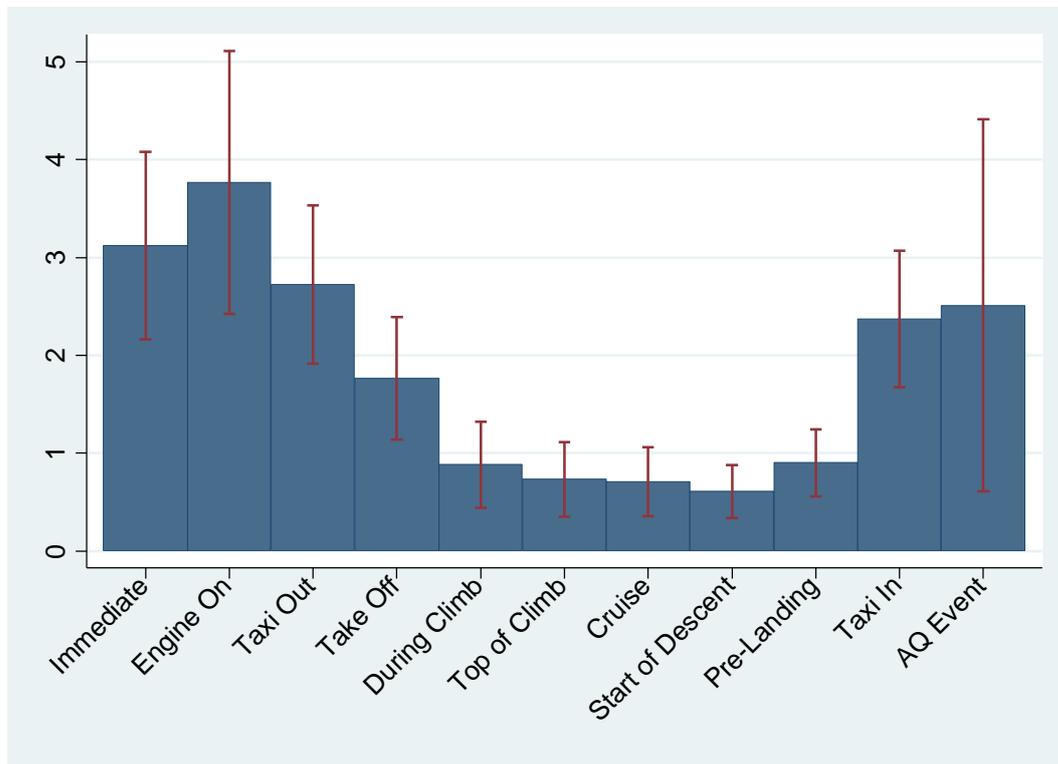
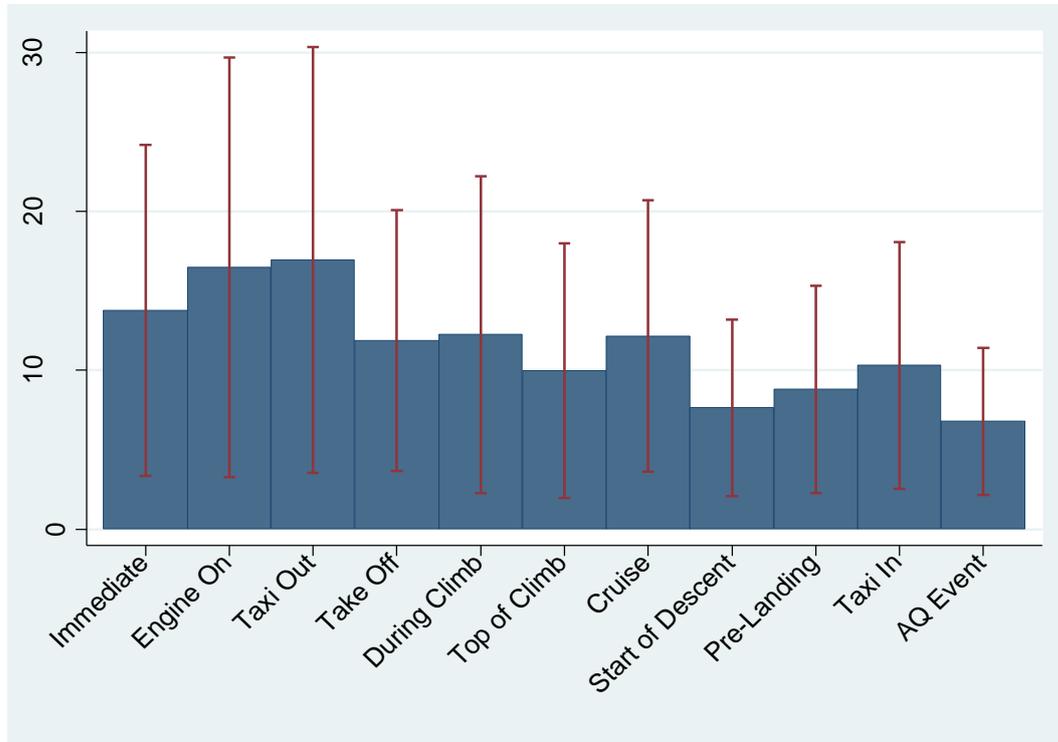


Figure J6. Mean concentration (and 95% confidence interval) of m+p-xylene ( $\mu\text{g m}^{-3}$ ) during different phases of flight.



**Figure J7.** Mean concentration (and 95% confidence interval) of limonene ( $\mu\text{g m}^{-3}$ ) during different phases of flight.



**Figure J8.** Mean concentration (and 95% confidence interval) of TCE ( $\mu\text{g m}^{-3}$ ) during different phases of flight.

