EASA
European Aviation Safety Agency

Final Report EASA_REP_RESEA_2014_4

Research Project:

CAQ
Preliminary cabin air quality measurement campaign

An agency of the European Union

Fraunhofer ITEM

FRAUNHOFER INSTITUTE FOR TOXICOLOGY AND EXPERIMENTAL MEDICINE, ITEM

PRELIMINARY CABIN AIR QUALITY MEASUREMENT CAMPAIGN (CAQ) EASA.2014.C15

AND

PRELIMINARY CABIN AIR QUALITY MEASUREMENT CAMPAIGN – CAQ II EASA.2014.C15.SU01

FINAL REPORT

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PRELIMINARY CABIN AIR QUALITY MEASUREMENT CAMPAIGN – CAQ II EASA.2014.C15.SU01

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Project numbers: EASA.2014.C15 and EASA.2014.C15.SU01
Project partners: ***Hannover Medical School (MHH)**, Lufthansa Technik AG / Deutsche Lufthansa AG, Condor Flugdienst GmbH, British Airways

Acknowledgements

We greatly appreciate the participation of Lufthansa Technik AG / Deutsche Lufthansa AG (LH), Condor Flugdienst GmbH (CFG), British Airways (BA) and their management, flight crews, and technical staff on this cabin air quality (CAQ) project. Especially Kirsten Winter (LH), Walter Emmerling (CFG) and Oliver Angell (BA) and their colleagues were particularly helpful with organization, campaign implementation and technical support. We are also grateful to Manfred Elend (Fraunhofer ITEM), Frank Günther (Fraunhofer ITEM), Anja Kaul (Fraunhofer ITEM), Bibiana Beckmann (MHH), Erik Hanff (M. Sc. Biochemistry, MHH) and Arinc Kayacelebi (M. Sc. Biochemistry, MHH) for assistance with the data handling, analytical and technical support, respectively. Without their congenial and professional participation, it would not have been possible to accomplish this complex in-flight measurement campaign.

Sven Schuchardt and Wolfgang Rosenberger

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Abbreviations

ACGIH	Association Advancing Occupational and Environmental Health
AGW	German: Arbeitsplatz Grenzwert; English: Occupational exposure limit
AH	aldehydes
APU	auxiliary power unit
BA	British Airways
BDPP	butyldiphenyl phosphate
CAC	cabin/cockpit air contamination
CAQ	cabin air quality
CBDP	2-(o-cresyl)-4H-1:3:2:benzo-dioxaphosphoran-2-one
CFG	Condor Flugdienst GmbH
DBPP	dibutylphenyl phosphate
DIN	German: Deutsches Institut für Normung; English: German industrial standard
DLH	Deutsche Lufthansa AG
DNEL	Derived No Effect Level
DNPH	dinitrophenyl hydrazine
DoTCP	diortho-tricresyl phosphate
DPEHP	diphenyl-2-ethylhexyl phosphate
EASA	European Aviation Safety Agency
ECHA	European Chemicals Agency
EI-MS	electron ionization mass spectrometry
GC	gas chromatography
HEPA	high-efficiency particulate air
IDA	Indoor Air Level
ISO	International Organization for Standardization
Fh-ITEM	Fraunhofer Institute for Toxicology and Experimental Medicine
LOD	limit of detection
LOQ	limit of quantitation
MHH	Hannover Medical School
MoTCP	monoortho-tricresyl phosphate
MS	mass spectrometry

NDIR	nondispersive infrared detector
NIST	National Institute of Standards and Technology
OEL	occupational exposure limit
OPC	organophosphorous compounds
PAX	passenger
PFC	perfluorinated compounds
PID	photo ionization detector
PUR	poly urethane foam
RCR	Risk Characterization Ratio
SVOC	semi volatile organic compounds
TBEP	tris(butoxy-ethyl)phosphate
TBP	tributyl phosphate
TCAC	Technical Cabin Air Contamination
TCEP	tris(chloro-ethyl)phosphate
TCPP	tris(chloro-isopropyl)phosphate
TD	thermal desorption
TDCPP	tris(1,3-dichloroisopropyl phosphate
TEHP	tris(ethyl-hexyl)phosphate
TiBP	triisobytyl phosphate
TmCP	tri-m-cresyl phosphate
TmmpCP	mmp-tricresyl phosphate
TmppCP	mpp-tricresyl phosphate
ToCP	tri-o-cresyl phosphate
ToopCP	oop/omm-tricresyl phosphate (DOCP)
ToomCP	oom-tricresyl phosphate (DOCP)
ToppCP	opp-tricresyl phosphate (MOCP)
TommCP	omm-tricresyl phosphate (MOCP)
TompCP	omp-tricresyl phosphate (MOCP)
oTCP	group name for all cresyl phosphates containing at least one ortho group
TpCP	tri-p-cresyl phosphate
TLV	threshold limit value
TMPP	trimethylopropane phosphate
TPP	triphenyl phosphate
TVOC	total volatile organic compounds

TWA	time-weighted average
TXP	trixylyl phosphates (mixture of isomers)
VOC	volatile organic compound

Executive Summary

The preliminary cabin air quality (CAQ) measurement campaign on board of commercially operated large transport aircraft was carried out by the consortium of Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e. V. (lead) & Hannover Medical School. Deutsche Lufthansa AG/Lufthansa Technik AG, Condor Flugdienst GmbH and British Airways were subcontracted to the project.

The project has been implemented through the award of two contracts by EASA. 1. EASA.2014.C15: main study (hereinafter referred as main study) contract awarded to the consortium following the call for tender EASA.2014.OP.16. This contract provides measurements on aeroplanes equipped with traditional engine bleed air systems. 2. EASA.2014.C15.SU01: supplementary study (hereinafter referred as B787 study) direct contract awarded to the consortium to provide measurements on Boeing 787 which are equipped with electrical air compressors instead of engine bleed air systems.

In total, 69 measurement flights were performed between July 2015 and June 2016 on 8 types of aircraft/engine configurations. In the main study only bleed air supplied aircraft (61 flights) were investigated, while the B787 part covered 8 flights with the alternative no-bleed air supply system of the Boeing 787 (B787, Dreamliner). Two sets of measurement equipment were installed in the flight deck and the cabin respectively during regular passenger in-flight operations. Overall, samples were taken at defined flight phases (taxi-out, take off and climb, descent and landing, complete flight). Additional required CAQ parameter such as climate data, total volatile organic compounds, carbon dioxide, carbon monoxide and ozone content were recorded continuously.

Essential results of the substances/group of substances of particular interest obtained in both parts of the study (main study and B787 study) can be summarized as follows: Total volatile organic compounds (VOC) concentrations ranged from 0.024 – 2.1 mg/m³ (main study) and 0.012-0.489 mg/m³ (B787 study). In this study low amounts of formaldehyde (range 0.03-48 µg/m³ (main study) and 0.02 - 17 µg/m³ (B787 study)), acetaldehyde (range 0.02-42 µg/m³ (main study) 0.01- 15 µg/m³ (B787 study)) and other aldehydes mostly at trace levels were detected. Organophosphates were analysed in all samples (n = 516). In the group of tricresyl phosphates (TCP) only traces of meta- and para-isomer were detected (mean 0.009 (main study) and 0.020 µg/m³ (B787 study), max 1.515 (main study) and 0.403 µg/m³ (B787 study)). No ortho isomers were detected. The most prominent airborne organophosphorous compounds (OPC) in this study were tri-n-butyl phosphate (TBP) which amounted in the main study from

0.037 to 2.484 µg/m³ (mean 0.430 µg/m³); and in the B787 from 0.037 to 1.482 µg/m³ (mean of 0.237 µg/m³), and tris(chloro-isopropyl)phosphate, a typical flame retardant, which amounted in the main study from 0.023 to 9.977 µg/m³ (mean 0.506 µg/m³), and in the B787 study from 0.041 to 2.633 µg/m³ (mean of 0.502 µg/m³). Other OPC were detected in trace amounts in most of the samples.

Overall, the results of this measurements campaign are consistent with findings of other published CAQ campaigns [1–3]. The observed frequency, pattern and concentration levels were similar to findings of other indoor environments.

Taking into account, that an aircraft is a complex technical system with a couple of potential emission sources of contaminants, high air exchange rates are necessary to provide good air quality. Crucial findings in this study were the documentation and proof of a general valid "air contaminant thinning effect" exclusively observable while performing flight phase dependent air sampling and the introduction of a classification between primary and secondary technical cabin air contamination-events. With the help of the "thinning effect" and this new classification, the ubiquitous OPC burden observable in almost all investigated aircraft types (including the B787) can be easily differentiated from contamination with engine oil.

1 Background

Concern has been raised with regard to a number of chemical substances which are suspected to be present in cabin/cockpit air and which may contribute to long and/or short-term health (toxic/physiological) effects. Although efforts have been undertaken to determine the chemical contaminants in cabin air by air sample measurements or wipe samples, a comprehensive measurement campaign is needed to provide measurement results with a sufficient statistical confidence level. The objective of this project was to implement a preliminary measurement campaign thereby setting the scene for a large-scale measurement campaign on-board of commercially operated large transport aircraft.

In general, the indoor environment of aircraft is a special issue in the view of health and safety. In cruise flight of commercial aircraft, cabin air is characterized by very low humidity and reduced air pressure (typically equivalent to approx. 2500 m in cruise). In comparison to other indoor air environments such as dwellings or classrooms in schools, aircraft have a high density of occupants and a high load of furnishings. To ensure suitable air quality, the pressurized cabin is operated with very high air exchange rates (~ 15^{-h} - ~ 35^{-h}). Other physical factors potentially affecting the well-being of crew and passengers in aircraft are noise, vibration and radiation. With regard to chemical exposures, the air quality could be affected by the following factors:

- Outdoor air in general
- Airport environment (e.g., fuel, exhaust gases, particles etc.)
- De-Icing procedures (e.g., propylene glycol)
- Ozone at high altitude
- Bio-influenced emissions by occupants in aircraft, predominantly carbon dioxide (CO_2), certain volatile and semi volatile organic compounds (VOC/SVOC) and, occasionally offensive smell
- VOC/SVOC emissions by entertainment devices
- Technical dysfunctions of aircraft systems, e.g. sealing failures (engine oil, hydraulic liquids, combustion products of overheated oils)
- VOC/SVOC emissions by maintenance and cleaning (cabin equipment, galley, engines, environmental control system, furnishings etc.)

Since decades, complaints with cabin air quality in commercial aircraft, reinforced through different odour perceptions and health complaints from flight personnel, occasionally even with

passengers, have been raised e.g. in Germany. The issue focuses neither on specific airlines nor specific aircraft or turbine types. The investigations regarding “fume events” in Europe by the Federal Bureau of Aircraft Accident Investigation (2010-2013, only completed investigations) showed that the subject is not only important on a national level but also concerns a number of European countries. Their study of events in connection with cabin air, BFU 803.1-14 [4], revealed a heterogeneous picture in terms of frequency and distribution of these incidents in the European countries. While the data show a consolidation of the absolute number of cases (“fume events”) in the countries Great Britain, France and the Netherlands, these case numbers were not adjusted for example in regard to total flight numbers in the respective countries, making a direct comparison difficult. Shehadi et al. [5] calculated an average frequency of 2.1 events in 10,000 flights. The author pointed out, that there were uncertainties in respect to the database [5].

However, in recent years crew members and – in rare cases – passengers of bleed-air technology-supplied aircraft occasionally reported health concerns in association with potentially acute neurotoxic and other, mostly non-specific symptoms after a so-called smell or fume events. These symptoms are sometimes referred to as an “aerotoxic syndrome” [6]. However, the so-called “aerotoxic syndrome” has not been considered as a medical syndrome [7, 8]. It has been repeatedly suspected that the release of hazardous neurotoxic substances, especially organophosphorus compounds (OPC), originating from the engines or the auxiliary power unit (APU) into the aircraft cabin might be responsible for the reported health effects. Especially, ortho cresyl phosphates (ortho TCP) were suspected as cause of the symptoms [6, 9]. In individual cases health complaints by crewmembers were evident, but to date the correlation between air contaminations and the occurrence of symptoms has not been established. For example, in all up to date examined cases of health complaints of crew members by employer's liability insurance coverage (e.g., BG Verkehr, Germany), no incidences of ortho TCP intoxication was observed [8]. On the other hand, a link between a fatal disease and exposure to neurotoxic compounds in the aircraft has been suggested [10]. Overall, there is a controversial, sometimes very emotional discussion about the air quality in bleed-air powered aircraft.

In the media, the Boeing 787 (B787, Dreamliner) was repeatedly mentioned as the solution to the pretended problem. Since the syndrome is neither scientifically defined nor recognised, and published data from measurements in the B787 are not available, there is therefore currently no evidence for this assertion. The cabin-air of most large transport aeroplanes is fed by air taped from low- and high-pressure parts of the engines (bleed air) and, on ground, from the auxiliary

power unit (APU). There is no filtration unit to remove particles or volatile organic compounds (VOC) from the engine bleed air before it enters the cabin; however most aircraft are equipped with High Efficient Particle Absorption-Filter systems (HEPA) used to filter recirculation air (approx. 40-60% recycled air). Ventilation in aircraft cabin is very high, typically air-exchange rate in aircraft is higher than 20 per hour. Depending on the type of aircraft, there are differences in the distribution of bleed-air in general. Certain areas, e.g. the cockpit can be provided with 100% bleed-air (e.g., in B757-300) or with a mix of bleed air and recirculation air (e.g., in Airbus 380 (A380) and A320-series).

The air composition in aircraft depends on various factors. Table 1 provides a brief overview of potential chemical pollutants. This compilation is just exemplary and can be extended if needed.

Table 1 Potential sources of cabin air contamination

Potential sources	Potential impact
Engine start during push back	Exhaust gases (e.g., CO, CO_2, NO_X, fuel, particles)
Bleed air switch off during engine start	Short time increase of CO_2
Cabin cleaning in general **Interior cleaning**	VOC, e.g. alcohols, flavors (terpenes), aldehydes Residual of tetrachloroethene
No ozone converters installed	Ozone, particularly in cruise
De-icing fluids	1,2-Propanediol (major constituent) and various additives (e.g., dyes, thickener, antioxidants)
Aircraft traffic at the airport	Exhaust gases (e.g., CO, CO_2, NO_X, fuel, particles)
Car traffic at the airport	Exhaust gases (e.g., CO, CO_2, NO_X, gasoline, particles)
Passengers	Emission of CO_2, various VOCs, offensive smell
Restrooms	Smell, VOC from cleaning products
Furnishings	VOC/SVOC, particulate organic matter (POM), flame retardants e.g. organophosphates
Maintenance	Various VOCs, lubricants
Lubricants	Oil base stock, organophosphates, POM
Hydraulic fluids	e.g. Tributyl phosphate (TBP), triphenyl phosphate (TPP)
Engine oils	Tricresyl phosphate (TCP), trixylyl phosphate (TXP), Amines
In case of thermal degradation	VOCs, organic acids, aldehydes, CO, CO_2, potential unknown products

Already at this point, it is clear that the reasons for chemical contamination in the cabin air are complex and focusing investigations solely on bleed air could possibly be misleading. Specifically in the group of SVOC/POM, the isomers of tricresyl phosphate (TCP, tritolyl phosphate, CAS 1330-78-5), which are used as an additive in aviation jet oil, have been in the

focus of previous and current research. If jet oil reaches hot parts of the engine, thermal degradation and pyrolysis of the oil may occur, with typical reaction products being CO, CO_2, aldehydes and various VOCs. Laboratory experiments have shown that the tricresyl phosphates survive the thermal stress and may enter the environmental control system of the aircraft. Tri-*n*-butyl phosphate (TBP) and triphenyl phosphate (TPP) are compounds of aircraft hydraulic lubricants and further applications. Typically, tri-*n*-butyl phosphate is a common ingredient with marginal impurity caused by tri-*iso*-butyl phosphate. In addition, other OPC are used as flame-retardants e.g. in furnishing, carpet, plastic and electronics (e.g., entertainment devices). In general, they have an important safety function by mitigating flames propagation. According to present knowledge it is indisputable that inadvertent release of oil into the bleed air system due to technical problems on the labyrinth seals of the turbine shafts or by overfilling the oil reservoir may occur. According to other allegations, the contaminants, predominantly TCP, are emitted constantly from the bleed-air even during normal operation [11]. However, the usage of organophosphates as flame-retardants is not an aircraft-specific feature, as they are also used in various other fields and enter different environmental compartments [12–14].

2 Aims and Objectives

The overall objective was to determine if there are cabin air contaminants, which represent a safety and/or potential long/short-term health risks. These investigations were carried out particularly with regard to possible bleed air contaminants from engine oil. Therefore a powerful trace analysis of TCP and other OPC was of particular importance. The investigation of the chosen flight phases aimed at identifying possible increase in oil release during the change in engine performance (e.g., take-off and landing). However, the sampling of an engine oil triggered cockpit/cabin air contamination (CAC) event was considered unlikely due to low likelihood of occurrence and the limited number of measurement flights performed [4, 5, 15, 16].

The following aspects should be considered for the oils or lubricants: Major types of the lubricant chemical esters make up trimethylol propane (TMP) and pentaerythritol (PE) esters. For example, according to the manufacturer's datasheets, Mobil Jet Oil II, Mobil Jet Oil 254 and Mobil Jet Oil 291 are broadly similar and are predominantly composed of TMP and PE esters. Engine oils further include additives that are used as flame retardants, anti-wear or antioxidant agents. More recently, several concerns have been raised about the possible health impacts due to air contaminations. Specific concerns have been raised with respect to organophosphate compounds (OPC) in cabin air. OPC are used as anti-wear and high

temperature additives in aviation engine oils and hydraulic fluids. These additives improve the flame retardancy of the oils and fluids, as well as enhancing their lubricant and anti-corrosion properties. The types and concentrations of different organophosphates within fluids vary depending on the manufacturers' specifications. Common compositions for engine oils and hydraulic fluids include mixtures of tri-aryl, tri-alkyl and alkyl/aryl phosphate esters including TCP, TBP, TPP etc. TCP is used with concentrations in the range of 1-5%. TCP is a mixture of 10 isomer molecules (6 ortho- and 4 meta/para isomers). Engine oils further include additives that are used as antioxidant agent such as N-phenyl-1- naphthylamine. N-phenyl-1-naphthylamine is reported to have a purity of about 99 % and isomeric impurities of <1%. Furthermore, low molecular weight organic acids, esters and ketones which are reported as thermal breakdown products of the lubricant esters or contaminants present after manufacture [9, 17, 18].