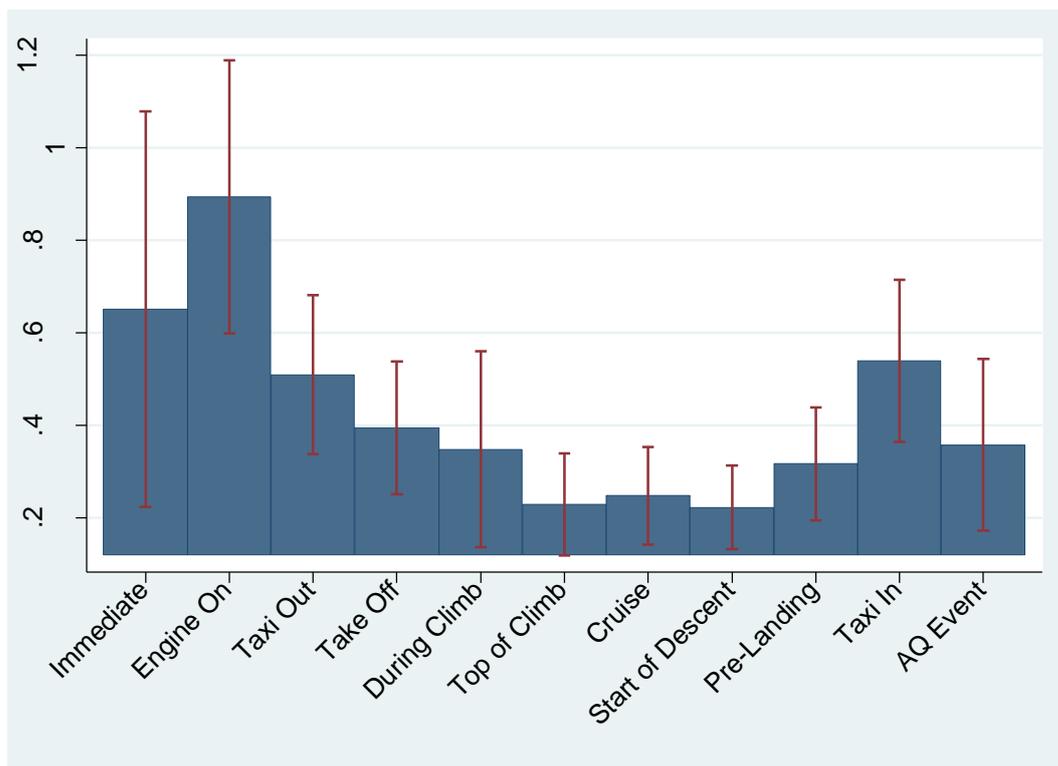
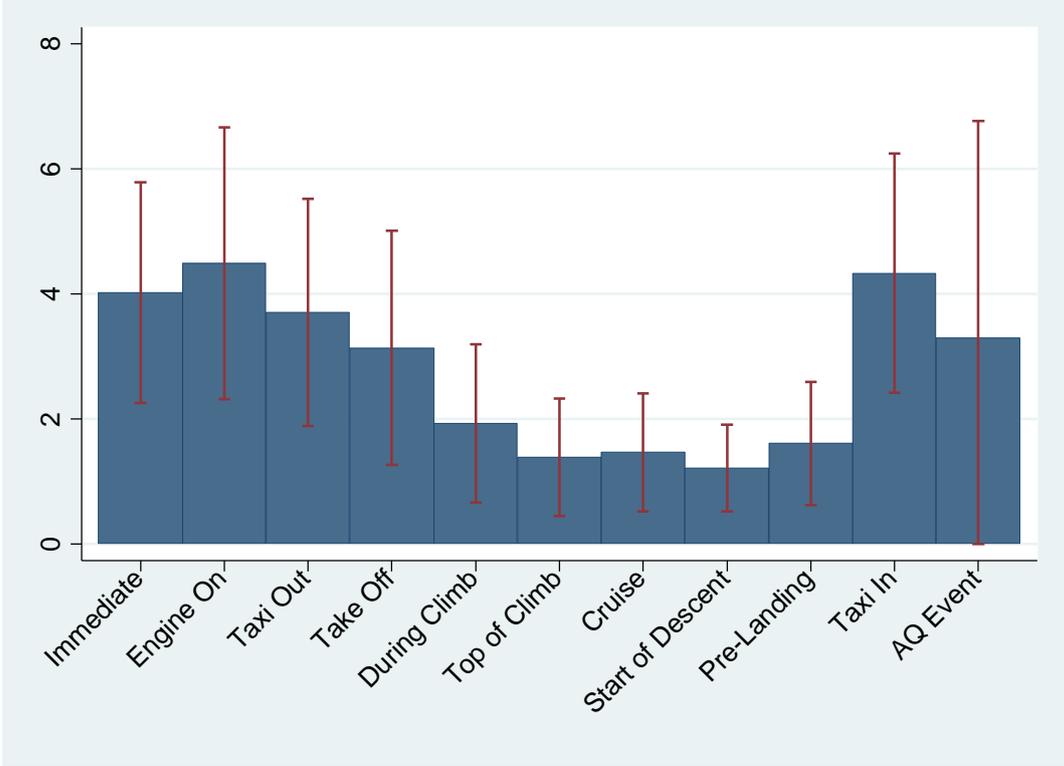


Figure J9. Mean concentration (and 95% confidence interval) undecane ( $\mu\text{g m}^{-3}$ ) during different phases of flight.



## **Appendix K – Concentration of VOCs/SVOCs during each Part of the study and during different phases of flight for each Part of the study**

**Appendix K-1; Mean concentrations (and 95% confidence intervals) during each Part of Study**

Figure K1-1. Mean concentration of TOCP ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

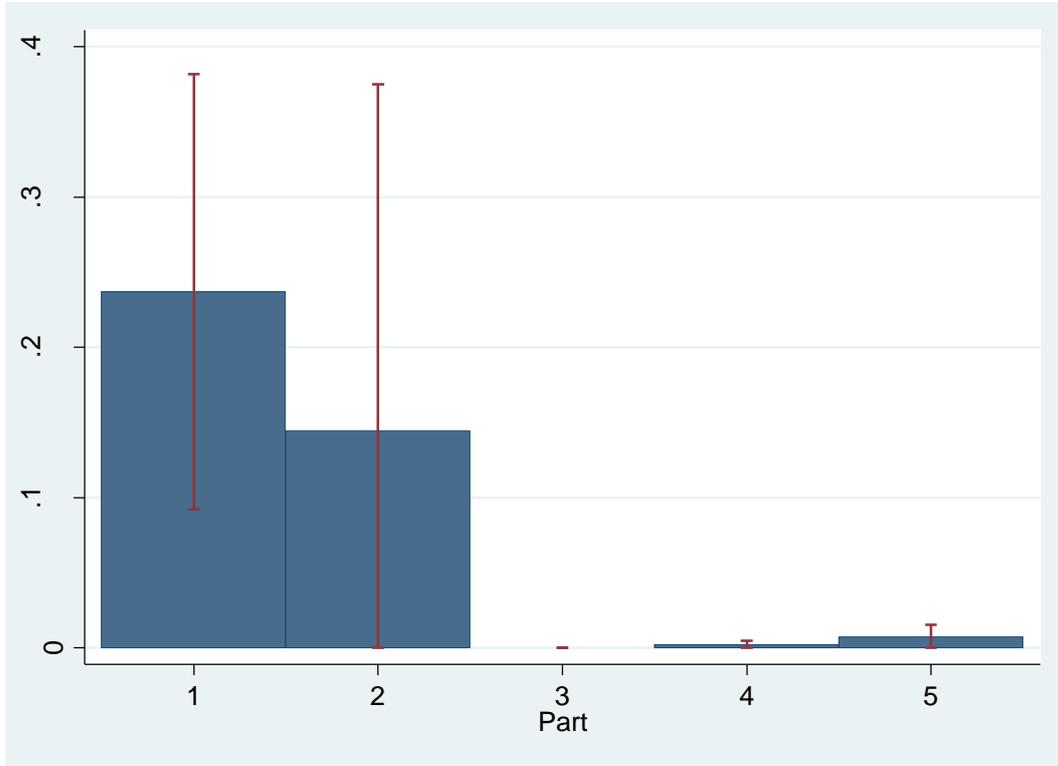


Figure K1-2. Mean concentration of TCPs ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