However, during use the oil composition may be altered by thermal stress. Thermally degraded oil was reported to have a small increase in the percentage of low molecular weight organic acids and esters. The percentage of the anti-oxidant N-phenyl-1-naphthylamine and the additive agents such as tricresyl phosphates appeared to be only slightly affected by either use or thermal degradation [19]. Potential pyrolysis products represent aldehydes, carbonyls, carbon acids as well as carbon dioxide (CO_2) nitrogen oxides and carbon monoxide (CO) ([19, 20]. Mair et al [18] found maximum emission of VOCs at 300 °C, containing combustion products from the base stock of the oil (e.g., short and middle chained organic acids). Wyman reported the formation of trimethylol propane phosphate (TMPP) in a heating of TMP based stocks after 20 min at 500°C [21]. Up to now it is not certain whether and in what extent the turbine oils are exposed to these extreme thermal conditions. During an experimental shipboard fire the formation of TMPP has further be confirmed under the conditions of this study [22]. However, the rat bioassay neurotoxic activity related to TMPP was not observed for used aviation engine oils or lubricants [21].

However, altogether a large variety of sources, internal or external to the aeroplane, may trigger the contamination of cockpit or cabin air. Note that the mentioned oil degradation products are well detectable with the detection methods applied in this study.

3 Literature review

A literature search has been conducted for scientific open literature in journals and books cited in electronic bibliographic databases or full text journals in PubMed, TOXline/TOXNET, Scopus and Web-of-science.

Citations from search hits in these databases have been retrieved as full text and directly imported into the EndNote data documentation system for literature.

Many studies on cabin air quality were identified by the literature search. However, the evaluation of this topic cannot be regarded as complete or even exhaustive at this point of time. As targeted approach to focus of the most relevant data the combination of relevant keywords was applied; the references chosen for evaluation include reports on analytical measurement of cabin air, biomonitoring, toxicological effects and clinical case reports. The monitoring studies either evaluated general air quality parameters such as O_2, CO and CO_2 concentrations or focused in particular on tricresyl phosphate. It became clear very soon in literature evaluation that there are some biases and critical points which should be considered carefully:

Due to the topicality of this topic (aerotoxic syndrome) there is a multitude of publications but:

- Only few publications are primary data sources and many are secondary literature or review articles
- „new studies“ --- have mostly a focus only on organophosphates but often do not consider confounders
- „old studies“ --- air quality was affected by other factors such as smoking
- data represent often indirect evidence for poor air quality or pollution and/or exposure of crew and passengers. Indirect information also sometimes represents a correlation between observed effects and known toxic properties of pollutants such as organophosphates
- the literature search identified a lack of data to evaluate the exposure to certain air contaminants that result from fume events as only in two study fume events were recorded [23, 24].

As already mentioned above, specific concerns have been raised with respect to organophosphate compounds (OPs) in cabin air. Thus, especially in the more recent literature measurements and observations indicating indirectly towards air contamination are focusing on organophosphates.

3.1 Cabin air monitoring in literature

Nadga & Rector [25] published a critical review of six prominent monitoring study within the years from 1997 to 2001. Publications of 71 flights in total conducted on 18 air craft types were reviewed. Nearly all of studies focused on cabin air quality under normal operating conditions none of them included unusual or episodic events that could affect cabin air quality. Parameters analysed included humidity, CO, CO_2, VOC, SVOC and particulate matter. Amongst the VOC and SVOC about 20 different substances were noticed and attributed to different source origins such as bio-effluents, consumer products and petroleum fuels. Neither TMPP nor ToCP was determined in the cabin or the bleed air of any aircraft for which results are reported. Study results indicate that under routine aircraft operations, contaminant levels in aircraft cabins are mostly similar to those in residential and office buildings. Exceptions are higher levels of ethanol and acetone in aircraft and higher levels of certain chlorinated hydrocarbons in residential/office buildings.
The review was used as a starting point for the evaluation of monitoring studies that were conducted later than the studies considered in this review

The following major cabin air monitoring studies that were conducted later than 2003 should be considered with respect to measurement set-up, analytical methods and results:

- Cranfield, 2011
- Solbu 2011
- DeNola 2011
- IOM 2012
- Spengler
- Guan

The so-called Cranfield study [1] investigated 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). An additional focus was on the detection and characterization of anomalous elevations of VOC, SVOC and particle concentrations during „fume events or „air quality events where unusual smells or similar incidents were reported. Cabin air contamination was analysed in 100 flights of 5 different air crafts (Boeing 757 cargo, Boeing 757, Airbus A320/1, BAe 146 and Airbus A319). The timeline was between 2008 and 2010. Besides the “normal” sampling additional „air quality event“

samples initiated by the researcher conducting the measurements whenever any change in air quality was detected or reported was foreseen.

The most abundant VOC/SVOCs were generally limonene and toluene. 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. TBP, limonene, m and p-xylene and undecane showed the highest concentrations during first engine start, highest levels of TCPs and toluene occurred during take-off, climb and prelanding. During taxi-out, take-off and landing levels of VOC concentrations were increased by about 2 fold (limonene) to 3 fold (undecane, TCE), and by 5 fold for xylene.

In more than 95% of all cabin air samples, no detectable amounts of ToCP or other TCPs were found and no 95th-percentile could be determined. A high variance of ToCP detects over the different flights was reported. Only very few ToCP detects were determined in the different flight phases of each part. The findings were independent and not determined in a relationship on the same flight. Unexpected high concentrations of ToCP and TCP were reported during climb in Boeing 757 PAX. No air quality event and no smell/fume by the flight crew or researcher were reported on this flight and the increase was not associated with an accompanying increase of tributyl phosphate or undecane. In addition, there is a little doubt about the suitability of sampling and TD-GC-MS for the determination of TCP. In the flight section before and after this point value no ToCP was determined.

During the study flight crew, cabin crew and researchers were requested to complete a post-flight questionnaire for all flights. Thirty-eight flights had smells reported as air quality events by at least one crew member or researcher in a post flight questionnaire. Sixty out of 552 questionnaires reports reported smells or fumes and the dominant smell descriptor was described as “oil” or “oily” by 26 persons. Events were largely concentrated at engine start and take-off, and only few occurred at top of climb or during cruise. Thirty so termed “air quality event sorbent tube samples” were collected during the study. The results showed that the concentrations of target analytes were not elevated during these events compared with the routine samples.

In the report of this Cranfield study some important critical point with regard to analytical methods i.e. for ToCP were discussed:

(1) duration of sampling needs special consideration: a longer sampling time improves sensitivity but might be less representative for a very short phase of flight (e.g., take-off). Comparability between samples required the same duration for all sampling phases

(few samples had a shorter duration and some flight phases were even too short to allow appropriate sampling)

(2) TD-GC-MS allows identification of a very wide range of compounds present in a sample, in particular when compounds mixture poorly defined in advance. On the other hand, quantification of an individual compound by TD-GC-MS requires calibration against a high-purity standard, which is clearly impracticable for every compound which might be present (in the study retrospective quantification was foreseen).

(3) An important consideration is the ability of the sorbent Tenax TA to retain the compounds. The breakthrough volume, which is the volume of air required to elute a given compound from the sorbent is strongly temperature-dependent. These breakthrough volumes for Tenax are well characterized for the majority of the target analytes. But the retention of organophosphates on Tenax TA has not been investigated to the same extent.

In the study performed by Solbu et al. [23] the presence of a range of VOC and organophosphate (OPC) contaminants was investigated in cabin and cockpit air.

The study distinguishes between jet aeroplanes (model A and B), propeller aeroplanes (model C and D) and helicopters. The used hydraulic oils contained <1% TPP, a combination of 1–5% TPP and 60–80% TnBP, or a combination of 20% TnBP and 40–70% DBPP (according to the material safety data sheets MSDS). All turbine oils contained ≤5% TCP. Determinations of VOC and OPs were performed using gas chromatography electron ionization mass spectrometry (GC-EI-MS). The general limit of quantification (LOQ) for OP in air was 75 ng/m³ based on a four hour sampling time. Sampling methods are described in detail in the publication.

In none of the aircraft included in the study contamination incidents were reported during the study period. Thus, the measured levels reported here are considered representative for normal flight conditions.

TCP was determined in four out of 95 samples (4.2%), all of them from model C-propeller aeroplanes; however, no ortho-isomers were identified. TPP was detected in one out of 43 (2.3%) of these samples (model C). The DBPP concentration levels in the model B jet aeroplanes were significantly lower ($p < 0.001$) than in model C and model A aeroplanes. TnBP was detected in all samples collected during aeroplane flights. Here the levels varied between different aircraft models which might be explained by their differences in hydraulic systems.

In addition a passive long-term sampling using wipe sampling, activated charcoal cloth sampling and analysis of HEPA filters was performed. Wipe sampling techniques were

expected to favour the collection of non-volatile organophosphates. TCP was determined in 92% of the collected samples of model C and in 31 and 8% of the samples collected from model A and D aeroplanes. TCP was determined in only two activated charcoal cloth sampling. The activated charcoal cloth sampling method was hence not considered to be suitable. The authors explained this by the lower LOQs and higher extraction recoveries for the wipe sampling method. Furthermore, new HEPA-filters were installed into six aeroplanes and exposed for a period of 1–3 months; TCP was determined in all filter samples, supporting an assumption of the general presence of TCP in the cabins.

During the study one oil leak with subsequent contamination of the cockpit/cabin air occurred in a propeller aeroplane. The arithmetic mean of TCP concentrations was an order of magnitude higher before (5.1 ± 1.1 µg/m³) than after (0.47 ± 0.04 µg/m³) replacement of the engine ($p = 0.02$). No TCP ortho-isomers were identified.

In model C propeller aeroplanes were identified with increased TCP exposure during inflight measurements. Measurements revealed that TCP levels >LOQ were determined in 33% of the samples in aeroplane model C. The TCP concentrations were ≤ 0.29 µg/m³. Deposited TCP concentrations were determined in 92% of the wipe samples. The passive long-term sampling methodology showed that TCP was detectable in the cabin of some aircraft. However, the measured values of one accidental case are not representative, but indicate that TCP concentrations are significantly elevated during a turbine oil leak incident and may result in an exposure, which is increased by factor of 10.

The exposure of maintenance personnel to airborne organophosphates originating from hydraulic and turbine oils was determined in a parallel set-up of this experiment. For engine and hydraulic maintenance, sampling was performed during the complete work operation (60–400 min). Oil filling operations included often sequential repetition of one procedure; air sampling was performed throughout all repetitions during one continuous procedure sequence (6–40 min). Peak sampling (1–5 min) was performed for wheel well maintenance to identify concentration levels during pressure drop in advance of the following wheel well work operations (20–255 min). In general, the many of the measured exposure levels were below the limit of quantification (LOQ); the air concentration ranges for all samples related to technician work were <LOQ-0.24 (oil aerosol) and <LOQ-9.4 (OPC) mg/m³.

Monitoring of tricresyl phosphate (TCP) contamination of cockpit air in three types of military aircraft was undertaken by DeNola et al. [24]. The air crafts [hawk fighter trainer (FT), fighter bomber (FB), and cargo transport (CT) aircraft] were monitored in the cockpit/flight deck

during ground engine runs and inflight. A total of 78 air samples were analysed, from 46 different aircraft. During this study several smoke events were reported, on ground runs as well as in flight. The highest concentrations of TCP measured were 21.7 and 51.3 μg/m³ during ground testing of the Hawk fighter trainer for time intervals of 10 to 15 min. Measurement for F-111 and Hercules C-130 cockpit air was performed during ground engine power runs and in flight. The concentrations of TCP measured during ground power runs were ≤3.5 μg/m³ (F-111) and ≤0.3 μg/m³ (Hercules C-130); those obtained during flights were ≤2.068 μg/m³ and ≤0.243 μg/m³ respectively.

The highest measured values of 2.068 μg/m³ was assumed to be associated with smoke in the cockpit and comparable to the concentration determined by former incident measurements [23]. The highest TCP level during ground run measurements (51.3 μg/m³) was determined and associated with an oils spill in the vicinity of the engine. The concentrations of toxic o-cresyl phosphate isomers were below the level of detection in all samples. The results possibly indicate that the personnel at a greater risk from TCP exposure are the engine maintenance workers who have skin contact with jet oil containing 3% TCP rather than the flight crews.

The study by Lamb et al. [26] (Cabin Air – surface residue study; Research Report TM/11/06 2012) was commissioned by the Aviation Health Working Group of the Department for Transport. The goal was to complement contemporary research on cabin air quality, by providing information on chemical surface residues in aircraft as a potential indicator of previous fume events. Whilst there are many compounds potentially contained within surface deposits, four organophosphates were chosen as index compounds for oil fume deposit- tri-n-butyl phosphate (TBP), tricresyl phosphate (TCP), butyl diphenyl phosphate (BDPP) and dibutyl phenyl phosphate (DBPP). The measurement was performed as wipe sampling and analytical methods for collecting and evaluating residues were validated within the course of the project. Sampling was undertaken on aircraft, together with airport-based and office control sites. A total of seventeen aircraft, five airport-based vehicles and two offices were evaluated. In total 86 sample sets were obtained from different aircraft types, ground vehicles and offices. Samples were analysed by gas chromatography/mass spectrometry for TCP, TBP, butyl diphenyl phosphate (BDPP) and dibutyl phenyl phosphate (DBPP). With only one exception TBP, BDPP and DBPP measured on the surfaces in cockpits of the aircraft were in general higher than those from the passenger areas. The amounts of TBP, BDPP and DBPP were higher in aircraft and airport-based vehicles than in offices. TCP concentration above control levels was detected in 34 of the 86 samples (40%). TCP was found in B757, BAe 146 and vehicles

but not in other planes or buildings. Increased levels of TBP, DBPP and BDPP were observed in Bae146 compared to the other tested aeroplane types. No significant difference between different types of aircraft was detected for TCP levels. With the exception of the BAe 146, the multiple wipe sample analyses indicated that the mean levels in the rear of the aircraft were lower than those in the cockpit and this effect was more pronounced in Airbus aircraft than in the Boeing planes. Overall, the IOM study gives insight in the question whether detectable quantities of TCP are present on the wipe samples but does not address the question for underlying air concentrations and events.

In the study of Spengler et al. [27] monitoring of cabin air was performed in the passenger cabin of 83 commercial flights (3 additional flights as a part of the Onboard Pressure Study) in 6 aircraft models (2 Airbus and 4 Boeing) which varied by passenger load factor and other flight-specific characteristics. The flights were either on U.S. domestic routes or on international routes.

Environmental conditions and air quality, including carbon monoxide, carbon dioxide, particles, ozone, volatile organic compounds (VOCs), semi-VOCs, carbonyls, and tricresyl phosphate were investigated. For environmental conditions relative humidity, cabin pressure, temperature, and cabin sound levels were determined.

As results the median values of continuous one-minute measurements as well as the overall flight averages and the ranges of these median values were given; VOCs, SVOCs, TCPs and aldehydes were summed separately. The five carbonyls investigated were acetaldehyde, acetone, acrolein, formaldehyde, propionaldehyde but not all of them in each flight. Acetaldehyde, formaldehyde, propionaldehyde were in. 81% of the samples (acetaldehyde), in 79% of the samples (acetone and 71% of the samples (acrolein); formaldehyde was detected in 49% of the samples (in two airlines only) and propionaldehyde was detected in only 17% of the samples.

The ozone level approached in only one flight the maximum level for instantaneous ozone exposure which is 0.25 ppm (250 ppb, and three flights exceeded the maximum allowable 1-hour level (100 ppb). Carbon dioxide levels were above the recommended level but below 5,000 ppm; the maximum values were slightly higher than values reported in the literature. Many of the VOC compounds concentrations were lower in the passenger cabin than what is typically reported of offices and residences. However, the maximum levels of formaldehyde, xylenes and acetone, were higher than values previously reported inside aircraft cabins.

TCP was detected in only one sample, in a concentration of 0.1 ppt TmCP, ToCP was not detected in 71 samples.
The authors (Spengler et al [27]) discussed some limitations of their study as follows: "*While continuous measurements were conducted for all the environmental conditions and most of the air contaminants, measurements on aldehydes and VOCs were performed only once, using integrated samplers. Notably, the sensors and samplers were positioned only in one location inside the cabin. … Spatial variations in environmental conditions within the cabin could not be assessed in this study.*"

Another research group investigating the cabin air quality is the group of Guan et al. [2, 28, 29] who conducted in-flight measurements in 107 commercial flights operating from August 2010 to August 2012. The flights were operated in China and world-wide, cover a multitude of aircraft types and were randomly selected. The intention was to obtain a better understanding of the occurrence of VOC species, levels and influencing factors in the aircraft. In this measurement campaign in total 346 VOC were detected; about 59 VOCs in each flight. 41% of these VOCs belong to the chemical group of alkanes and alkenes, 15% were esters and alcohols, 11% ketones and aldehydes, 6% halides, 20% aromatics and 6% other VOCs. A correlation analysis showed an interconnection between some VOCs, e.g. o-xylene, tetrachloroethene and benzene and others. Tetrachloroethene is widely used for dry cleaning of fabrics and as degreaser for oils, wax, etc.; it might occur more frequently in winter when people wear heavy clothes. 1,4-dichloro-benzene is often used for disinfectant, deodorant in cabin or other occasions, and on-board lavatories could be one of the sources of this compound.
A comparison of VOCs in buildings and in aircraft cabins revealed that some of them such as the aromatics benzene, toluene, xylene, ketones and aldehydes (e.g., acetone), esters and alcohols and alkanes and alkenes are present in both – buildings and cabins. Others that mainly derived from a reaction of ozone with unsaturated hydrogen compounds (i.e. 6-Methyl-5-hepten-2-one) were found in aircraft cabins only.
Concentrations of detected VOCs and a search for their potential sources within cabins are conducted by quantitative analyses, which are presented in a second paper: in-flight measurements in 51 randomly selected flights were analysed by statistical and contrastive methods for several potential influencing factors. Concentration levels for most of the investigated VOCs had significant differences at three different phases of the tested flights; peak values commonly occurred during before take-off and cruise phases. The effect of meal service was considered to be limited due to its short service duration in spite of its dominant

contribution to the concentration increase of total VOCs during meal time. And concentrations of some specific VOCs in supply air were significantly lower than those in recirculated air indicating the evident dilution effect of bleed air on cabin VOCs. All in all the results provided in these publications fit well to other VOC measurements on this topic.

3.2 Human biomonitoring as indicator of pollutants in cabin air

Concern for the health and safety of air quality in the aircraft cabin environment has been raised during the past years either by flight crews or by passengers. Specific concerns are focusing on oil/hydraulic fluid smoke/fume contamination incidents in pressurized aircraft and a potential exposure towards toxic organophosphate compounds (OPs) in the cabin air environment. Some crewmembers reported incidents experience and a variety of symptoms; however, the exposure situation remained still unclear.

Therefore, a set of studies differing from the air monitoring campaigns tried to verify the exposure by human monitoring data – either as urine metabolites or by studies of blood or serum.

Schindler et al. [30] investigated 332 urine samples of pilots and cabin crewmembers in common airliners, where a fume/smell event during their last flight was reported. Urine samples were analysed for three isomers of tricresyl phosphate metabolites and the dialkyl and diaryl phosphate metabolites of four flame retardants.

The authors did not find any ToCP metabolites in the 332 urine samples; only one sample contained metabolites of m- and p-tricresyl phosphates with levels near the limit of detection, which was at 0.5 µg/L. LOD. The levels of metabolite of tributyl phosphate (TBP), tris-(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPP) (DBP 0.28 µg/L; BCEP 0.33 µg/L; DPP 1.1 µg/L) were found to be significantly higher than in unexposed persons from the general population. These elevated levels were assumed to be due a release from flame-protected material in the aircraft and from hydraulic fluids (TBP, TPP). The values for TBP metabolites are in good accordance with previously published values for TBP in aircraft

Median tris-(2-chloropropyl) phosphate (TCPP) metabolite levels were elevated in crewmembers compared to controls. Health complaints reported by the aircrews could not be associated to o-TCP exposure in cabin air. Only a slight exposure of aircrews to certain organophosphates was shown in this study. However, possible limitations of the study have been discussed [31, 32].

The research group of Liyasova et al. published two papers on human biomonitoring in 2011 and 2012 [33, 34]. Goal of the research was to develop a laboratory test for human exposure to tricresyl phosphate – a biomonitoring assay. Their investigations refer to ToCP as main toxicant in cabin air and ToCP is known to inhibit the activity of butyrylcholinesterase in animal experiments. ToCP undergoes in vivo metabolic activation by the microsomal cytochrome P-450 system to the potent neurotoxic 2-(2-cresyl)-4H-1-3-2-benzodioxaphosphorin-2-oxide (CBDP) which is called cresyl saligenin phosphate.

Therefore, Liyasova et al. [33] based their assay on the fact that the active-site serine of butyrylcholinesterase reacts irreversibly with the active metabolite of tri-o-cresyl phosphate, cresyl saligenin phosphate. The stable phosphorylated adduct shows an added mass of 80 Da which is discussed to be unique and could serve as a biomarker for exposure to tri-o-cresyl phosphate, as demonstrated in the present report. 12 aeroplane passengers were tested and 6 were shown to be positive for exposure to tri-o-cresyl phosphate; the level of exposure was very low; only 0.05 to 3% of plasma butyrylcholinesterase was modified. The passengers did no show toxic symptoms; four of the positive passengers were re-tested 3 to 7 months after their last flight and found to be negative for phosphorylated butyrylcholinesterase. Some criticism to this study was published by Schindler et al. [30]: they argued that the measured phosphorylated butyrylcholinesterase adduct is known undergo ageing and was not specific to ortho TCP per se. And they stated that the specific o-cresyl saligenin phosphate butyrylcholinesterase adduct was not measured and "*it must remain questionable, if ortho TCP is the only agent capable to form those adducts in man*."

In their second study Liyasova et al. [34] investigated the reaction of CBDP with butyrylcholinesterase and acetylcholinesterase (AChE). These reactions result in inhibition of their enzymatic activities and formation of organophosphorylated adducts on the active site serines (Ser-198 for human BChE and Ser-203 for human AChE). However, aerotoxic syndrome cannot be explained by inhibition of either of these enzymes. CBDP is a unique organophosphorus with respect to its two electrophilic centres: the phosphorus and the benzylic carbon. Nucleophilic attack on the phosphorus resulting in the ring-opened CBDP-adduct and subsequent displacement of the saligenin moiety will be referred to as organophosphorylation. Liyasova et al. tried to identify the amino acids capable of reacting with CBDP and to characterize the types of adducts formed; finally they identified two types of adducts on histidine residues, five types of adducts on lysine residues and for tyrosine a ring-opened form and three o-cresyl phosphotyrosine adducts are identified.

The research group of Abou-Donia et al. [35] showed another approach for biomonitoring. They tried to detect circulating autoantibodies in serum samples of 12 healthy controls and 34 flight crew members (pilots and attendants) who had adverse effects after exposure to air emissions and, in addition, they had undergone thorough medical monitoring. Seven proteins associated with the nervous system, which are associated with neuronal degeneration of nerve cells, were selected and immunoglobin (IgG) was measured using Western blotting against: neurofilament triplet proteins (NFP), tubulin, microtubule-associated tau proteins (tau), microtubule-associated protein-2 (MAP-2), myelin basic protein (MBP), glial fibrillary acidic protein (GFAP), and glial S100B protein. A significant increase in levels of circulating IgG-class autoantibodies was found in flight crew members compared to controls. A healthy 50-year-old male professional airline pilot, with 25 years and approximately 15,000 cumulative hours of flying, had been on vacation for 2 month, this pilot was symptom-free. He agreed to participate in the study and samples were taken before his flight and then several times afterwards. This pilot developed clinical problems after flying for 45 h in 10 days. Significant increases in autoantibodies were noted to most of the tested proteins in the serum of this pilot after exposure to air emissions. Average concentration of TCP isomers in cabin air during these flights was 0.65 ng/m³. His complaint at that time was bad memory, the levels of autoantibodies rose with worsening of his condition but after he stopped flying for a year, this pilot's clinical condition improved, and eventually he recovered and his serum autoantibodies against nervous system proteins decreased.

The authors of this study discussed a possible association between neurologic deficits and the levels of autoantibodies against nerve cell specific proteins circulating in sera. They concluded that the presence of circulating autoantibodies could serve as a confirmation of chemical-induced nervous system injury in the absence of other neurologic diseases as well as a monitor for the progression of disease or recovery. Finally, the autoantibodies could help to identify cellular mechanisms underlying neurotoxicity and determine individual differences. On the other hand the authors discussed the limitations of this more descriptive study which includes one case study. I.e. the sample size in this study was much too small to investigate covariates like age and exposure; in addition, there is a lack of correlation with respect to chemical identity of chemicals and the levels to which the flight crew members were exposed.

Other compounds such as polybrominated diphenyl ethers (PBDEs) which are used as flame-retardants as well have to be identified by reference compounds and analysed i.e. by GC-MS. There are two studies available for PBDEs and both show a clear elevation of blood serum

levels after flying (Christiansson et al. [36], Strid et al. [37]). However, in one study also investigated the maintenance personnel at the airport and thereby showed much higher blood levels for this group.

3.3 Occupational exposure limits for organophosphates

As especially organophosphates are in the public and occupational interest some actual occupational exposure limits are summarized here. Occupational exposure limits set for TBP, DBPP and the ortho-isomer of TCP in a number of countries are shown below in Table 2 as 8 hour time weighted averages (TWA) according to the IOM report. No exposure limit values for BDPP could be found in the literature.

Table 2 Exemplary international occupational exposure limits for organophosphates; 8h TWA mg/m^3

	Tricresyl phosphate	*Tributyl phosphate*	*Dibutyl phenyl phosphate*
Austria	0.1	2.5	3.5
Belgium	0.1	2.2	3.6
Canada	0.1	2.2	3.5
Denmark	0.1	2.5	3.5
France	0.1	2.5	-
Germany	-	11	-
Hungary	0.1	-	-
Poland	0.1	-	-
Singapore	0.1	2.2	3.5
Spain	0.1	2.2	3.6
Sweden	-	-	-
Switzerland	0.1	2.5	-
USA NIOSH	0.1	2.5	-
USA OSHA	0.1	5	-
UK	0.1	5	-

However, it should be mentioned here that in some countries there are attempts to re-evaluate these values at present.

Most recently ACGIH (2016) derived a new threshold limit value TLV-TWA for ToCP of 0.02 mg/m³ for the inhalable fraction and vapour. This value is described to be intended for minimizing the potential for cholinergic effects, neuropathies and other adverse effects.

Even more critical for this class of substances is the present data demand presented by ECHA (European Chemicals Agency) 26 July 2016 in the “DECISION ON SUBSTANCE EVALUATION PURSUANT TO ARTICLE 46(1) OF REGULATION (EC) NO 1907/2006)

for tris(methylphenyl) phosphate, CAS No 1330-78-5 (EC No 809-930-9)“. Here a clear lack of data was identified which makes it impossible to derive a health-based safe concentration – the so-called derived no effect level (DNEL). The request for data includes information on toxicity from: 1) an *in-vitro* dermal absorption study using well characterised human skin, an appropriate solvent and doses which are representative of relevant human exposure situations, and 2) a 90-day repeated dose neurotoxicity study in the rat, by inhalation nose only using a representative composition of the test substance. The prerequisites for an acceptable 90 day test with the TCPs include an assessment of learning and memory (Morris Water Maze test or avoidance tests), a histopathology for neuro-inflammation and neural degeneration, identification of inflammation as microgliosis and astrogliosis, cholinesterase activity in the brain and a recovery group. Based on the results of this study a new DNEL derivation should be performed.

Another information requirement addressed in the ECHA opinion is about valid and robust data on exposure for pilots and cabin crew which should include the data on “registered” substances during flights followed by a calculation of inhalation and dermal exposure and the calculation of a risk characterization ratio (RCR) for both routes. This latter should be based on the newly derived DNELs. Here it should be mentioned that the process of risk characterization at ECHA differs slightly from the German derivation of OELs in this context.

All in all an extensive new evaluation of the class of substances is necessary, however the present preliminary measurement campaign will give some valuable contribution to the requested information on exposures.

4 Methodology

Two almost identical measurement boxes were built for the in-flight measurements (cockpit and cabin). The measurement boxes of previous campaigns served as a starting point. The holders for the sampling systems and the attachment loops for the seat assembly were optimized or replaced. In the cockpit box a particle counter (Aerosol Sensing System developed by Fraunhofer) was installed additionally. The particle counter was coupled directly to the bleed air inlet through a hose. Figure 1A shows an unassembled measurement box in the cabin. Figure 1B-C describes, as an example, the exact location of the two measurement boxes in cockpit and cabin of an A321.

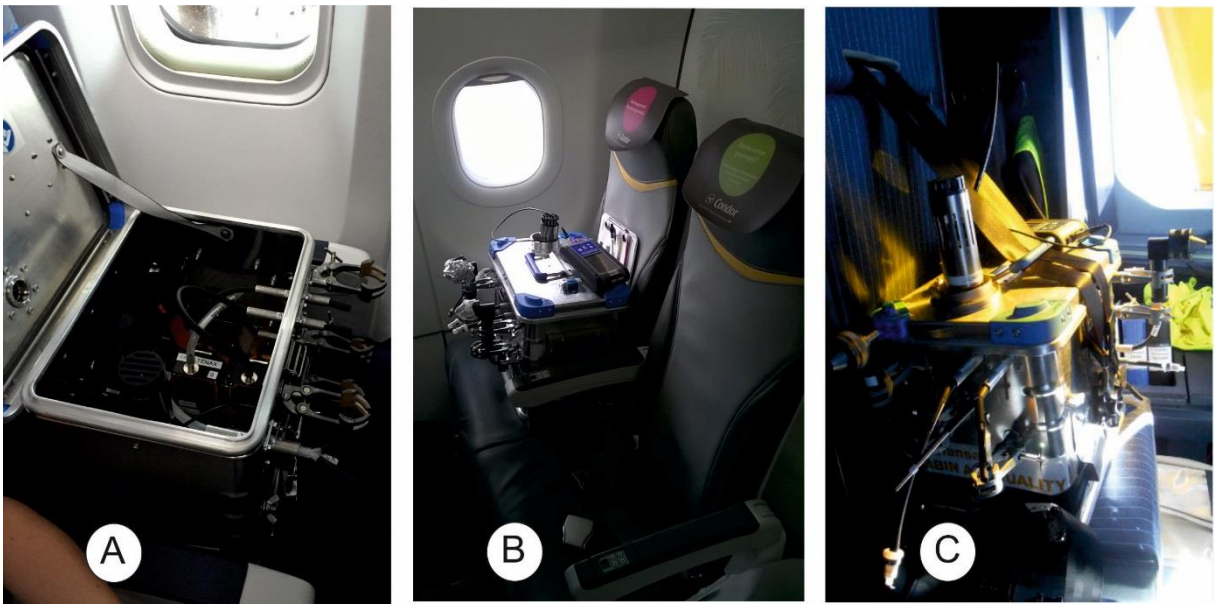


Figure 1 (A) Open measurement box on the window seat of a B767-300 (Condor). Pumps, connectors and measuring instruments (GrayWolf, climate data logger and particle counter) were explicitly designated for the measurement tasks with labels. (B) Closed measuring box fully stocked and ready for measurement on the window seat of an A321 (Condor). (C) Closed measuring box with additional particle counter in the flight deck of an A321 (Condor).

All sampling devices for carbon monoxide, carbon dioxide, ozone and VOC (Advanced Sense, GrayWolf Sensing Solutions, with 10.6 eV-photo-ionization detector, infrared detector, electro chemical detector, USA), the data logger for temperature, pressure and humidity (MSR-145, PCI, Germany), and the sampling pumps were assembled in a special measurement box to avoid interferences with the avionics. This sampling device was successful tested in a special physical laboratory. Sample handling before, during, and after the measurement flights was organized in a mode to minimize transport time and storage time. Cooling devices on aircraft, at the project base, and for sampling transport to the analytical laboratories ensure suitable conditions (4 °C).

4.1 Sample devices

4.1.1 Aerosol sensing system (Particle counter)

The sensor principle used in this study is based on the (Rayleigh) scattering of light at small particles. It consisted of a laser diode emitting polarized light (λ=680 nm) and a photo detector measuring the scattered light of aerosol particles inside an optically defined measuring volume (Figure 2). Two sensors were used in series one operating with a laser diode with polarization direction perpendicular, the second one with light polarized parallel to the scattering plane. The signal from the perpendicular polarization was a measure for the aerosol concentration, the ratio of the scattered signals (parallel/perpendicular) was an indicator for the particle size. Submicron particles were prevailing when this ratio was smaller than 1. This parameter was used to discriminate oil fumes from other aerosol sources generating coarser particles.

The advantage of the photometric sensor is its low weight and size and low power consumption. It is virtually maintenance free and there is no need to exactly control the air flow through the sensor. Since the sensing principle is independent of the flow rate and the sampled air is passing straight through the sensor without being filtered, the unit can be operated by a small fan with minimum power consumption without any flow control.

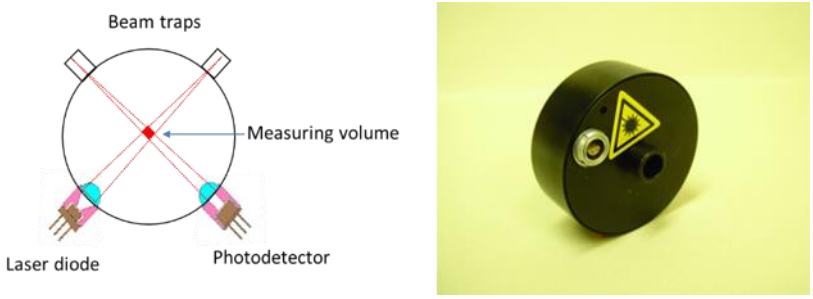


Figure 2 Light scattering sensor: operating principle and hardware

The sensor has been developed by Fraunhofer ITEM. The detection limit as determined for environmental aerosol conditions was 2 µg/m³ provided constant temperature of the sensor environment. Two light scattering sensors with different polarization mounted in series were incorporated into a frame and installed in the common measurement box (Figure 3). The data was sampled by a multichannel data logger. This unit served also as power supply for the optical sensors.

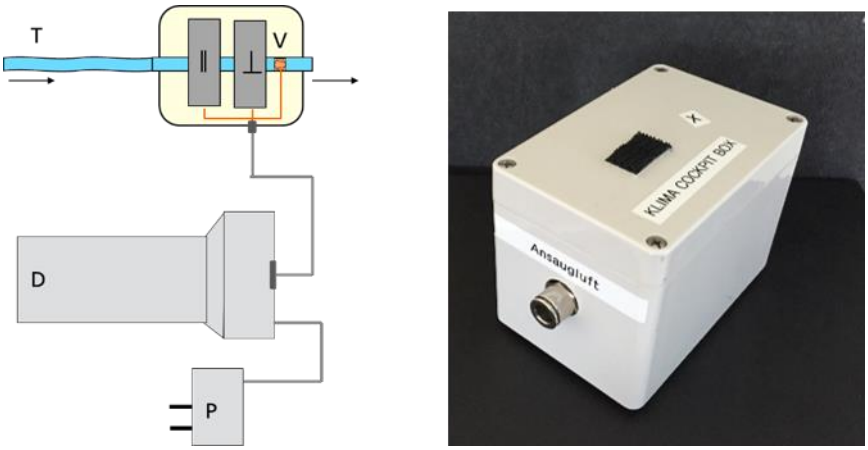


Figure 3 Particle detection system used in the study. T: tube, V: ventilator, D: data logger, P: power supply. The sensors were mounted in a frame. The entire system was integrated in the in-flight measurement and sampling box operated in the cockpit of the aircraft.

4.1.2 Sampling devices, pumps and ab-/adsorption materials

In Table 3, the devices for continuous and discontinuous sampling are listed.

Table 3 List of sampling devices, pumps, airflow rates, and ab-/adsorption materials, [1]GrayWolf Advanced Sense by Sensing solutions, Shelton, CT 06484, USA, [2]MSR 145 climate data Logger obtained from PCE Deutschland GmbH (PCE Inst.), 59872 Meschede, Germany, all pumps have a flow stability of ± 5%, to set the pump to the desired flow rates a DryCal DC-Lite calibration unit (Bios Corporation International, USA) was used, ozone and carbon monoxide sensors were replaced and annually, VOC, CO and CO_2 were calibrated weekly or after longer breaks before the next flight with certified calibration gases; in addition, the instrument was sent annually to the factory tour.