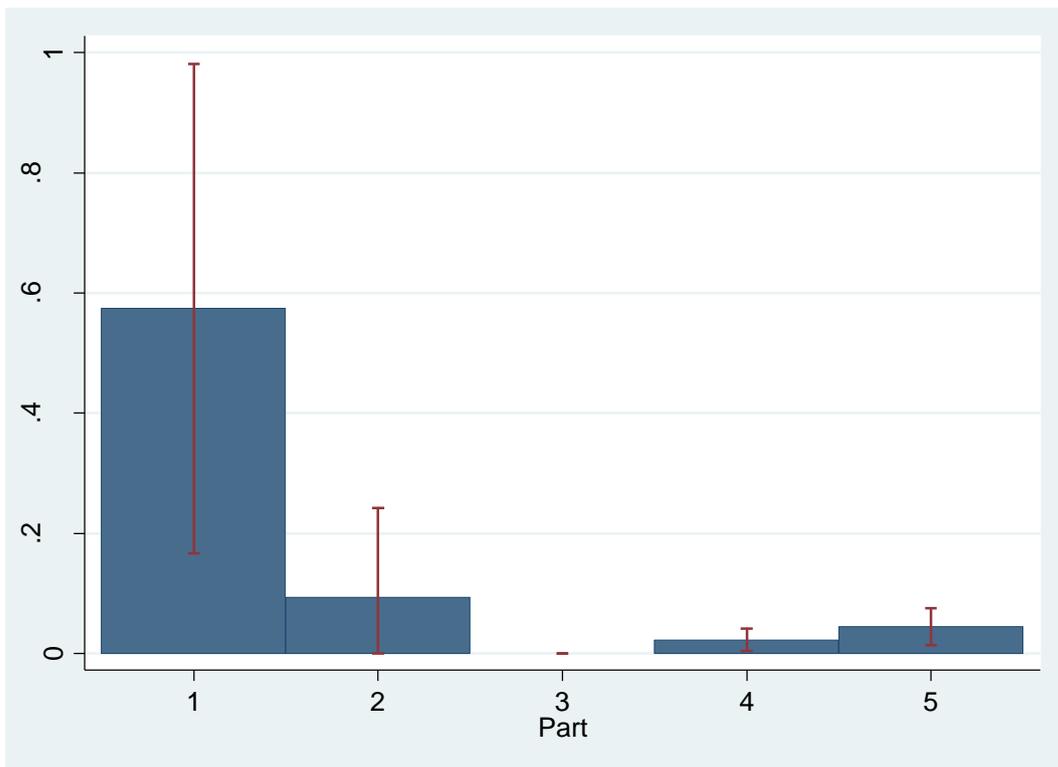


Figure K1-3. Mean concentration of other TCPs and TOCP ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

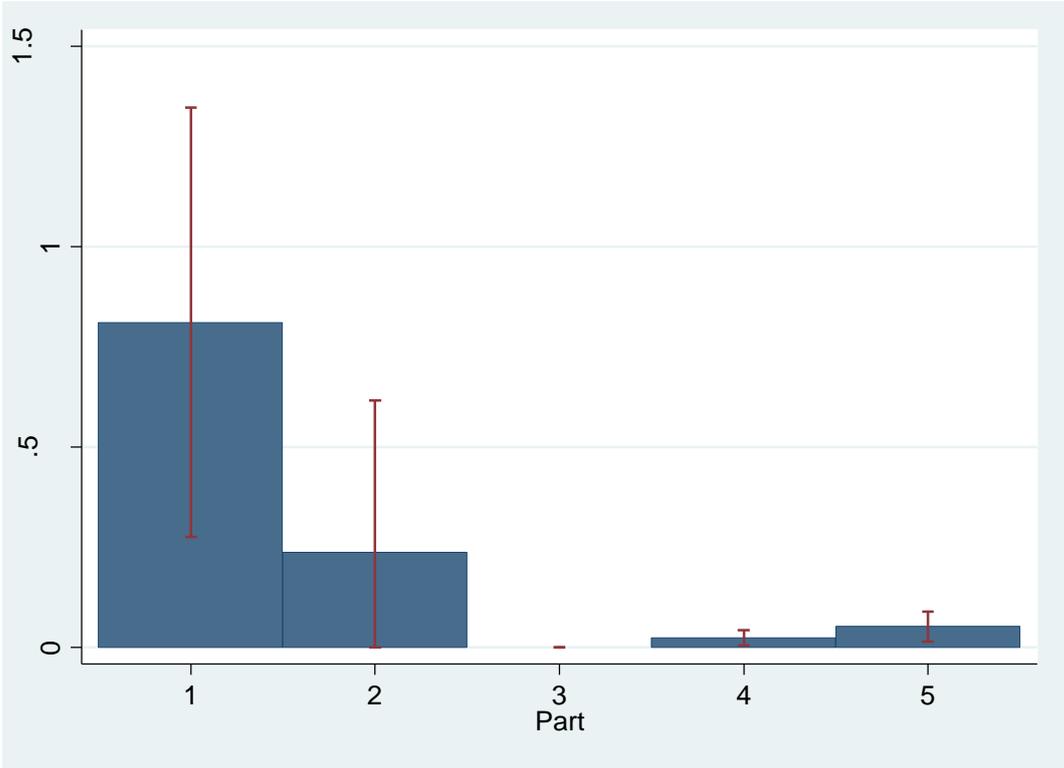


Figure K1-4. Mean concentration of TBP ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