Sensor	Resolution	Range
VOC (PID, 10.6 eV)[1]	1 ppb	5 to 20.000 ppb
carbon dioxide, CO (NDIR) [1]	±3 % rdg ±50 ppm	0 to 10.000 ppm
carbon monoxide, CO_2 (electro chemical) [1]	0.5 ppm	0.5 to 5000 ppm (LOD = 0.5 ppm)
Ozone (O_3) (electro chemical) [1]	0.01 ppm	0.02 to 1.0 ppm (LOD = 0.02 ppm = 20 ppb)
Temperature[2]	±0,5 °C (-10…+65 °C)	-20…+65 °C
Air pressure[2]	±2.5 mbar (750…1100 mbar, +25 °C)	0…2000 mbar
Humidity[2]	±2 % (10…85 %, 0…+40 °C)	0…100 %
Sample type	Sampler (pumps)/adsorbents	Flow rate [L/min.]
OPC	Gilian 5000, GSA-SG 10, SG- 5100 quartz filter and polyurethane foam, GGP-System (BIA)	10; 3.5 or 1
VOC	SG 350 (GSA, Germany) or Tenax TA tubes (Supelco or Perkin Elmer, USA)	0.100 (each tube)
AH	SG 350 (GSA, Germany) or DNPH-cartridges (Sep-Pak XPoSure, Sep-Pak ozone scrubber, Waters, USA)	0.300…0.500

4.2 Analytical techniques

4.2.1 Determination of VOC in air with TD-GC-MS

The VOC analysis was conducted at Fraunhofer ITEM according to the international standard methods for measuring organic compounds in indoor air (DIN ISO 16000-6 "Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA™ sorbent, thermal desorption and gas chromatography using MS or MS-FID"). Deuterated toluene as an internal standard was spiked by a gas loop. Note the method DIN ISO 16000-6 comprises the detection of typical VOCs from the indoor environment. This includes a wide range of alkanes, aromatics, terpenes, aldehydes, etc., which are also known to be present in cabin air. Unknown VOC were identified by mass spectrometry with this non-targeted approach.

4.2.2 Determination of aldehydes with HPLC-UV-absorption

This method is based on DIN ISO 16000-3. The principle of the method is based on the specific reaction of a carbonyl group present in an aldehyde or ketone with DNPH in the presence of an acid. This procedure provides stable derivatives (hydrazones) of lower vapour pressure than the trapped aldehydes/ketones. Aldehydes were collected by drawing air through a cartridge containing a substrate (silica gel) coated with the 2,4-dinitrophenyl-hydrazin (DNPH) reagent. SG-350 pumps were used for this purpose and their flow rate was set to 0.3 L/min. Transport and storage of the samples were carried out in aluminum bags at 4 °C. The hydrazones were separated, identified and quantified by HPLC with UV absorbance detection at 360 nm. Aldehyde/ketone hydrazones were eluted from DNPH-cartridges with 3.5 mL acetonitrile. The extracts were filtered using syringe filters (pore size, 0.2 µm) prior to analysis. Uncertainties are known for unsaturated aldehydes.

4.2.3 Determination of organophosphate based flame retardants and plasticizers

A suitable method based on "ISO 16000-31:2014 Indoor air - Part 31: Measurement of flame retardants and plasticizers based on organophosphorus compounds -Phosphoric acid ester" was developed further for use of in-service measurements on aircraft. The method permitted the determination of chlorinated and non-chlorinated trialkyl and triaryl phosphates in workplace air and indoor air. This method allowed the simultaneous determination of gaseous and particulate OPC. Sampling was carried out by drawing ambient air through a quartz filter spiked with tributyl phosphate-d_{27} and triphenyl phosphate-d_{15} with poly urethane foam (PUR). The adsorbed OPC were extracted with dichloromethane according to the Soxhlet procedure. Samples were evapourated by means of a rotary - and a nitrogen evapourator. Afterwards the

residue was diluted in toluene/ethyl acetate and determined by gas chromatography with a mass-selective detector (GC-MS). The GC parameters are given in Table 4. Mass spectrometer data are shown in Table 5. Two GC systems are used in parallel with different columns to obtain maximal information. The quantitative evaluation was carried out on the basis of calibration functions, whereby the quotients of the peak areas of the respective OPC to tributyl phosphate-d_{27} or triphenyl phosphate-d_{15} were plotted versus the corresponding OPC concentrations of the calibration standards used. Additionally, a mixture of all 10 TCP isomers, diphenyl cresyl phosphates (DPhCP) isomers and dicresyl phenyl phosphates (DCPhP) isomers as well were synthesized via reaction of ortho- meta-, para-cresol and phenol with phosphorus oxychloride and subsequently analysed with GC-MS to identify the retention times and the mass spectra. The method allowed the required differentiation between the TCP-isomers.

In total, the following substances were implemented in the analysis:
Triisobytyl phosphate (TiBP), tributyl phosphate (TBP), tris(chloro-ethyl)phosphate (TCEP), tris(chloro-isopropyl)phosphate (TCPP), tris(1,3-dichloroisopropyl phosphate (TDCPP) , triphenyl phosphate (TPP), tris(butoxy-ethyl)phosphate (TBEP), diphenyl-2-ethyl-hexyl phosphate DPEHP), tris(ethyl-hexyl)phosphate (TEHP), tri-o-cresyl phosphate (ToCP), omp-tricresyl phosphate (MoTCP), oom-tricresyl phosphate (DoTCP), oop/omm-tricresyl phosphate (DoTCP/MoTCP), opp-tricresyl phosphate (MoTCP), tri-mcresyl phosphate (TmCP), mmp-tricresyl phosphate (mmpTCP), mpp-tricresyl phosphate (mppTCP), tri-p-cresyl phosphate (TpCP), trixylyl phosphates (TXP, mixture of isomers). The list of compounds for qualitative determination was further extended by trimethylopropane phosphate (TMPP) and 2-(o-cresyl)-4H-1:3:2: benzo-dioxaphosphoran-2-one (CBDP).

Table 4 GC conditions for OPC analysis

Column:	Material:	Fused silica
Column 1:	Coating material:	Silarylene phase with polarity similar to a 5 % diphenyl – 95 % dimethylpolysiloxane phase (Optima 5 MS accent, M&N)
Column 2:	Coating material:	50%-diphenyle-50%-dimethylpolysiloxane (HP 50 +, J&W)
Column 1 and 2	Length:	30 m
	Inner diameter:	0.25 mm
	Film thickness:	0.25 µm
Injector:	PTV - injector:	80 °C ramp 12 °C/s to 300 °C
	Split ratio:	Split less (2 min)

	Solvent delay time:	6 min
	Injection volume:	1 µL
Carrier gas:	Helium 5.0	1.0 mL/min
Temperature program	Step	Ramp
Column 1	100 °C (2 min)	10 °C/min
	320 °C (11 min)	
Temperature program	step	ramp
Column 2:	60 °C (1 min)	20 °C/min
	250 °C	0.25 °C/min
	260 °C	20 °C/min
	300 °C	
Transfer Line:	300 °C (column 1) 280 °C (column 2)	

Table 5 MS conditions for OPC analysis

Ionization type:	Electron impact (EI)	
Ionization energy:	70 eV	
Dwell time:	50 ms	
Temperature:	Quadrupole:	150 °C
	Ion source:	230 °C
Single ion monitoring mode	Compound	Quantifier/qualifier (u)
	d_{27}-TBP	103 / 231
	d_{15}-TPP	341 / 243
	TiBP	99 / 155
	TnBP	99 / 155
	TMPP	150 / 178
	TCPP	125 / 99
	TCEP	249 / 205
	TEHP	99 / 113
	TBEP	125 / 299
	CBDP	276 / 178
	TDCPP	381 / 191
	DPEHP	251 / 249
	TPP	326 / 215
	TCPs	368 / 165
	DCPhP	354 / 165
	DPhCP	340 / 165
	TXP	410 / 193
Scan mode	Full scan	40-800

4.2.4 Aerosol sensing system (particle counter)

Since the sensor was used to detect possible aerosol events associated with the bleed air, the air sample was sucked into the sensor directly from the outlet of one of the fresh air feed nozzles on the flight deck. A flexible, electrically conductive tube was used to lead the air from the air nozzle outlet into the sensing unit.

Carrying out in-flight measurements: The aerosol sensor was operated on all flights. For long distance flights two pre-charged data loggers were used: one for the outbound and one for the return flight. The measurements were started immediately after the installation of the measurement box on a jump seat in the cockpit and was switched off after the passengers left the aircraft.

5 Implementation

5.1 Flight phases and sampling procedure

A detailed overview of the compounds, particles and physical parameters collected during sampling of cockpit/cabin air is summarized in Figure 4.

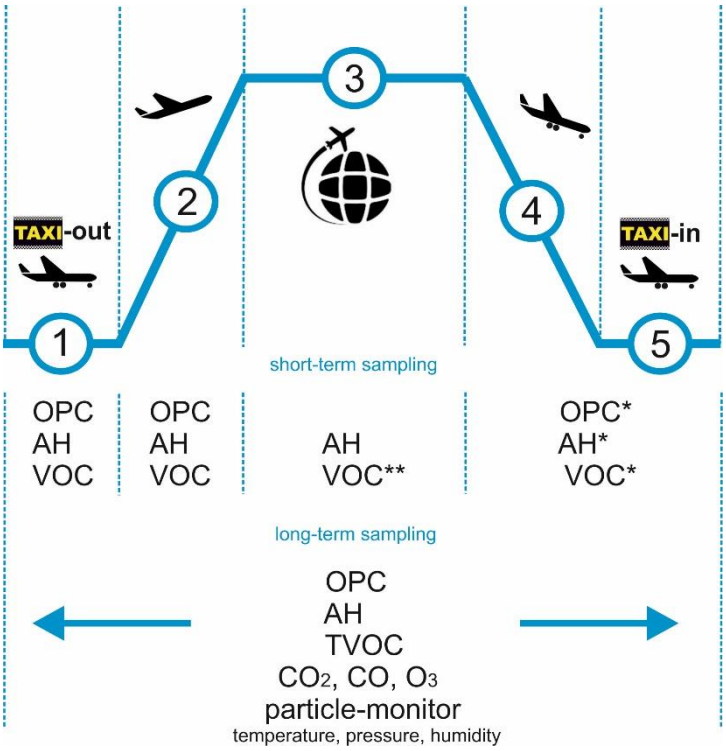


Figure 4 Considered measurement tasks on the individual phases of flight. 1. Taxi-out; 2. Take-off and climb; 3. Cruise; 4. Descent and landing; 5. Taxi-in; Phases 4 and 5 were combined to a single measurement phase due to logistical reasons; **optional VOC measurement in case of CAC-events. The following components were analytically determined: organic phosphorous compounds (OPC), aldehydes (AH), volatile organic compounds (VOC), total volatile organic compounds (TVOC), carbon dioxide (CO_2), carbon monoxide (CO), ozone (O_3), climate parameter and airborne particles.

General Sampling Procedure: Sampling procedures generally started when the doors of aircraft were closed. Long-term sampling (whole flight) and first short-term sampling (taxi-out) started simultaneously. Upon reaching the runway, second short-term sampling started after disassembling first phase short-term samples and installing the second set of sampling-tubes for take-off/climb phase. Upon reaching cruise altitude or latest after 40 minutes, the second short-term sampling was considered to be completed. The third short-term sampling started at the beginning of descent and stopped – in parallel with long-term sampling after reaching the parking position at the destination. Transport and storage of the samples were carried out in cooling containers at 4 °C.

5.2 Aircraft and engine selection

To optimize logistical performance, all flights of the main study were operated from/to Frankfurt Airport. All flights on Boeing 787-8 (B787-8) were performed with BA on the route London Heathrow ↔ Newark. In the main study, five types of bleed air equipped aircraft, with different engine types, were selected. Additionally, one Boeing 757-300 provided by CFG was added to the study, after a "smell event" happened to this aircraft (cycle 19a).

Table 6 Overview of investigated aircraft and engine types in main study

Cycle	Airline	Type	Plane age years	Engines
1	CFG	B767-330ER	22.8	2 x PW PW4062
2	CFG	B767-330ER	22.3	2 x PW PW4062
3	CFG	B767-330ER	23.6	2 x PW PW4062
4	CFG	B767-330ER	25	2 x PW PW4062
5	CFG	B767-330ER	23.8	2 x PW PW4062
6	DLH	B747-830	2.4	4 x GEnx-2B67
7	DLH	A320-211	15.8	2 x CFMI CFM56-5A1
8	DLH	A320-214	2.4	2 x CFMI CFM56-5B4/P
9	DLH	B747-830	1.5	4 x GEnx-2B67
10	DLH	B747-830	3.9	4 x GEnx-2B67
11	DLH	A340-642	9.7	4 x RR Trent 556-61
12	CFG	A321-211	1.1	2 x CFM56-5B3/3
13	CFG	A321-211	1.1	2 x CFM56-5B3/3
14	CFG	A321-211	1.2	2 x CFM56-5B3/3
15	CFG	A321-211	1.2	2 x CFM56-5B3/3
16	CFG	A321-211	1.2	2 x CFM56-5B3/3
17	DLH	B747-830	3.1	4 x GEnx-2B67
18	DLH	A320-211	26.6	2 x CFMI CFM56-5A1
19	DLH	A340-642	12.9	4 x RR Trent 556-61
19a	CFG	B757-330	16.4	2 x RR RB211-535E4B
20	CFG	B767-31BER	22.1	2 x GE CF6-80C2B6F
21	CFG	B767-31BER	22.3	2 x GE CF6-80C2B6F
22	DLH	A340-642	7.4	4 x RR Trent 556-61
23	DLH	A320-211	26	2 x CFMI CFM56-5A1
24	DLH	A340-642	9.7	4 x RR Trent 556-61
25	DLH	B747-830	3.3	4 x GEnx-2B67
26	DLH	A320-214	2.5	2 x CFMI CFM56-5B4/P
27	CFG	B767-31BER	22.3	2 x GE CF6-80C2B6F
28	CFG	B767-330ER	23.6	2 x PW PW4062
29	CFG	B767-31BER	22.3	2 x GE CF6-80C2B6F
30 out	DLH	A320-214	2.8	2 x CFMI CFM56-5B4/P
30 in	DLH	A320-214	3.5	2 x CFMI CFM56-5B4/P

Table 7 Overview investigated aircraft and engine types in B787 study

Cycle	Airline	Type	Plane age Years	Engines
1	BA	B787-8	3.1	2 x RR Trent 1000
2	BA	B787-8	3.3	2 x RR Trent 1000
3	BA	B787-8	2.2	2 x RR Trent 1000
4	BA	B787-8	3.3	2 x RR Trent 1000

6 Results and discussion

It should be mentioned, that indoor air measurement is typically characterised by low concentrations of target substances (ng/m³ to µg/m³ range). This can lead to known and generally accepted uncertainties of about 30 – 50 %, covering the entire procedures including sampling. However, stable and reliable results were achieved using suitable quality control instruments e.g. calibration and recovery experiments or comparing results from in field measurement.

6.1 Volatile organic compounds (VOC)

6.1.1 Online VOC measurement

Tables 8-10 summarize the results of online VOC measurement with PID in the main study. The data was recorded in minute steps at both sampling points (flight-deck and cabin). Altogether more than 24.000 minutes were recorded for each sampling point during the 69 flights investigated.

Table 8 Descriptive statistical data of online VOC measurement with PID, calculated as toluene equivalent. The values presented are the mean values of all flights investigated.

	Flight deck Mean µg/m³	Cabin Mean µg/m³
Mean	108	273
Min	59	137
Max	1205	851
Median	84	225
95th-percentile	221	549

Table 9 Compared online VOC data from flight deck of short haul and long haul aircraft, calculated as toluene equivalent from main study, [a)]Airbus A32x series; [b)]Airbus A340, Boeing 747, 767

Short haul aircraft[a)] Flight deck	Mean µg/m³	Long haul aircraft[b)] Flight deck	Mean µg/m³
Mean	109	Mean	107
Min	66	Min	54
Max	354	Max	1701
Median	95	Median	77
95th-percentile	210	95-percentile	228

Table 10 Compared online VOC data from cabin of short haul and long haul aircraft, calculated as toluene equivalent from main study, [a)]Airbus A32x series; [b)]Airbus A340, Boeing 747, 767

Short haul aircraft[a)] Cabin	Mean µg/m³	Long haul aircraft[b)] Cabin	Mean µg/m³
Mean	273	Mean	273
Min	159	Min	123
Max	634	Max	988
Median	239	Median	216
95th-percentile	483	95-percentile	590

Note, VOC data for B787 flights are not available due to malfunction of PID`s.

6.1.2 VOC data from Tenax sampling

In Tables 11 (main study) and Table 12 (B787 study) are detailed results of VOC sampling with Tenax TA presented. Overall, a similar VOC distribution was observed in both studies. Slightly higher amounts were measured in the main study (Figure 5 and Figure 6). Most likely, this observation is due to the use of an activated charcoal filter in the recirculation system of B787 aircraft.