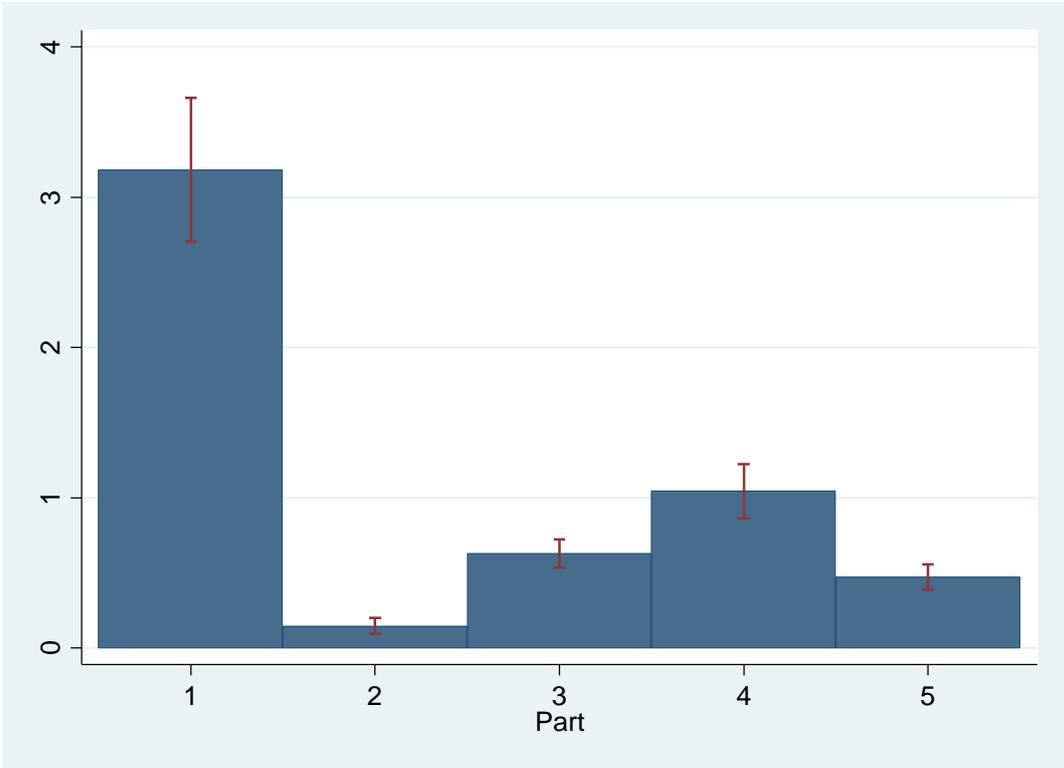


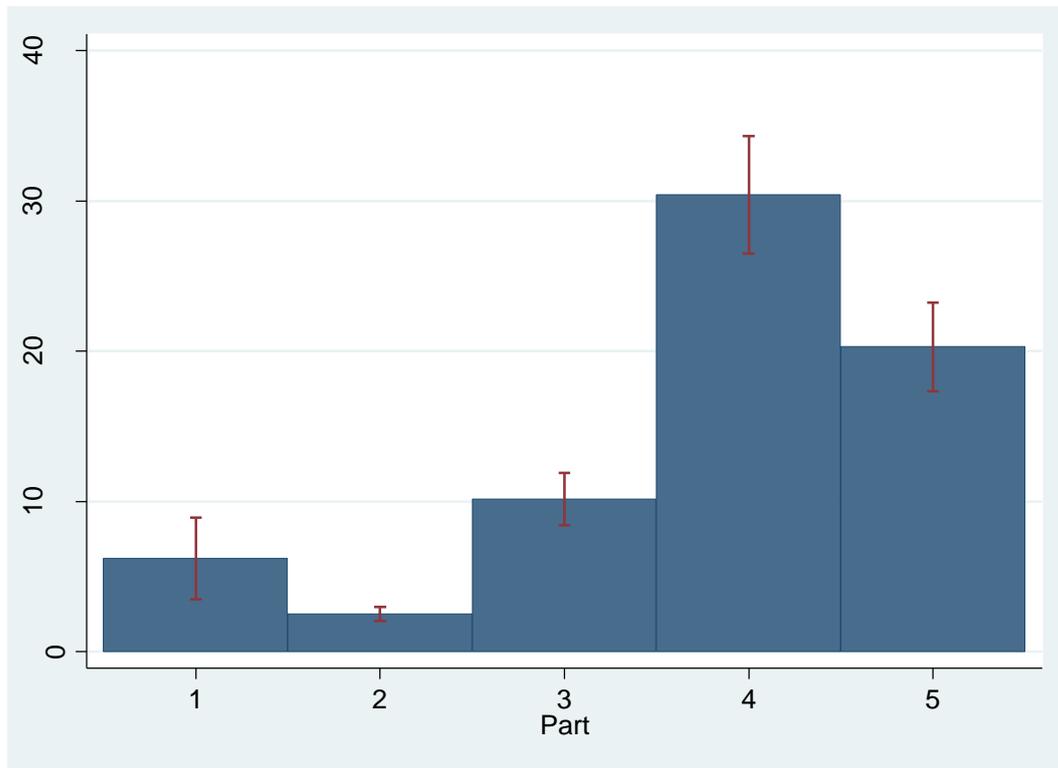
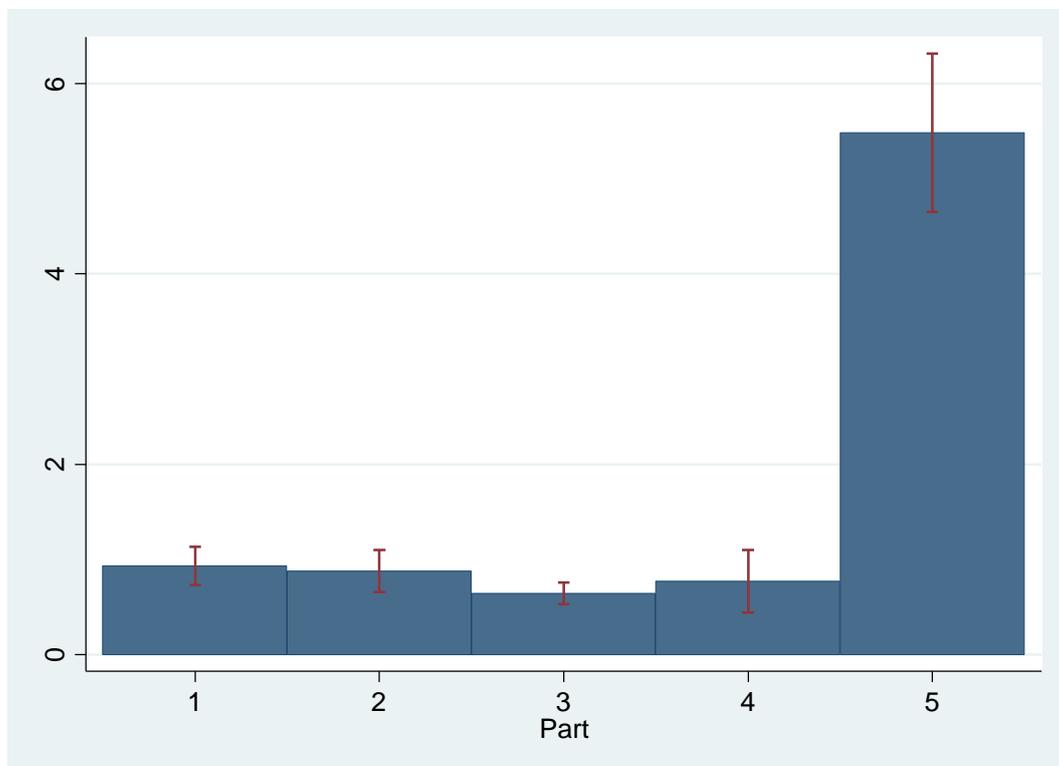
Figure K1-5. Mean concentration of toluene ( $\mu\text{g m}^{-3}$ ) during each Part of the study.Figure K1-6. Mean concentration of m+p-xylene ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

Figure K1-7. Mean concentration of limonene ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

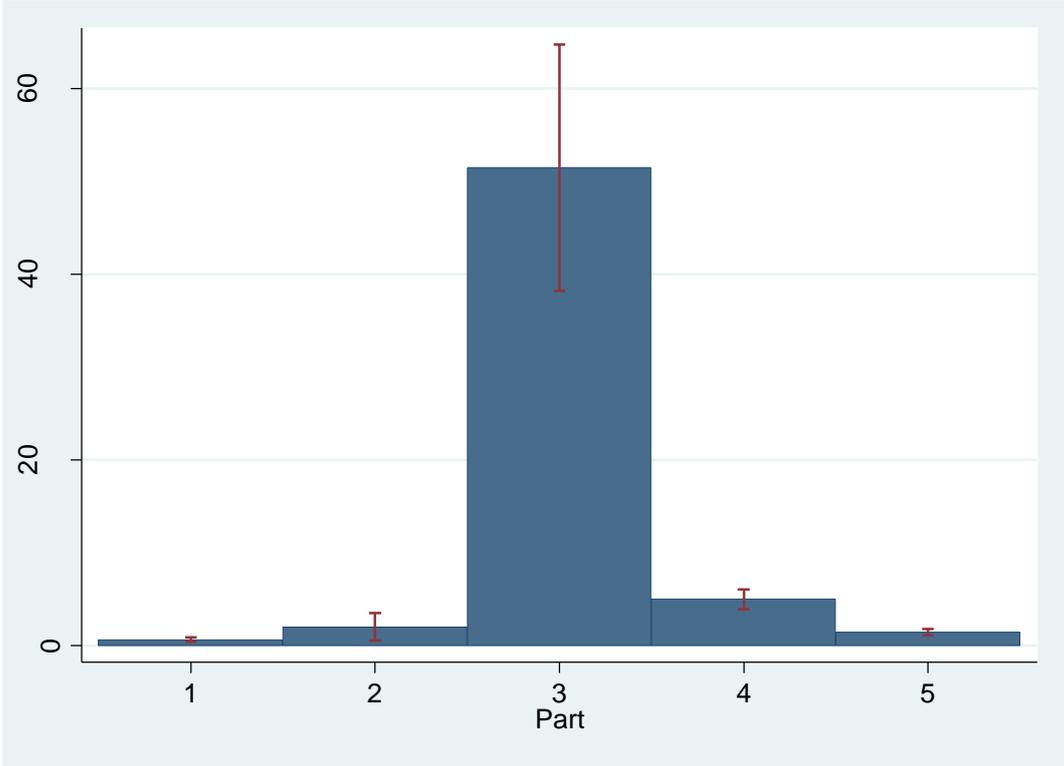


Figure K1-8. Mean concentration of TCE ( $\mu\text{g m}^{-3}$ ) during each Part of the study.

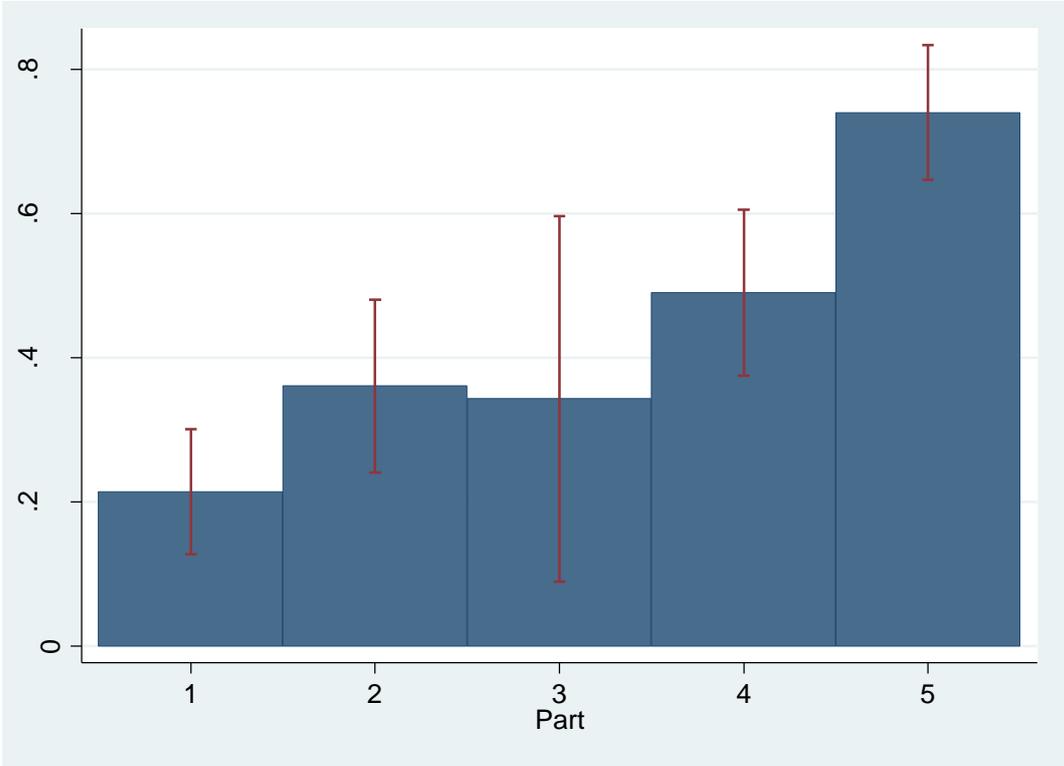
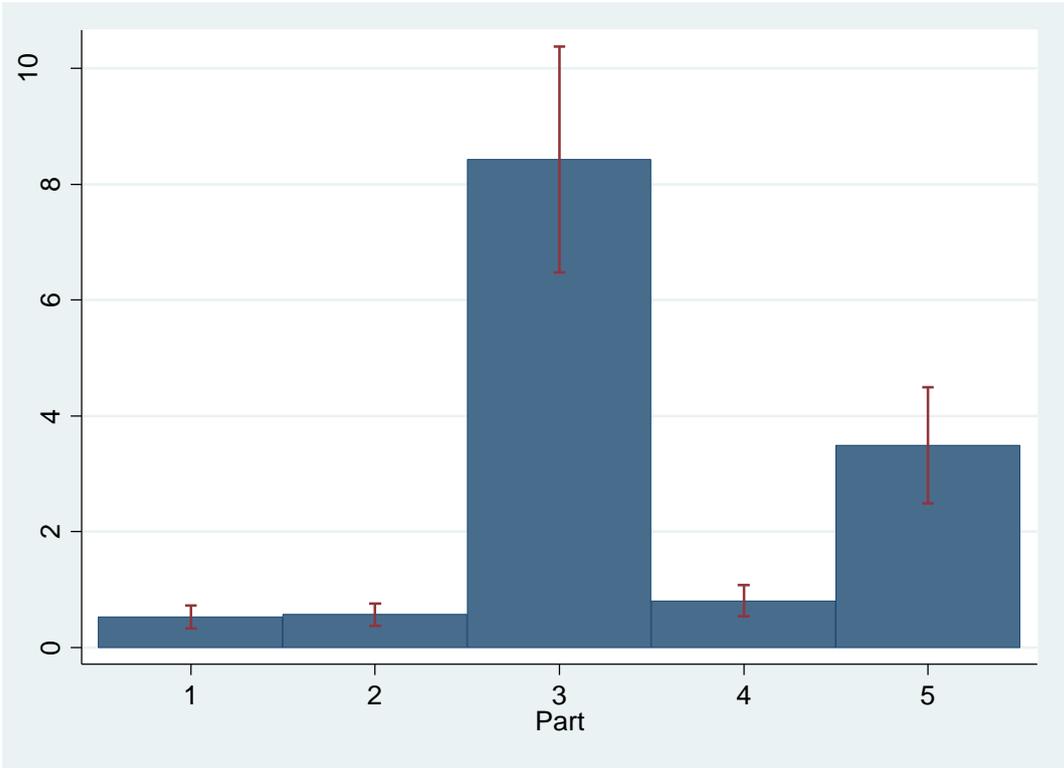