Table 11 VOC results main study overview

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
Acetic acid	96.8	11.8	0.1	59.4	9.1	30.1
Benzoic acid	90.9	5.3	0.1	72.8	3.7	14.7
Hexanoic acid	89.4	3.8	0.0	16.6	3.3	9.2

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
Octanoic acid	75.9	2.1	0.1	8.1	1.7	5.3
Nonanoic acid	80.0	1.9	0.1	6.1	1.7	4.2
Decanoic acid	24.4	0.8	0.0	5.4	0.6	1.9
Formic acid	17.9	0.7	0.0	33.9	0.0	3.5
Phenylmaleic anhydride	7.9	0.3	0.0	6.1	0.1	1.4
Sum Acids		26.6	0.3	185	22.1	57.8
Tetradecane	87.4	2.6	0.0	13.3	2.1	6.3
2,2,4,6,6-Pentamethyl heptane	28.2	1.6	0.0	61.4	0.6	5.3
2,2,4,4,6,8,8-Heptamethyl nonane	55.0	2.4	0.0	49.3	1.2	7.6
Undecane	75.3	2.2	0.0	22.3	1.6	5.7
Nonane	60.0	2.0	0.1	12.9	1.3	6.9
Dodecane	67.9	1.9	0.0	17.6	1.4	4.4
Tridecane	68.2	1.7	0.0	12.2	1.4	4.2
Decane	51.8	1.7	0.1	16.9	1.1	5.1
Pentadecane	64.1	1.5	0.0	6.1	1.2	3.4
Pentane	17.1	1.4	0.0	63.7	0.2	3.9
Hexadecane	53.5	1.2	0.0	3.2	1.0	2.5
Heptadecane	48.2	1.1	0.0	3.1	1.0	2.3
Heptane	24.1	0.9	0.1	24.8	0.4	2.9
Methylcyclohexane	12.9	0.9	0.0	73.8	0.2	2.2
Cyclohexane	14.7	0.8	0.0	48.1	0.2	2.0
Hexane	12.1	0.5	0.0	4.8	0.3	1.7
3-Methylpentane	3.8	0.3	0.0	18.9	0.0	0.5
2,2,4-Trimethyl pentane	1.5	0.1	0.0	2.3	0.0	0.3
Sum Alkanes		24.6	0.8	211	19.5	60.7
Decanal	85.9	10.5	0.0	54.0	9.3	26.1
Nonanal	84.1	5.4	0.1	31.2	4.5	13.6
Hexanal	90.9	4.4	0.0	14.4	3.9	10.2
Octanal	71.8	2.9	0.0	31.4	2.2	8.5
Heptanal	71.8	2.3	0.1	13.6	1.7	6.0
Benzaldehyde	67.6	2.0	0.0	15.0	1.5	5.6
Undecanal	66.5	1.4	0.1	5.2	1.3	2.6
Butanal	17.1	0.7	0.1	4.5	0.5	1.7
2-Hydroxybenzaldehyde	6.8	0.5	0.0	8.0	0.3	1.3
Sum Aldehydes		30.1	0.2	124	26.8	70.1
Ethanol	100.0	82.3	7.0	616	56.6	246
1-Propanol	97.9	80.7	0.6	1524	16.2	378
1,2-Propanediol	98.2	45.2	0.0	363	22.7	174
Isopropyl alcohol	88.2	12.6	0.1	248	3.5	51.0
1,3-Butanediol	70.0	5.2	0.0	70.2	1.8	24.8
2-Phenoxyethanol	95.0	4.6	0.1	29.4	3.6	11.4
2-Ethylhexanol	93.8	4.0	0.1	14.3	3.6	8.5
1-Butanol	57.6	2.4	0.1	31.5	1.2	9.7
Benzyl alcohol	55.0	1.4	0.0	7.3	1.1	3.3
3-Methylbutanol	23.2	0.8	0.0	10.2	0.5	2.4
Butylated hydroxytoluene (BHT)	16.2	0.6	0.0	12.2	0.3	2.1
Glycerine	1.5	0.4	0.5	127	0.0	0.0

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
tert.-Butanol	2.6	0.2	0.0	13.6	0.1	0.3
Sum Alcohols		240	12.7	1705	169	639
Isoprene	99.4	9.0	0.1	46.8	6.9	24.4
4-Cy-pentadien-1,3-dion4phenyl	1.8	0.1	0.0	3.6	0.0	0.3
Sum Alkenes		9.1	0.1	47.1	7.1	24.4
Toluene	96.2	11.5	0.0	62.0	8.3	32.4
Benzene	91.2	8.2	0.2	53.4	4.3	32.2
p+m-Xylene	49.4	1.6	0.0	11.7	1.0	5.3
Naphthalene	16.8	1.4	0.0	49.1	0.4	2.6
Phenol	47.4	1.2	0.1	5.0	1.0	2.5
o-Xylene	32.6	1.0	0.0	5.8	0.7	3.0
Ethylbenzene	18.5	0.7	0.0	10.8	0.4	2.0
Styrene	10.3	0.5	0.0	3.8	0.4	1.3
Sum Aromatics		26.1	0.5	174	20.0	67.8
Tetrachloroethene	57.9	3.8	0.0	73.9	1.2	14.6
Dichlormethane	11.2	1.1	0.0	71.9	0.2	2.8
p-Dichlorbenzene	9.7	1.0	0.0	34.1	0.2	4.8
Sum Chlorocarbons		5.9	0.2	75.7	2.4	20.8
Ethyl acetate	90.3	4.9	0.4	68.1	2.7	16.5
2-Ethylhexyl salicylate	61.8	2.3	0.0	19.1	1.5	7.1
Butyl acetate	55.3	2.2	0.0	44.8	1.2	6.6
Isopropyl myristate	65.3	1.7	0.0	8.6	1.4	4.2
2,2,4-Trimethyl-pentanedioldiisobutyrate	56.2	1.3	0.0	6.7	1.1	2.8
1-Methoxy-2-propylacetate	28.5	1.0	0.0	9.7	0.5	4.5
Isopropyl palmitate	32.9	1.0	0.0	19.3	0.7	2.5
Homosalate	17.9	0.7	0.0	4.1	0.5	2.1
Sum Esters		15.1	0.8	76.7	11.8	37.8
Dioctyl ether	93.2	6.4	0.0	42.8	4.5	19.4
Methoxy-bis-1,2'-dipropane-1,2-diol ether	3.5	2.4	18.5	142	0.0	0.0
1,1'-Dipropane-1,2-diol ether	3.5	1.7	9.2	124	0.0	0.0
1,2'-Dipropane-1,2-diol ether	3.5	1.6	8.9	114.8	0.0	0.0
Sum Ethers		12.0	0.0	403	4.5	24.2
Acetone	99.7	15.7	0.8	87.2	11.2	44.5
5,9-Undecandien-2-one-6,10-dimethyl	90.9	3.9	0.1	26.4	3.2	8.9
Hydroxyacetone	34.1	3.3	0.0	161.0	0.6	4.8
Butanone	86.2	2.9	0.1	31.8	2.1	7.4
Acetophenone	34.1	1.6	0.0	49.5	0.7	3.7
Sum Ketones		27.3	1.0	319	19.5	66.9
Acetonitrile	82.4	19.4	0.2	269	3.2	95.1
Dimethylformamide	3.5	7.7	63.9	541	0.0	0.0
Diethyltoluamide	16.8	0.9	0.0	19.2	0.3	4.3
Sum Nitrogenous		28.0	0.3	610	4.6	132
Isoalkanes C14 - C20	82.9	62.4	0.2	355	45.8	207
Tributyl phosphate	38.2	1.1	0.0	6.4	0.8	3.5
Triethyl phosphate	6.2	0.5	0.0	18.4	0.1	1.4

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
Sum Phosphates		1.6	0.0	21.4	1.0	5.2
Perfluoro derivates	14.4	5.5	1.1	110	0.0	43.6
Phthalic anhydride	9.1	0.9	0.0	48.9	0.3	2.0
Diethyl phthalate	22.1	0.7	0.0	4.1	0.6	1.7
Diisobutyl phthalate	4.4	0.5	0.0	7.1	0.4	1.0
Dibutyl phthalate	1.5	0.3	0.0	5.3	0.2	0.6
Sum Phthalates		2.4	0.1	62.0	1.5	4.4
Cyclopentasiloxane	96.5	18.0	0.1	277	11.8	51.4
Cyclotrisiloxane	55.0	1.8	0.0	42.3	1.1	4.7
Cyclotetrasiloxane	62.6	1.8	0.0	35.4	1.2	4.4
Cyclohexasiloxane	30.3	1.0	0.0	9.3	0.7	2.6
Cycloheptasiloxane	18.2	0.7	0.0	3.4	0.5	2.0
Sum Siloxanes		23.2	0.1	288	16.7	59.2
Limonene	93.8	12.3	0.0	216	8.4	29.6
Menthol	95.6	11.6	0.1	60.7	8.6	32.9
Eucalyptol	57.6	2.0	0.0	40.3	1.2	6.7
Menthone	48.5	1.5	0.0	13.5	1.0	4.4
a-Pinene	44.1	1.2	0.0	11.7	0.9	3.3
3-Carene	17.4	1.3	0.0	42.2	0.5	2.5
p-Cymene	7.4	0.8	0.0	33.4	0.4	1.3
b-Pinene	8.8	0.6	0.0	26.1	0.4	1.4
Sum Terpenes		31.3	0.2	265	25.2	72.8

Table 12 VOC results B787 study overview

Compound	Occurrence (>1 µg/m³)	Mean	Minimum (>0.005)	Maximum	Median	95-percentile
	%	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³
Acetic acid	97.6	7.5	0.3	27.1	5.7	19.4
Benzoic acid	82.9	3.3	0.3	9.1	2.9	8.0
Hexanoic acid	90.2	6.2	0.4	34.8	4.4	17.5
Octanoic acid	51.2	1.4	0.3	4.9	1.0	2.6
Nonanoic acid	43.9	1.2	0.2	4.0	0.9	3.1
Decanoic acid	0.0	0.1	0.0	0.4	0.0	0.1
Formic acid	0.0	0.0	0.0	0.0	0.0	0.0
Phenylmaleic anhydride	0.0	0.1	0.0	0.3	0.0	0.2
Sum Acids		19.7	1.9	77.7	18.5	39.9
Tetradecane	82.9	2.1	0.2	10.3	1.6	6.2
2,2,4,6,6-Pentamethyl-heptane	70.7	10.5	0.2	49.1	4.7	40.2
2,2,4,4,6,8,8-Heptamethyl-nonane	9.8	0.6	0.0	3.8	0.4	2.7
Undecane	51.2	1.5	0.2	8.5	1.1	3.2
Nonane	46.3	1.8	0.2	9.2	0.9	4.8
Dodecane	43.9	1.3	0.2	10.8	0.8	2.1
Tridecane	41.5	1.2	0.1	9.8	0.9	2.1
Decane	34.1	1.0	0.1	6.0	0.6	2.8
Pentadecane	34.1	0.9	0.1	5.4	0.8	1.5
Pentane	31.7	1.0	0.0	4.0	0.5	3.6
Hexadecane	12.2	0.7	0.0	3.3	0.7	1.1
Heptadecane	9.8	0.6	0.1	2.6	0.6	1.1
Heptane	29.3	0.9	0.1	5.0	0.4	2.3
Methylcyclohexane	19.5	0.7	0.0	2.9	0.3	2.3
Cyclohexane	7.3	0.3	0.0	1.5	0.2	1.2
Hexane	26.8	0.7	0.1	2.6	0.5	2.2
3-Methylpentane	2.4	0.2	0.0	1.3	0.1	0.5
2,2,4-Trimethyl pentane	0.0	0.1	0.0	0.8	0.0	0.4
Sum Alkanes		25.9	1.8	118.1	20.6	61.7
Decanal	61.0	2.7	0.1	7.9	2.6	7.3
Nonanal	65.9	1.9	0.0	5.4	1.6	4.7
Hexanal	75.6	2.4	0.1	10.3	2.3	4.7
Octanal	48.8	1.3	0.1	6.6	0.9	4.7
Heptanal	22.0	0.7	0.0	4.3	0.6	1.6
Benzaldehyde	56.1	1.7	0.4	5.2	1.3	4.4
Undecanal	43.9	1.0	0.2	3.0	0.9	1.6
Butanal	7.3	0.5	0.1	1.4	0.4	1.0
2-Hydroxybenzaldehyde	0.0	0.2	0.0	0.9	0.2	0.7
Sum Aldehydes		12.5	1.3	41.3	11.0	25.3
Ethanol	100.0	80.7	6.1	270.0	55.0	266.8
1-Propanol	24.4	0.6	0.0	2.8	0.4	1.6
1,2-Propanediol	97.6	10.9	0.3	33.3	7.9	27.4
Isopropyl alcohol	73.2	3.5	0.2	26.7	1.9	11.3
1,3-Butanediol	12.2	0.4	0.0	2.0	0.2	1.5
2-Phenoxyethanol	26.8	1.0	0.0	8.2	0.6	2.3
2-Ethylhexanol	78.0	2.9	0.2	15.1	2.3	5.9

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
1-Butanol	31.7	0.9	0.1	5.3	0.7	1.6
Benzyl alcohol	24.4	0.8	0.0	3.5	0.6	1.6
3-Methylbutanol	22.0	0.6	0.0	1.9	0.6	1.7
Butylated hydroxytoluene (BHT)	0.0	0.2	0.0	0.9	0.1	0.6
Glycerine	0.0	0.0	0.0	0.0	0.0	0.0
tert.-Butanol	0.0	0.1	0.0	0.3	0.1	0.2
Sum Alcohols		102.6	9.9	317.3	77.4	301.0
Isoprene	92.7	5.0	0.4	12.5	5.1	10.1
4-Cy-pentadien13dion4phenyl	0.0	0.0	0.0	0.3	0.0	0.1
Sum Alkenes		5.1	0.5	12.6	5.4	10.2
Toluene	82.9	3.5	0.1	17.0	2.2	8.5
Benzene	70.7	3.4	0.3	11.2	2.0	9.2
p+m-Xylene	36.6	0.9	0.0	4.5	0.6	2.4
Naphthalene	26.8	0.8	0.0	4.5	0.6	2.5
Phenol	29.3	0.9	0.2	2.6	0.8	1.9
o-Xylene	14.6	0.6	0.0	3.3	0.4	1.2
Ethylbenzene	4.9	0.3	0.0	1.5	0.2	0.8
Styrene	0.0	0.3	0.0	1.0	0.2	0.5
Sum Aromatics		10.7	0.7	44.6	9.4	22.6
Tetrachloroethene	80.5	8.5	0.2	42.4	2.7	25.1
Dichlormethane	14.6	0.8	0.0	18.8	0.1	2.1
p-Dichlorbenzene	0.0	0.1	0.0	0.5	0.1	0.3
Sum Chlorocarbons		9.4	0.4	43.0	6.6	25.5
Ethyl acetate	80.5	3.9	0.1	18.6	2.8	9.3
2-Ethylhexyl salicylate	7.3	0.3	0.1	1.2	0.2	1.0
Butyl acetate	17.1	0.7	0.1	4.3	0.5	1.9
Isopropyl myristate	7.3	0.5	0.1	1.8	0.4	1.1
2,2,4-Trimethyl-pentanedioldiisobutyrate	2.4	0.2	0.0	1.0	0.1	0.4
1-Methoxy-2-propylacetate	4.9	0.2	0.0	2.0	0.1	0.5
Isopropyl palmitate	2.4	0.3	0.0	1.9	0.2	0.8
Homosalate	0.0	0.2	0.0	0.6	0.2	0.5
Sum Esters		6.1	0.5	23.8	5.3	13.1
Dioctyl ether	9.8	0.4	0.0	2.1	0.3	1.7
Methoxy-bis-1,2'-dipropane-1,2-diol ether	0.0	0.0	0.0	0.0	0.0	0.0
1,1'-Dipropane-1,2-diol ether	0.0	0.0	0.0	0.0	0.0	0.0
1,2'-Dipropane-1,2-diol ether	0.0	0.0	0.0	0.0	0.0	0.0
Sum Ethers		0.4	0.0	2.1	0.3	1.7
Acetone	97.6	10.1	0.8	36.2	8.0	27.2
5,9-Undecandien-2-one-6,10-dimethyl	0.0	0.1	0.0	0.9	0.1	0.3
Hydroxyacetone	0.0	0.3	0.0	0.9	0.2	0.7
Butanone	51.2	1.2	0.1	4.3	1.0	2.1
Acetophenone	22.0	0.7	0.1	1.9	0.5	1.7
Sum Ketones		12.4	2.1	39.1	10.1	30.6
Acetonitrile	80.5	27.0	0.2	207.0	3.0	157.7
Dimethylformamide	0.0	0.0	0.0	0.0	0.0	0.0

Compound	Occurrence (>1 µg/m³) %	Mean µg/m³	Minimum (>0.005) µg/m³	Maximum µg/m³	Median µg/m³	95-percentile µg/m³
Diethyltoluamide	0.0	0.1	0.0	0.2	0.1	0.1
Sum Nitrogenous		27.1	0.2	207.1	3.1	157.8
Isoalkanes C14 - C20	65.9	25.3	10.0	211.0	19.2	51.3
Tributyl phosphate	0.0	0.0	0.0	0.2	0.0	0.2
Triethyl phosphate	0.0	0.0	0.0	0.2	0.0	0.1
Sum Phosphates		0.1	0.0	0.3	0.1	0.2
Perfluoro derivates	0.0	0.0	0.0	0.0	0.0	0.0
Phthalic anhydride	0.0	0.0	0.0	0.2	0.0	0.1
Diethyl phthalate	0.0	0.1	0.0	0.7	0.1	0.4
Diisobutyl phthalate	2.4	0.2	0.0	1.8	0.1	0.3
Dibutyl phthalate	4.9	0.3	0.0	3.1	0.1	1.0
Sum Phthalates		0.6	0.1	5.4	0.4	1.2
Cyclopentasiloxane	95.1	9.8	0.4	52.2	6.5	23.7
Cyclotrisiloxane	17.1	0.6	0.0	2.8	0.4	1.8
Cyclotetrasiloxane	17.1	0.6	0.1	1.9	0.5	1.5
Cyclohexasiloxane	12.2	0.5	0.0	2.1	0.4	1.2
Cycloheptasiloxane	39.0	1.1	0.1	4.6	0.7	2.8
Sum Siloxanes		12.7	0.7	53.5	10.3	27.9
Limonene	87.8	5.1	0.2	26.0	3.7	13.1
Menthol	75.6	3.3	0.1	9.5	2.9	7.9
Eucalyptol	14.6	0.5	0.0	2.4	0.4	1.4
Menthone	19.5	0.6	0.0	2.0	0.5	1.4
a-Pinene	17.1	0.5	0.0	1.9	0.4	1.6
3-Carene	0.0	0.1	0.0	0.3	0.1	0.1
p-Cymene	2.4	0.2	0.0	1.0	0.2	0.5
b-Pinene	7.3	0.3	0.0	1.0	0.3	1.0
Sum Terpenes		10.6	0.3	41.0	9.6	22.3