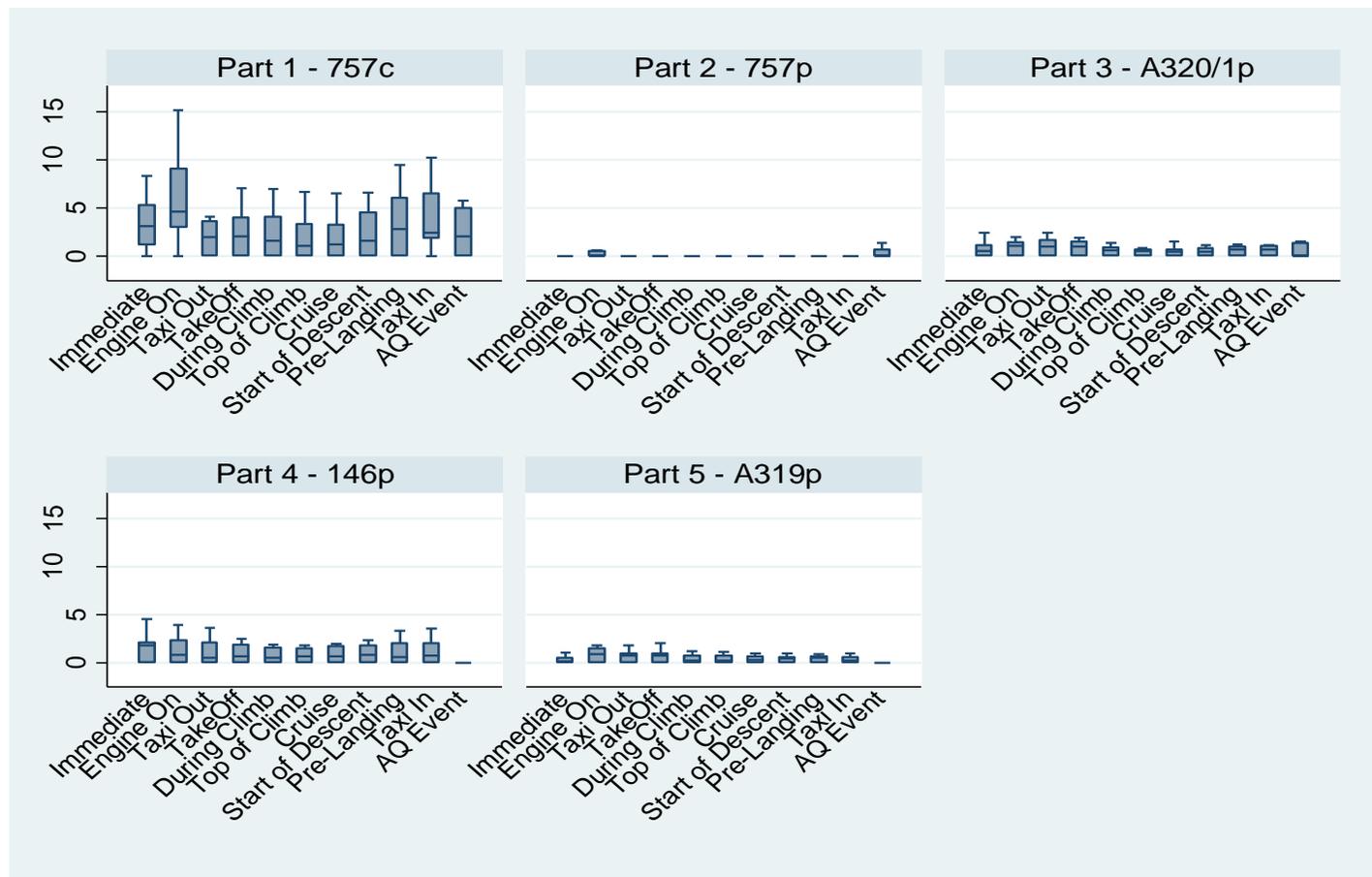
Figure K1-8. Mean concentration of undecane ( $\mu\text{g m}^{-3}$ ) during each Part of the study.



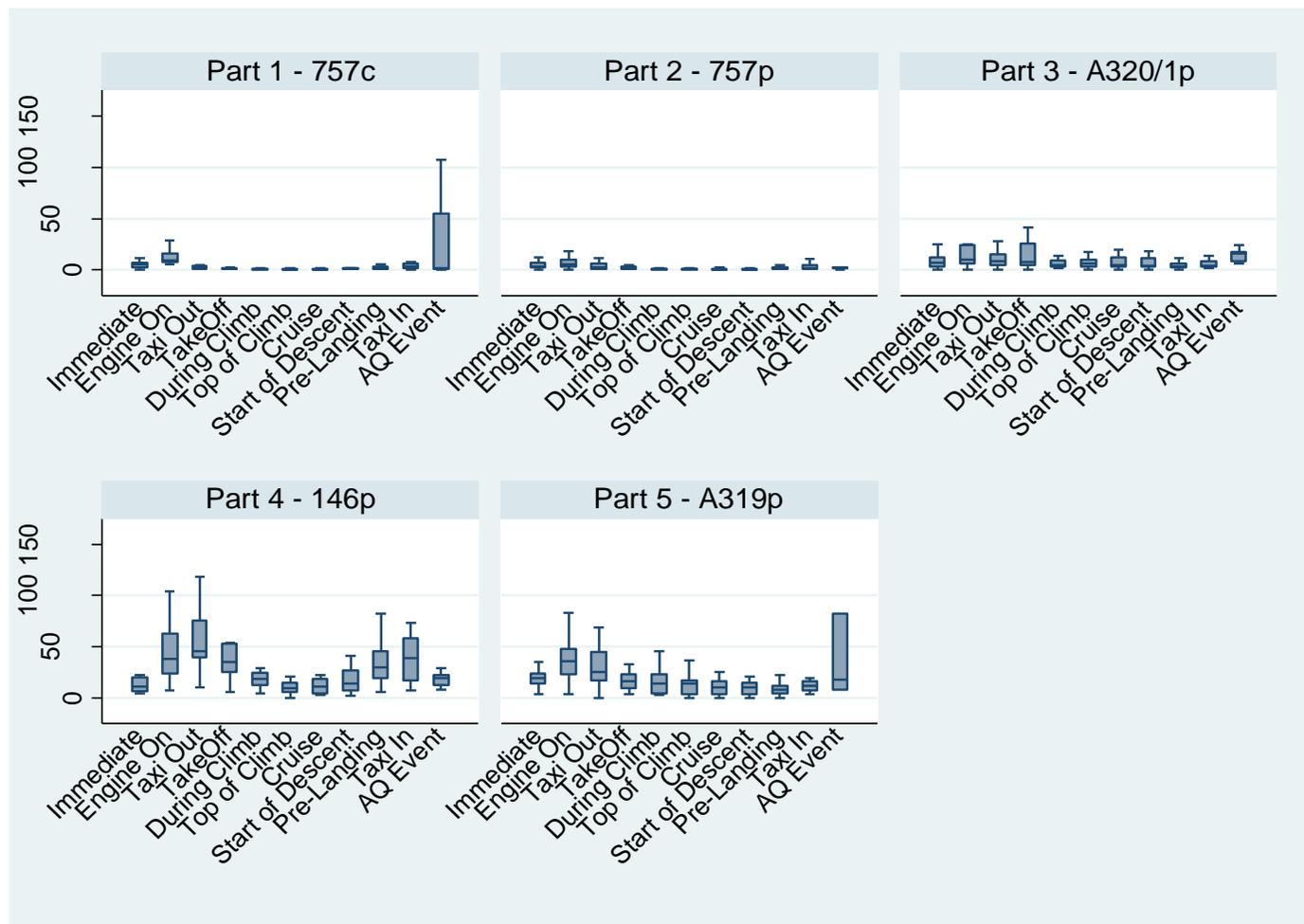


**Appendix K-2; Box plots of mean concentrations during each Part of Study and Phase of Flight**

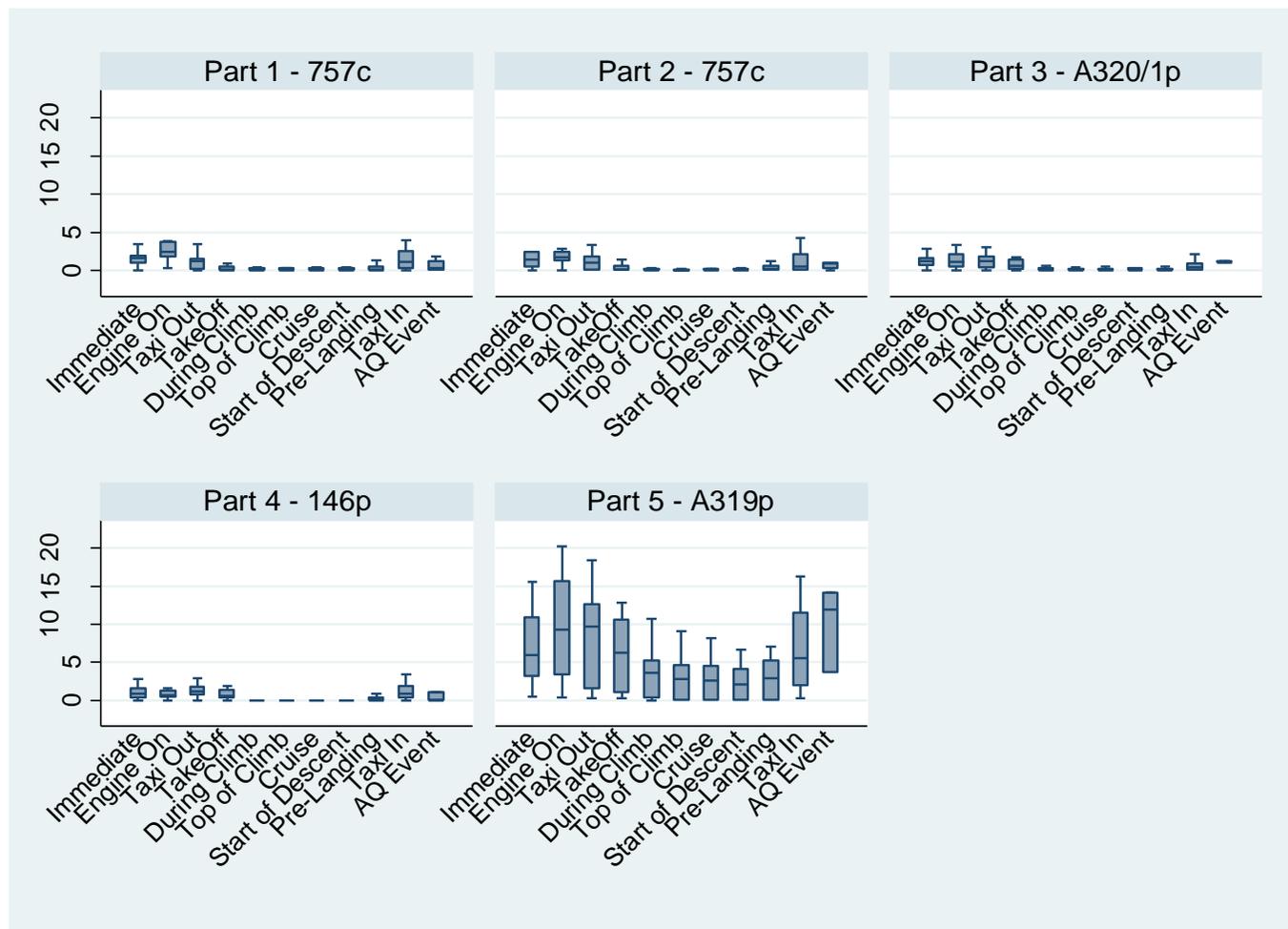
Figures K2-1(a-e). Box plot of TBP concentration ( $\mu\text{g m}^{-3}$ ).