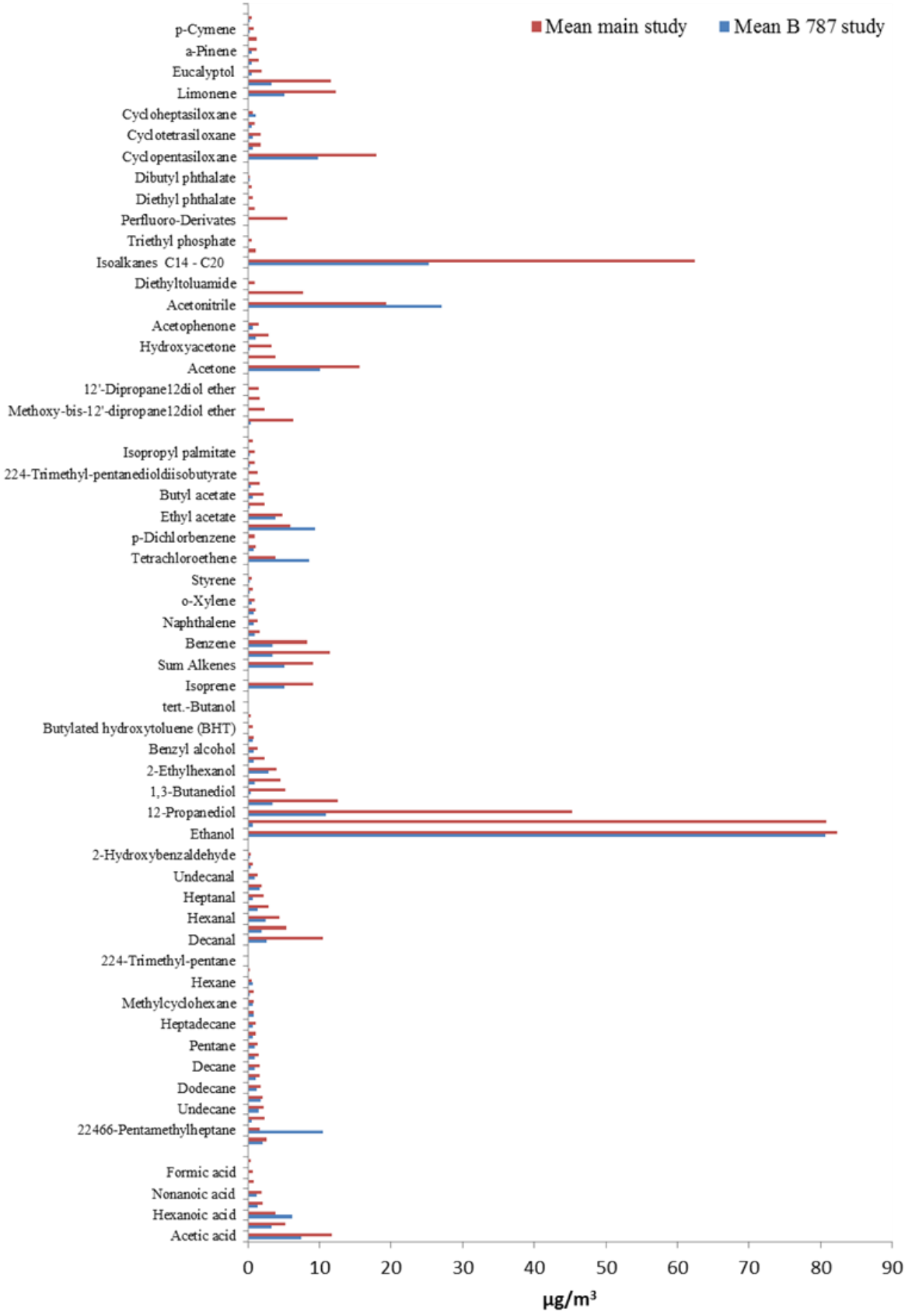


Figure 5 VOC main study vs. B787 study (mean values)

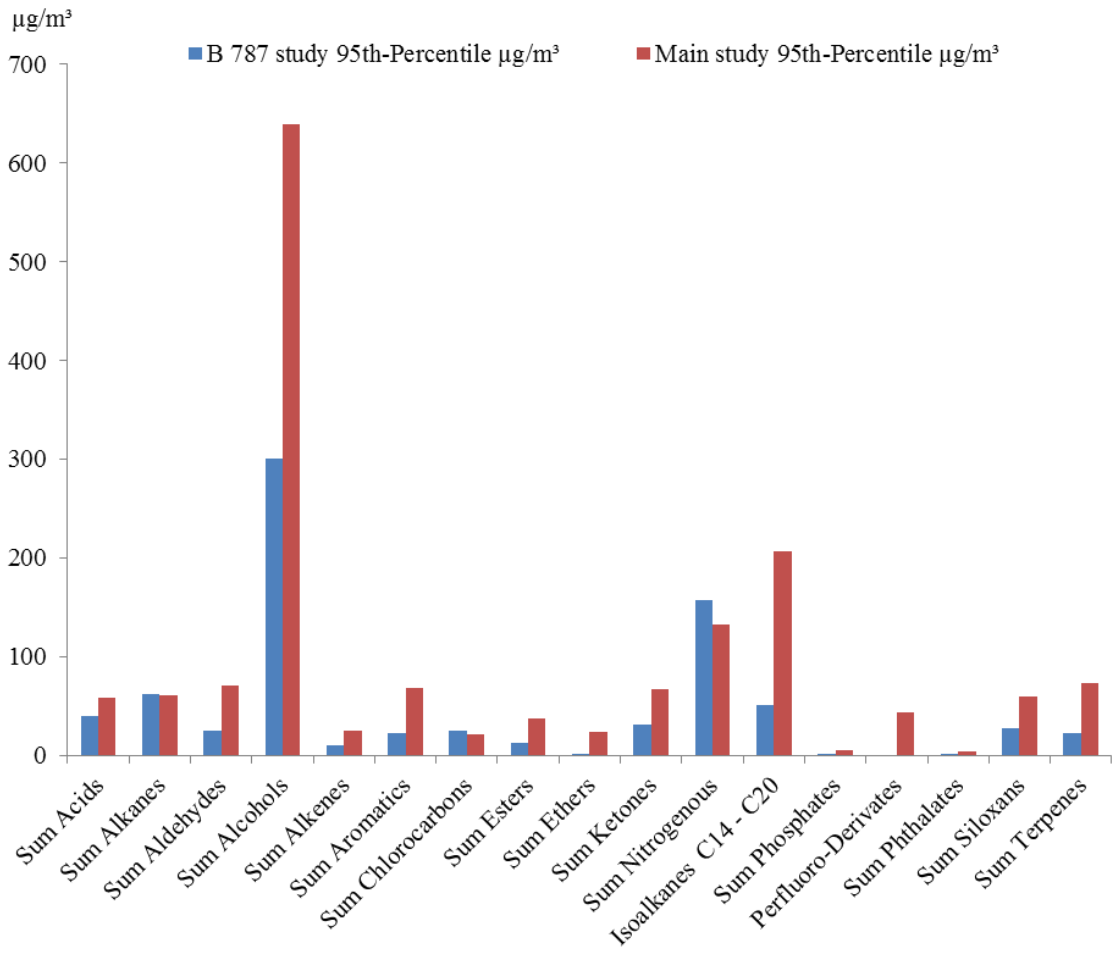


Figure 6 VOC substance groups, main study vs. B787 study (95th-percentiles)

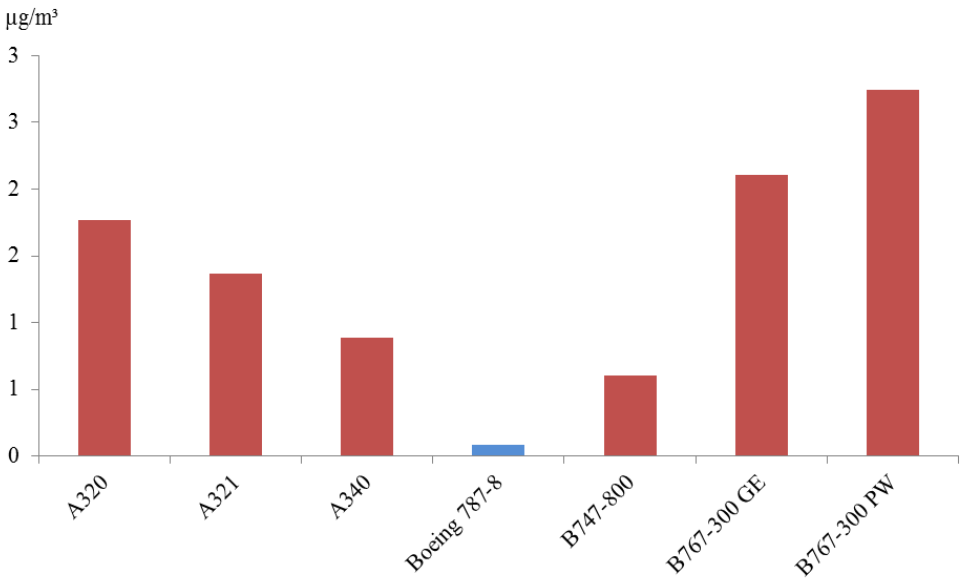


Figure 7 Semi volatile alkylphosphates, comparison of aircraft types, (mean values)

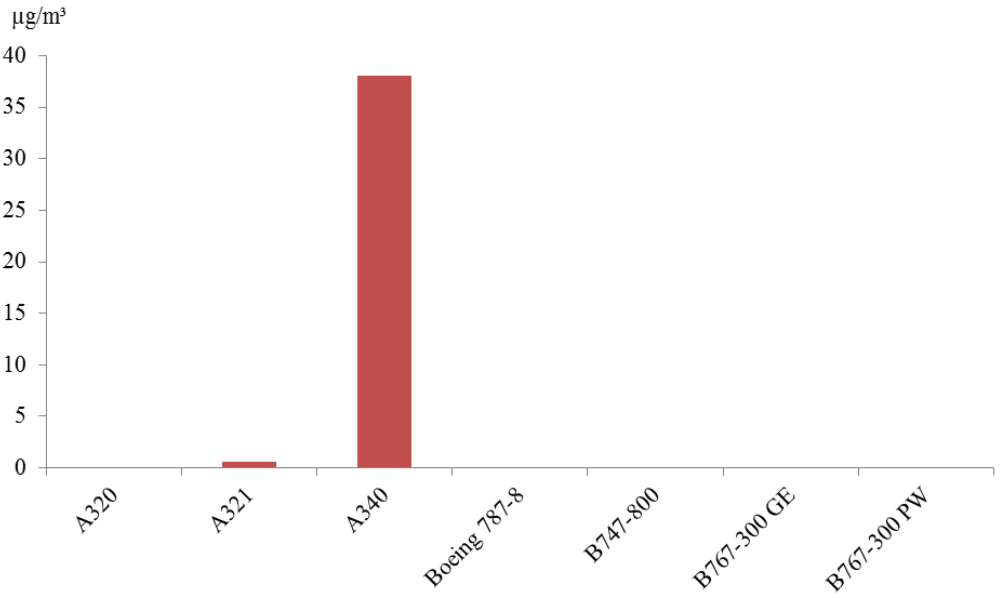


Figure 8 Perfluorinated compounds (PFC) comparison of aircraft types, (mean values)

Comparison of flight phases main study vs B787 study (mean values substance groups)

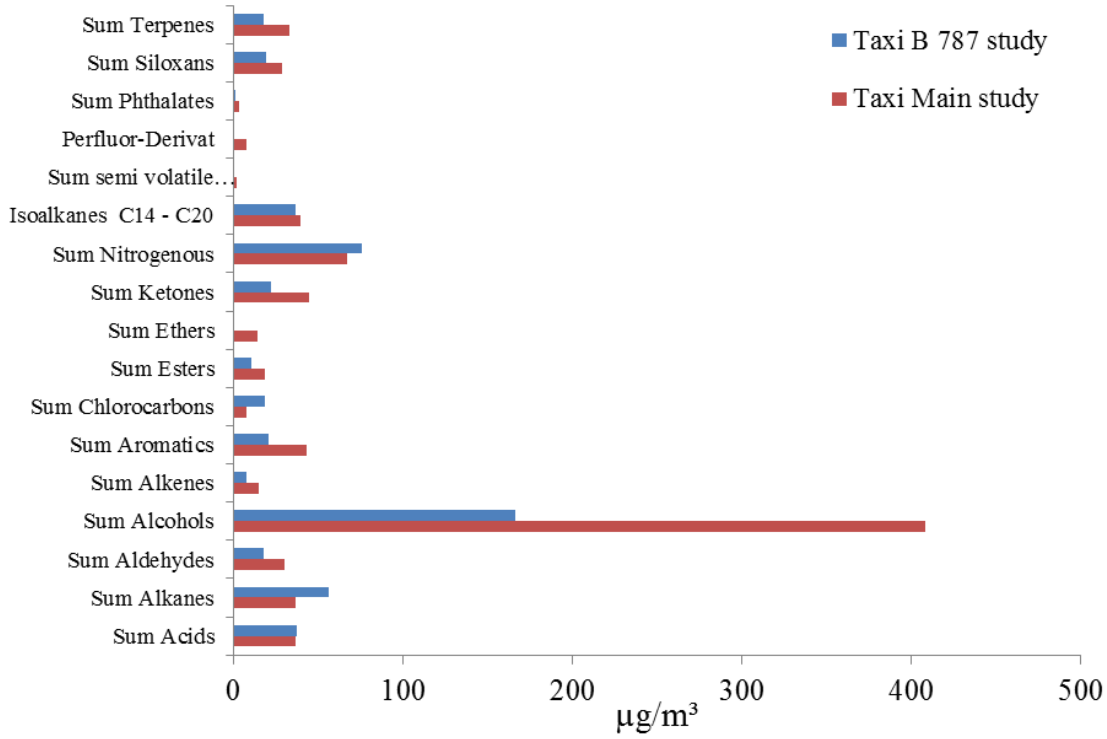


Figure 9 VOC during taxi-out (mean values) main study vs. B787 study

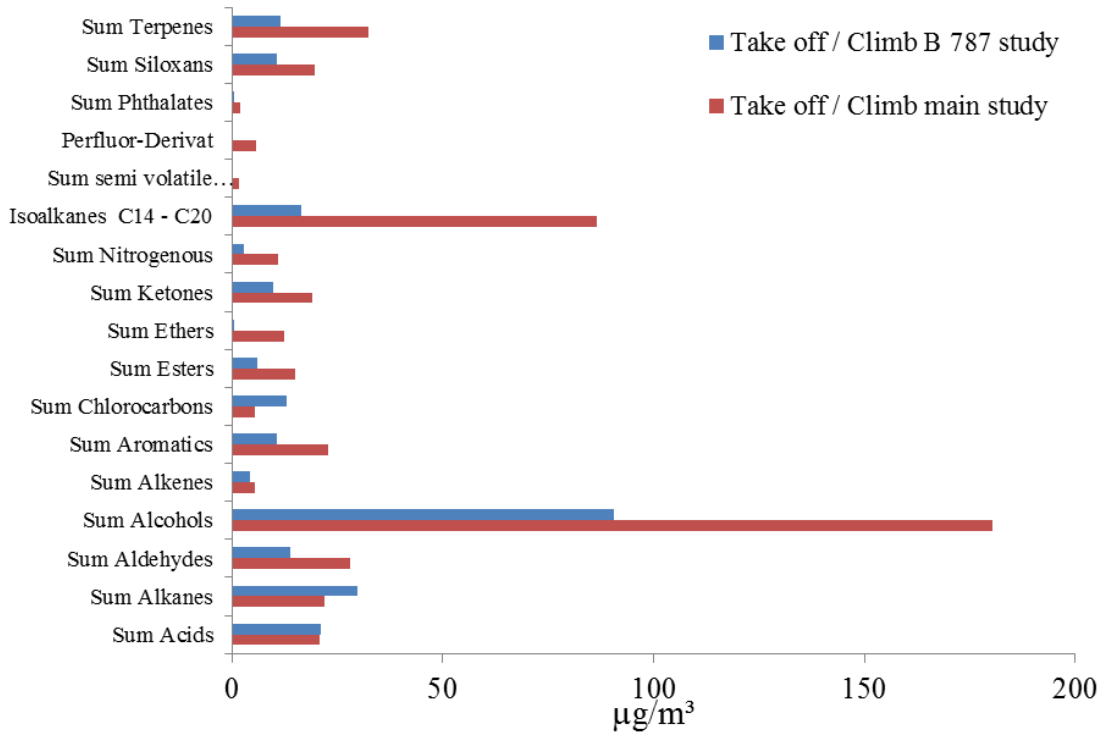


Figure 10 VOC during take-off/climb (mean values) main study vs. B787 study

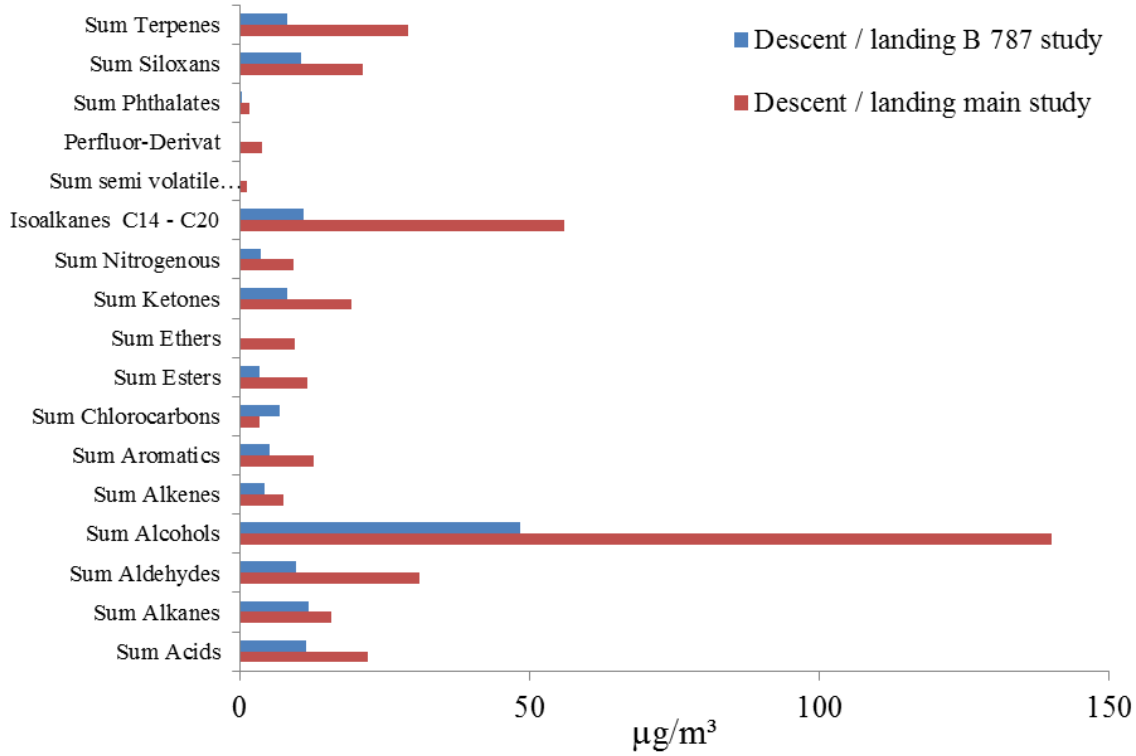


Figure 11 VOC during descent/landing (mean values) main study vs. B787 study

Comparison of certain VOC from different measurement campaigns.

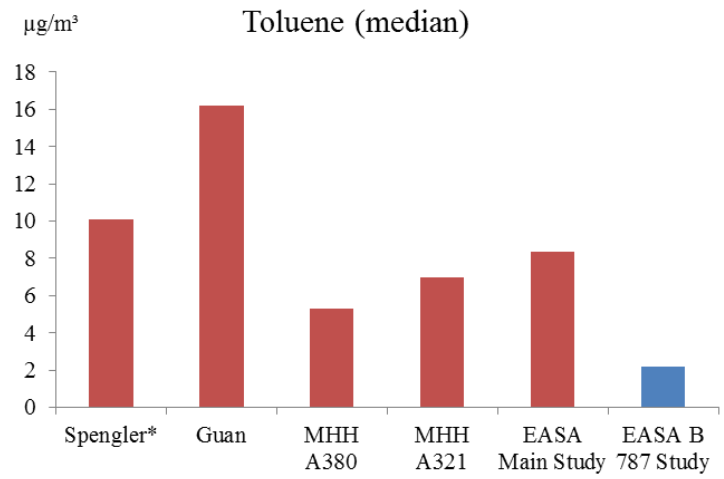


Figure 12 Toluene, comparison of different studies (median); *highest values from three investigated airlines

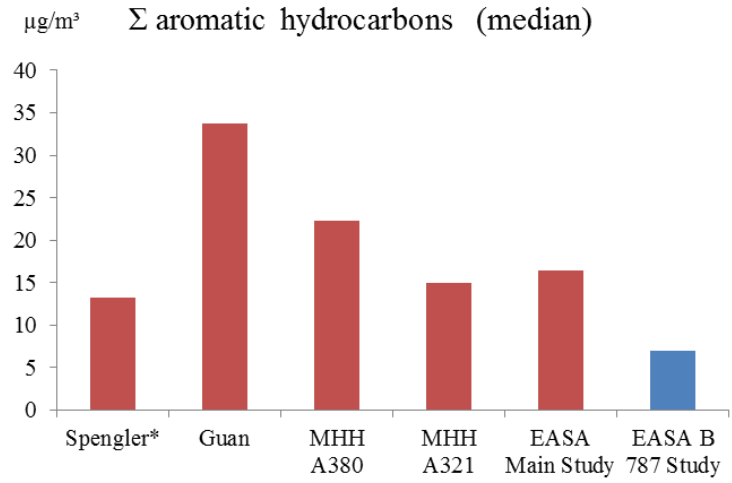


Figure 13 Σ aromatic hydrocarbons, comparison of different studies (median); *highest values from three investigated airlines

6.2 Aldehydes

Aldehydes were detected in all samples analysed. Analytical quality control was performed to ensure high analytical standards, covering the complete studies (main and B787 measurements) as exemplary illustrated in Figure 14 (other aldehydes show very similar results).

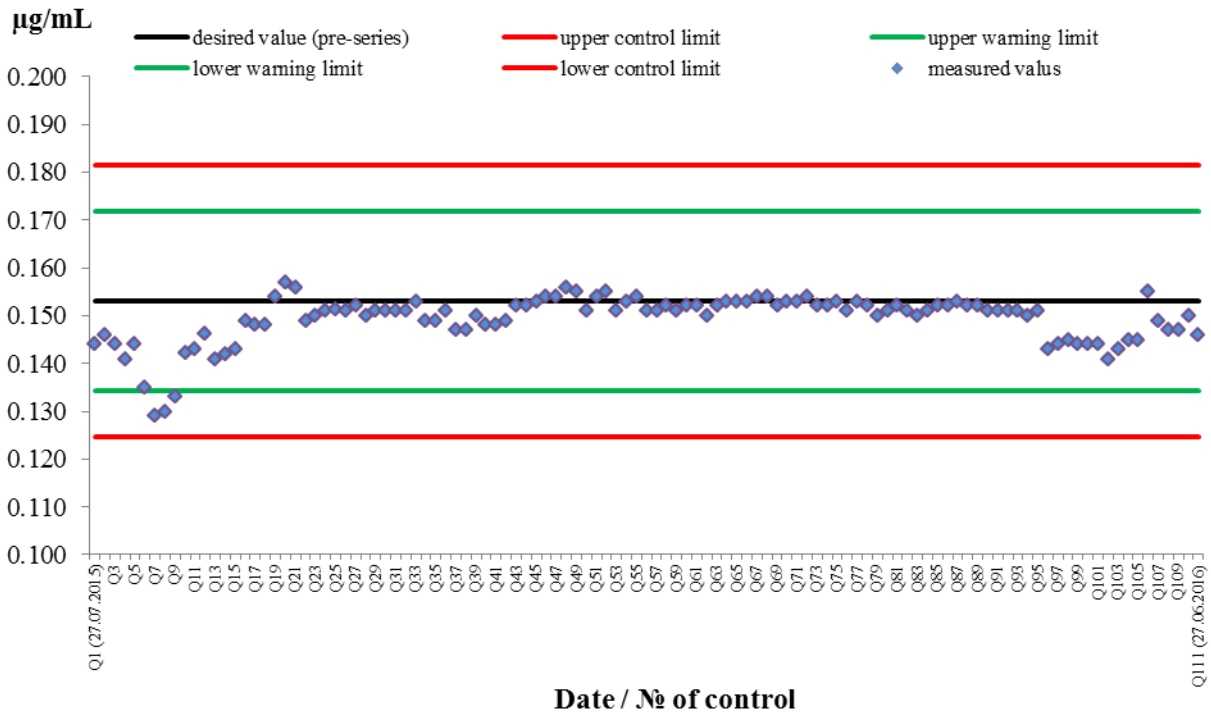


Figure 14 Exemplary quality control chart for formaldehyde from 07.2015 to 07.2016.

Table 13 Aldehydes main study comparison of flight phases (mean); entire flight represents long-term aldehyde sampling (Figure 4)

		Mean		
	µg/m³	µg/m³	µg/m³	µg/m³
Flight phases	taxi-out	take-off/climb	entire flight	descent/anding
Samples *n*	89	91	120	120
	taxi-out	take-off/climb	entire flight	descent/landing
Formaldehyde	13.9	7.0	2.7	4.8
Acetaldehyde	9.1	4.9	2.8	3.4
Acetone	55	31.4	19.5	35.2
Acrolein	1.0	0.8	0.1	0.4
Propionaldehyde	2.1	1.4	0.5	1.0
Crotonaldehyde (cis/trans)	< LOD	0.2	0.1	0.3
n-Butyraldehyde	1.5	0.8	0.4	0.7
Benzaldehyde	4.6	2.0	0.6	2.1
Isovaleraldehyde	2.4	1.2	0.5	3.5
Valeraldehyde	2.7	1.1	0.3	5.5
o-Tolualdehyde	2.5	1.5	0.4	1.2

m-Tolualdehyde	3.3	2.6	1.7	3.8
p-Tolualdehyde	1.8	1.9	1.3	2.7
Hexaldehyde	3.2	1.8	1.1	1.8
2,5-Dimethylbenzaldehyde	2.9	0.5	0.3	0.7
Sum Aldehydes (without acetone)	41.1	21.4	9.9	21.4

Table 14 Main study and B787 study, comparison of types of aircraft (mean)

				Mean			
	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³	µg/m³
Aircraft type	A320	A321	A340	B787-8	B747	B767 BE	B767 PW
Samples *n*	95	80	64	54	80	56	89
Formaldehyde	8.0	8.9	7.1	5.9	6.2	6.7	5.5
Acetaldehyde	5.3	6.3	5.3	5.2	5.2	5.5	3.8
Acetone	39	52	30.0	33.1	27.5	31.7	28.9
Acrolein	0.5	0.5	< LOD	< LOD	0.1	< LOD	0.5
Propionaldehyde	1.3	1.2	1.5	0.9	1.0	1.0	1.3
Crotonaldehyde (cis/trans)	< LOD	0.2	< LOD	< LOD	< LOD	< LOD	< LOD
n-Butyraldehyde	1.1	1.0	0.9	1.3	0.7	0.7	0.7
Benzaldehyde	3.2	2.7	2.6	2.8	2.2	1.7	1.8
Isovaleraldehyde	2.7	1.3	1.0	2.7	1.2	1.0	3.0
Valeraldehyde	2.0	1.8	2.1	3.5	2.6	2.5	2.2
o-Tolualdehyde	1.1	1.1	2.5	< LOD	1.5	< LOD	< LOD
m-Tolualdehyde	3.4	1.5	3.2	0.8	2.6	2.5	2.8
p-Tolualdehyde	0.3	1.4	2.5	< LOD	< LOD	< LOD	0.4
Hexaldehyde	2.5	2.4	1.8	2.4	1.5	1.6	1.9
2,5-Dimethylbenzaldehyde	1.8	0.6	0.2	< LOD	0.7	0.2	1.2
Sum Aldehydes (without acetone)	24.3	26.7	24.5	23.8	21.6	21.3	21.8

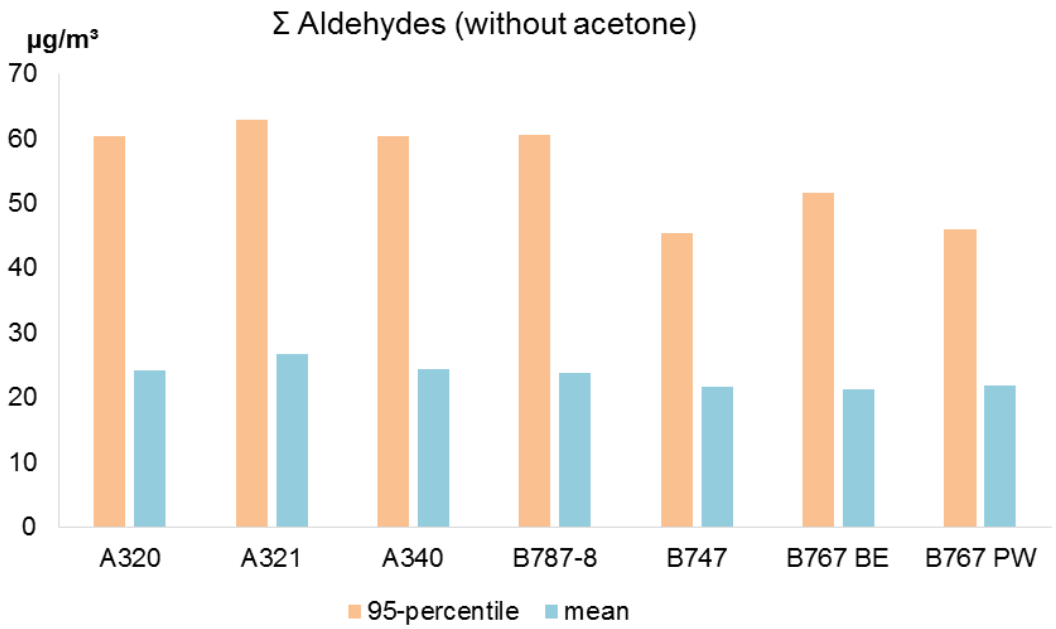


Figure 15 Sum of aldehydes (without acetone), comparison of aircraft types (mean values and 95th-percentiles)

The one-step sampling/derivatization technique on DNPH-cartridges is suitable for in-field measurement of volatile aldehydes. In the present work, very low amounts of aldehydes were detected in all types of aircraft and all flight phases as well. Nearly the same results were found in further studies [3, 27, 38].

Analytical uncertainty was present in the determination of acrolein and croton aldehyde, which are both unsaturated aldehydes. In all studies, no aldehyde concentrations were observed above workplace limits. Note indoor guide values were not reached in any flight phases in the present study. Moreover, the observed aldehyde concentrations are lower than or similar to those measured in other indoor air environments, such as in kinder gardens, schools and dwellings.

6.3 Organophosphates (OPC)

High sensitive analysis of OPC was performed with a limit of detection (LOD) of typically < 1 ng/m³ to 20 ng/m³ (Table 15). Quality control experiments with isotope labelled sampling systems (filter/PUR-foam) including sampling procedure (5 h at 3.5 L/min) revealed recovery rates in a range from 85 % to 120 % for all OPC. Filters were doped in to experimental settings: 1) with 50 ng/compound and 2) with 1000 ng/compound. The compounds 2-(o-cresyl)-4H-1:3:2: benzo-dioxaphosphoran-2-one (CBDP), trimethylo propane phosphate (TMPP) and all ortho isomers of TCP were not detected in all samples in this study. In contrast, traces of meta and para isomer of TCP, dicresylphenyl phosphates and diphenylcresyl phosphates were detected in nearly all samples.

Table 15 Determination of Detection limits (LOD) according to DIN 32654, calculated with B.E.N. Version 2.03

			Air-sample volume		
			60 L	240 L	500 L
			LOD at final sample volume of 100 µL		
Compund	CAS-Nr.	abbreviation	ng/m³	ng/m³	ng/m³
Tri-i-bytyl phosphate	126-71-6	T-i-BP	7	2	0.8
Tri-n-butyl phosphate	126-73-8	TBP	3	1	0.4
Tris(chloro-ethyl) phosphate	115-96-8	TCEP	5	1	0.6
Tris(chloro-isopropyl) phosphate	13674-84-5	TCPP	5	1	0.6
Tris(1,3-dichloro-isopropyl) phosphate	13674-87-8	TDCPP	7	2	0.8
Triphenyl phosphate	115-86-6	TPP	3	1	0.4
Tris(butoxy-ethyl) phosphate	78-51-3	TBEP	13	3	1.6
Diphenyl-2-ethylhexyl phosphate	1241-94-7	DPEHP	3	1	0.4
Tris(ethyl-hexyl) phosphate	78-42-2	TEHP	7	2	0.8
Tri-o-cresyl phosphate	78-30-8	T-o-CP	5	1	0.6
Tri-omp-cresyl phosphate[1]		T-omp-CP	5	1	0.6
Tri-oom-cresyl phosphate[1]		T-oom-CP	5	1	0.6
Tri-oop/omm-cresy lphosphate[1]		T-oop/omm-CP	10	3	1.2
Tri-opp-cresyl phosphate[1]		T-opp-CP	5	1	0.6
Tri-m-cresyl phosphate[2]	563-04-2	T-m-CP	2	0.4	0.2
Tri-mmp-cresyl phosphate[2]		T-mmp-CP	3	1	0.4
Tri-mpp-cresyl phosphate[2]		T-mpp-CP	3	1	0.4
Tri-p-cresyl phosphate[2]	78-32-0	T-p-CP	2	0.4	0.2
Trixylyl phosphate[3]	25155-23-1	TXP	8	2	1

[1]Mono- and Diortho-TCPs calculated with the response of ToCP

[2]Singe isomers calculated by constant percentage distribution of m/p-TCP-standard-mixture

[3]TXP may be used in engine oil as mixture of many isomers

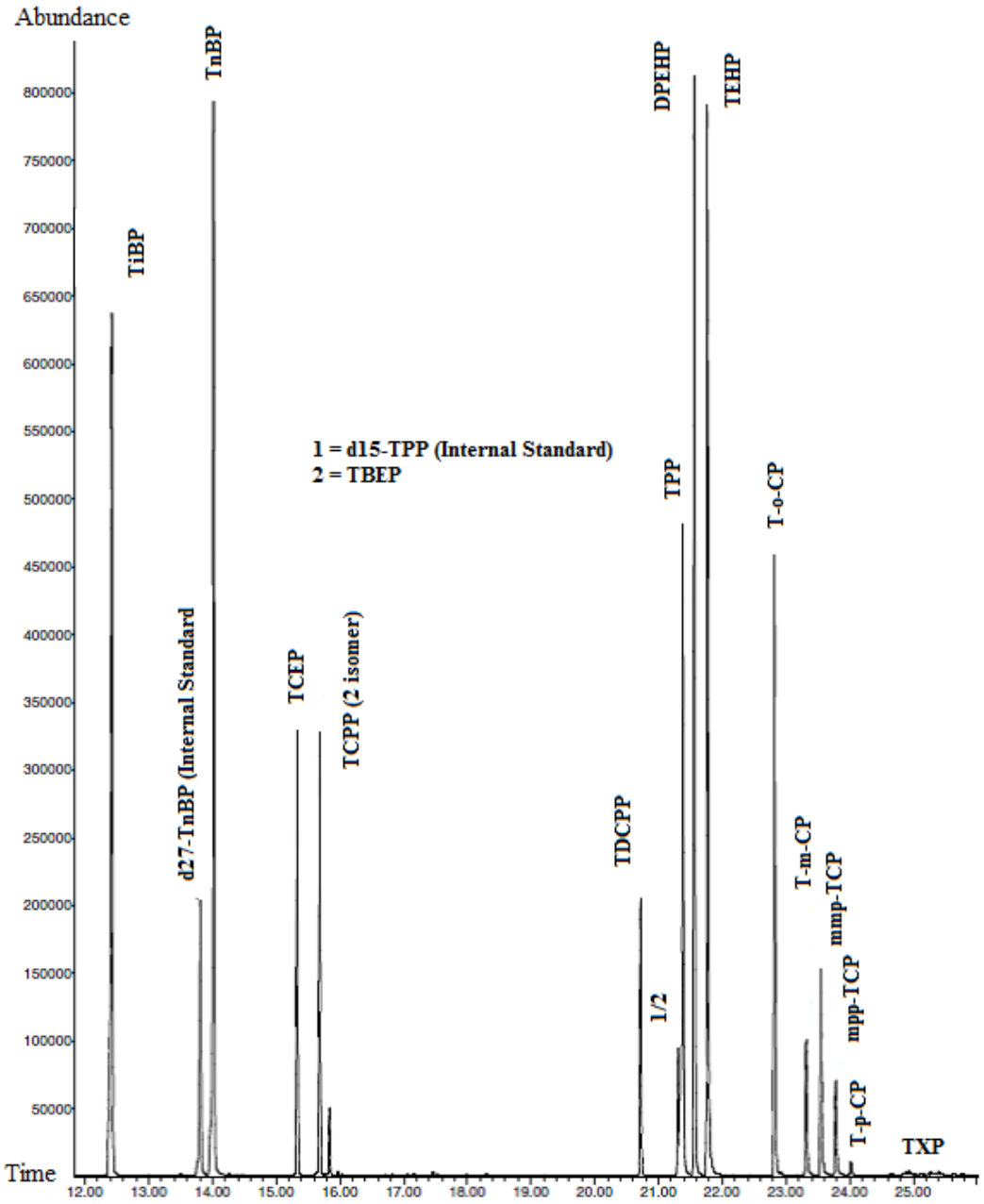


Figure 16 MS total ion chromatogram (TIC) of OPC calibration solution

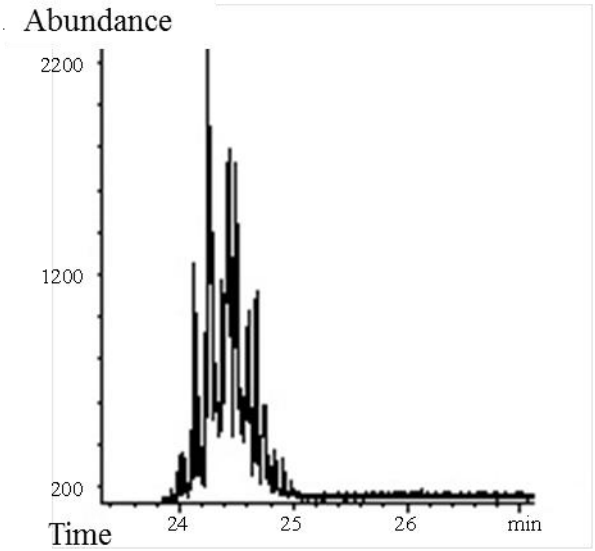


Figure 17 Peak cluster of Trixyly phosphate (TXP) at m/z 410; calibration standard