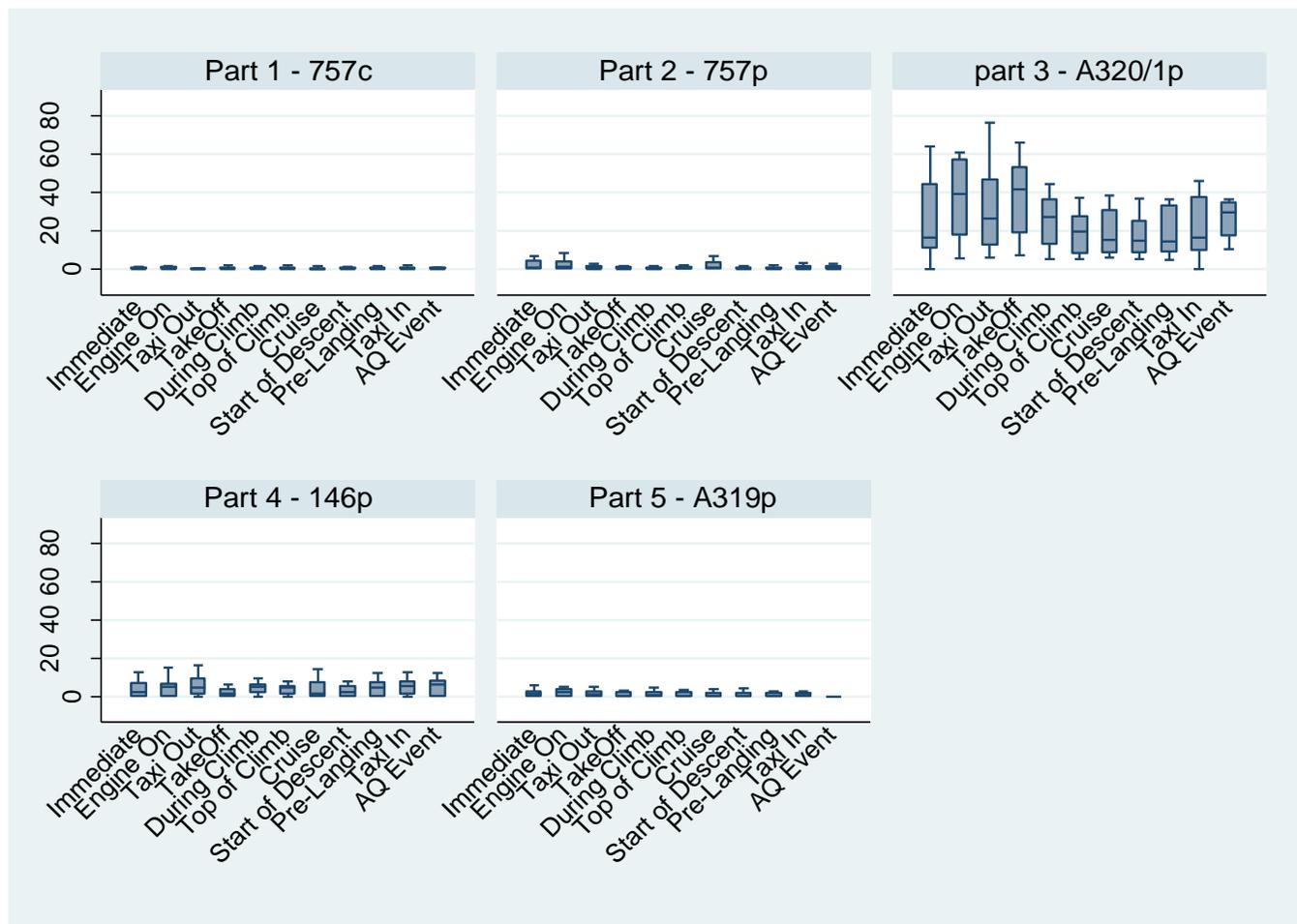
Figures K2-2(a-e). Box plot of toluene concentration ( $\mu\text{g m}^{-3}$ ).



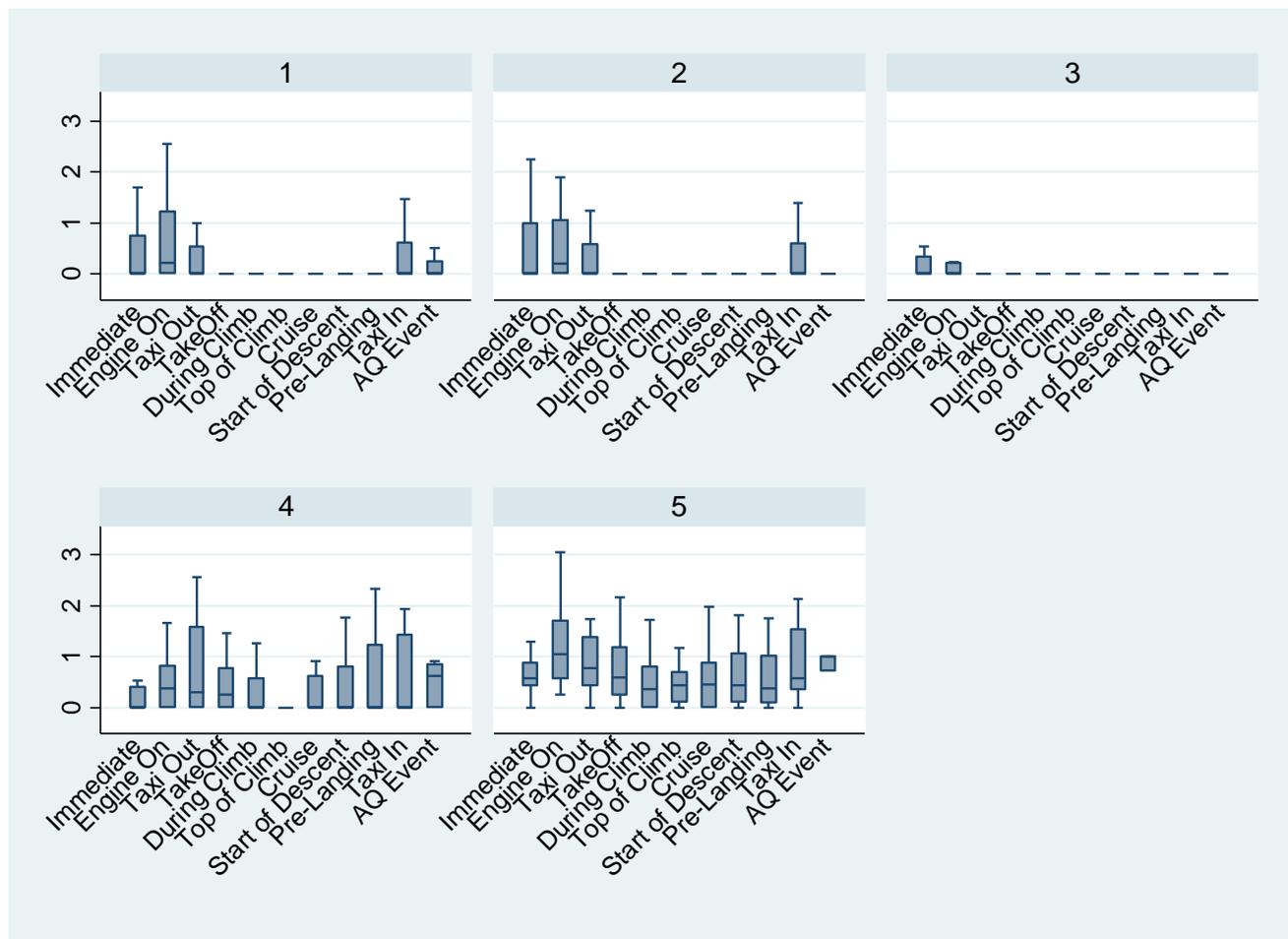
Figures K2-3(a-e). Box plot of m+p-xylene concentration ( $\mu\text{g m}^{-3}$ ).



Figures K2-4(a-e). Box plot of limonene concentration ( $\mu\text{g m}^{-3}$ ).



Figures K2-5(a-e). Box plot of TCE concentration ( $\mu\text{g m}^{-3}$ ).



Figures K2-6(a-e). Box plot of undecane concentration ( $\mu\text{g m}^{-3}$ ).