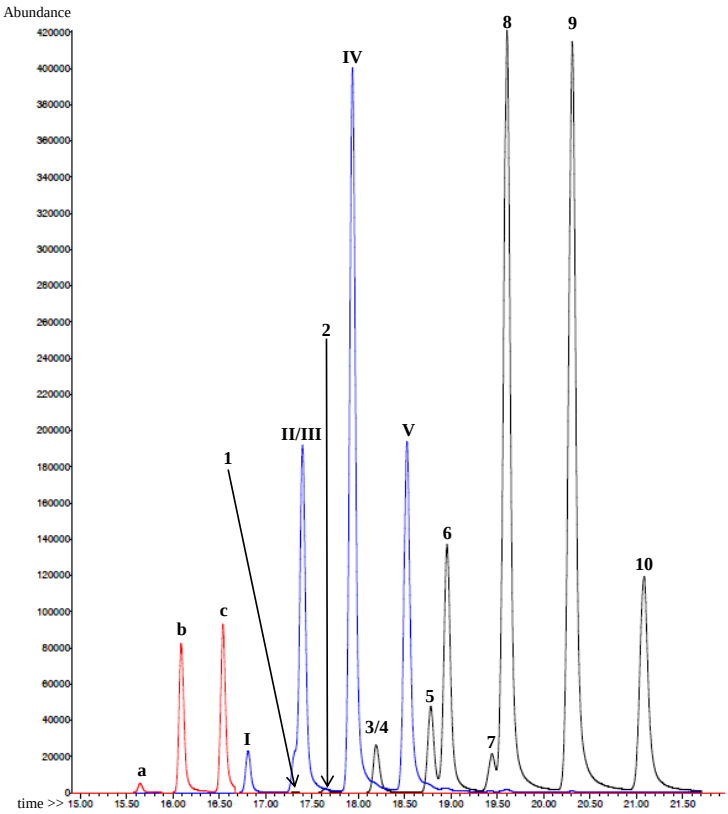


Figure 18 Chromatogram (SIM with mass 340 (a-c), 354 (I-V) and 368 (1-10)) on HP-50+ column, *a*) DPhCP (ortho isomer); *b*, *c*) DPhCP (meta/para isomers); *I*, *II*) DCPhP (ortho isomers); *III-V*) DCPhP (meta/para isomers); *1*) T-o-CP; *2-5 and 7*) ortho TCP isomers; *6*) T-m-CP, *8*) mmp-TCP; *9*) mpp-TCP and 10) T-p-CP

The identification of the isomer of mixed cresyl phosphates was performed using retention times and mass fragmentation pattern. The mass 165 was identified as base peak to all ortho

isomers. In contrast, molecule peaks (M^+: TCP = 368, DCphP = 354, DPhPC = 340) showed the highest intensity for all meta and para isomer.

However, all individual M^+ were used as quantification ions, and mass 165 served as qualifier ion. Identification of trimethylopropane phosphate (TMPP) was performed with GC-MS as shown in Figure 19 and Figure 20. Please note, that only qualitative analysis of TMPP was enabled (occurrence yes/no).

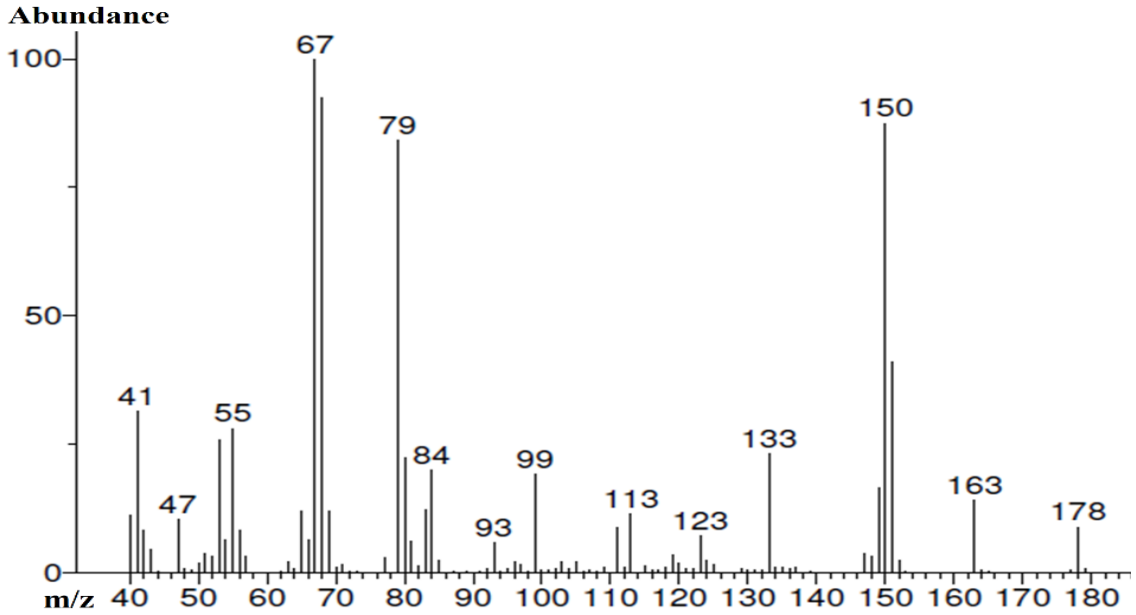


Figure 19 TMPP MS spectra of calibration standard

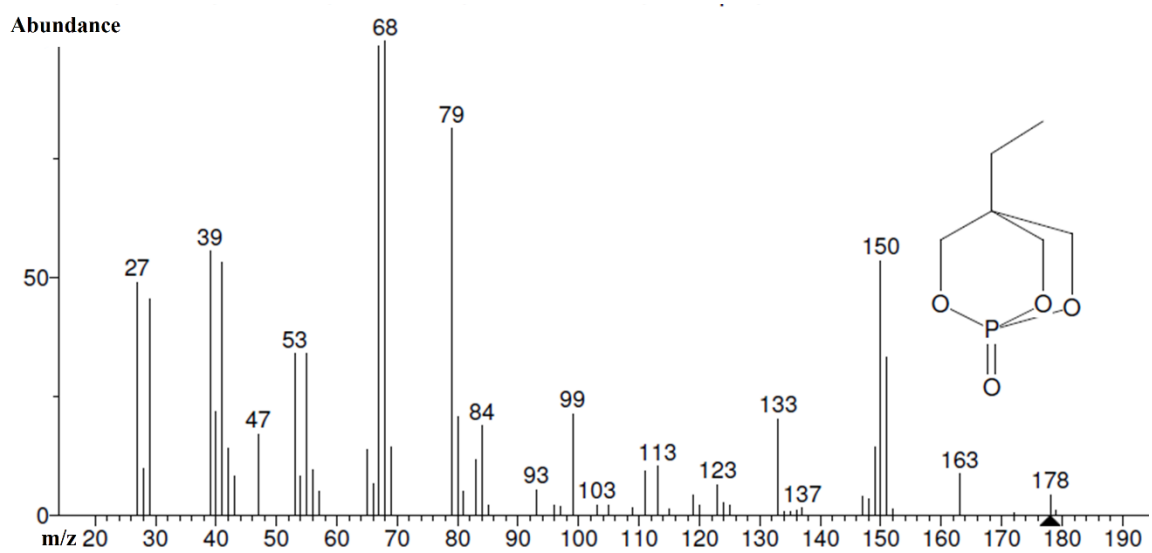


Figure 20 Reference TMPP MS spectrum of NIST data base

TMPP was not detected in all samples of main study and the B787 study.

Table 16 Overview and descriptive statistical data of OPC results from main study and B787 study

			Main study (n = 461)						B787 study (n = 55)					
Compound	CAS-Nr.:	Abbreviation	Mean µg/m³	Min µg/m³	Max µg/m³	Median µg/m³	95th-percentile µg/m³	Occurrence %	Mean µg/m³	Min µg/m³	Max µg/m³	Median µg/m³	95th-percentile µg/m³	Occurrence %
Triisobytyl phosphate	126-71-6	T-i-BP	0.102	< LOD	1.610	0.036	0.368	99%	0.016	0.003	0.093	0.010	0.031	91%
Tributyl phosphate	126-73-8	TBP	0.430	0.037	2.484	0.279	1.357	100%	0.237	0.037	1.482	0.153	0.569	100%
Tris(chloro-ethyl)phosphate	115-96-8	TCEP	0.016	< LOD	0.324	0.006	0.053	99%	0.007	0.001	0.056	0.004	0.013	91%
Tris(chloro-isopropyl)phosphate	13674-84-5	TCPP	0.506	0.023	9.977	0.200	2.247	100%	0.502	0.041	2.633	0.361	1.121	100%
Tris(1,3-dichloro-isopropyl)phosphate	13674-87-8	TDCPP	0.008	< LOD	0.049	0.005	0.025	95%	0.005	0.001	0.024	0.003	0.016	62%
Triphenyl phosphate	115-86-6	TPP	0.009	0.001	0.119	0.006	0.029	99%	0.006	0.001	0.052	0.003	0.016	96%
Tris(butoxy-ethyl)phosphate	78-51-3	TBEP	0.076	< LOD	0.642	0.035	0.298	62%	0.035	0.000	0.250	0.016	0.161	55%
Diphenyl-2-ethylhexyl phosphate	1241-94-7	DPEHP	0.015	< LOD	0.193	0.010	0.044	99%	0.013	0.000	0.282	0.004	0.034	100%
Tris(ethyl-hexyl)phosphate	78-42-2	TEHP	0.004	< LOD	0.088	0.002	0.015	47%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-o-cresyl phosphate	78-30-8	T-o-CP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-omp-cresyl phosphate		T-omp-CP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-oom-cresyl phosphate		T-oom-CP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-oop/omm-cresyl phosphate		T-oop/omm-CP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-opp-cresyl phosphate		T-opp-CP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Tri-m-cresyl phosphate	563-04-2	T-m-CP	0.004	< LOD	0.428	0.001	0.010	58%	0.007	0.001	0.119	0.002	0.014	60%
Tri-mmp-cresyl phosphate		T-mmp-CP	0.006	< LOD	0.691	0.002	0.014	64%	0.010	0.001	0.205	0.002	0.027	84%
Tri-mpp-cresyl phosphate		T-mpp-CP	0.004	< LOD	0.339	0.001	0.010	55%	0.006	0.001	0.075	0.002	0.021	80%
Tri-p-cresyl phosphate	78-32-0	T-p-CP	0.002	< LOD	0.057	0.001	0.008	31%	0.003	0.001	0.010	0.002	0.008	55%
Trixylyl phosphate	25155-23-1	TXP	< LOD	< LOD	< LOD	< LOD	< LOD	0%	< LOD	< LOD	< LOD	< LOD	< LOD	0%
Sum m/p-Isomer		Sum m/P-TCP	0.009	0.000	1.515	0.002	0.026		0.020	0.000	0.403	0.005	0.065	
Sum o-Isomer		Sum o-TCP	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.000	
Sum Total-TCP	1330-78-5	Sum TCP	0.009	0.000	1.515	0.002	0.026		0.020	0.000	0.403	0.005	0.065	
Sum of those contaminants which are restricted/have a threshold for indoor air concentrations		Sum TCEP, TCPP, TDCPP, TPP, TBEP, TEHP, TBP	1.015	< LOD	10.790	0.652	2.943		0.773	< LOD	4.348	0.645	1.531	
Sum all compounds		Sum OPC	1.139	< LOD	10.998	0.766	3.115		0.820	< LOD	4.560	0.717	1.734	

Table 17 OPC, comparison of flight phases in main study (mean values)

	Mean			
	µg/m³	µg/m³	µg/m³	µg/m³
n	111	110	118	118
Flight phase	taxi-out	take-off/climb	complete flight	descent/ landing
Triisobytyl phosphate	0.125	0.094	0.087	0.099
Tributyl phosphate	0.594	0.466	0.327	0.329
Tris(chloro-ethyl)phosphate	0.023	0.017	0.010	0.014
Tris(chloro-isopropyl)phosphate	0.666	0.546	0.357	0.450
Tris(1,3-dichloro-isopropyl)phosphate	0.011	0.007	0.005	0.007
Triphenyl phosphate	0.014	0.008	0.006	0.009
Tris(butoxy-ethyl)phosphate	0.113	0.075	0.054	0.062
Diphenyl-2-ethylhexylphosphate	0.024	0.014	0.008	0.012
Tris(ethyl-hexyl)phosphate	0.007	0.004	0.003	0.004
Tri-o-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-omp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-oom-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-oop/omm-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-opp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-m-cresyl phosphate	0.004	0.002	0.002	0.009
Tri-mmp-cresyl phosphate	0.006	0.003	0.002	0.013
Tri-mpp-cresyl phosphate	0.004	0.002	0.002	0.008
Tri-p-cresyl phosphate	0.002	0.002	0.002	0.003
Trixylyl phosphate	< LOD	< LOD	< LOD	< LOD
Sum m/p-Isomer	0.012	0.005	0.003	0.019
Sum o-Isomer	0.000	0.000	0.000	0.000
Sum total-TCP	0.012	0.005	0.003	0.019
Sum of those contaminants which are restricted/have a threshold for indoor air concentrations	1.377	1.095	0.739	0.849
Sum all compounds	1.535	1.206	0.837	0.978

Table 18 OPC, comparison of flight phases in B787 study (mean values)

	Mean			
	µg/m³	µg/m³	µg/m³	µg/m³
n	14	13	14	14
Flight phase	taxi-out	take-off/climb	entire flight	descent/ landing
Triisobytyl phosphate	0.025	0.015	0.012	0.010
Tributyl phosphate	0.433	0.213	0.149	0.153
Tris(chloro-ethyl)phosphate	0.014	0.005	0.003	0.005
Tris(chloro-isopropyl)phosphate	0.860	0.429	0.329	0.384
Tris(1,3-dichloro-isopropyl)phosphate	0.010	0.004	0.003	0.003
Triphenyl phosphate	0.012	0.004	0.003	0.003
Tris(butoxy-ethyl)phosphate	0.064	0.035	0.017	0.020
Diphenyl-2-ethylhexylphosphate	0.032	0.009	0.002	0.010
Tris(ethyl-hexyl)phosphate	< LOD	< LOD	< LOD	< LOD
Tri-o-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-omp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-oom-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-oop/omm-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-opp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD
Tri-m-cresyl phosphate	0.018	0.003	0.001	0.002
Tri-mmp-cresyl phosphate	0.032	0.006	0.002	0.002
Tri-mpp-cresyl phosphate	0.019	0.004	0.001	0.002
Tri-p-cresyl phosphate	0.005	0.002	0.001	0.001
Trixylyl phosphate	< LOD	< LOD	< LOD	< LOD
Sum m/p-Isomer	0.057	0.013	0.003	0.004
Sum o-Isomer	0.000	0.000	0.000	0.000
Sum total-TCP	0.057	0.013	0.003	0.004
Sum of those contaminants which are restricted/have a threshold for indoor air concentrations	1.472	0.710	0.509	0.580
Sum all compounds	1.360	0.674	0.492	0.557

Following pages show the comparison of each OPC focused on short-term samples (Figure 4) between main study and B787 study results in different flight phases (mean values and 95th-percentile of all samples.

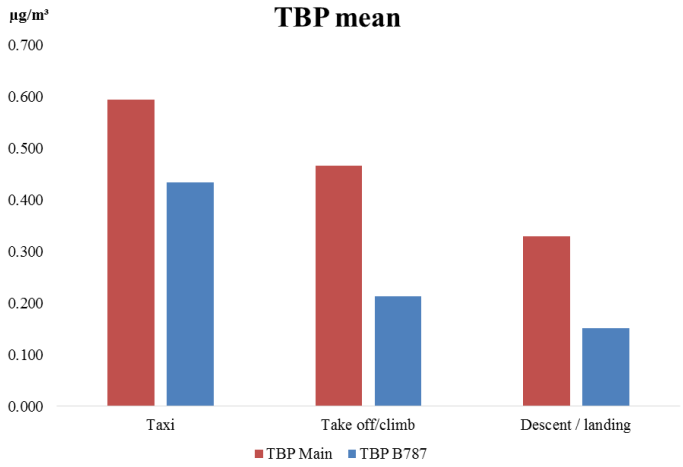


Figure 21 Mean values of tri-n-butyl phosphate, comparison of flight phases for main study and B787 study.

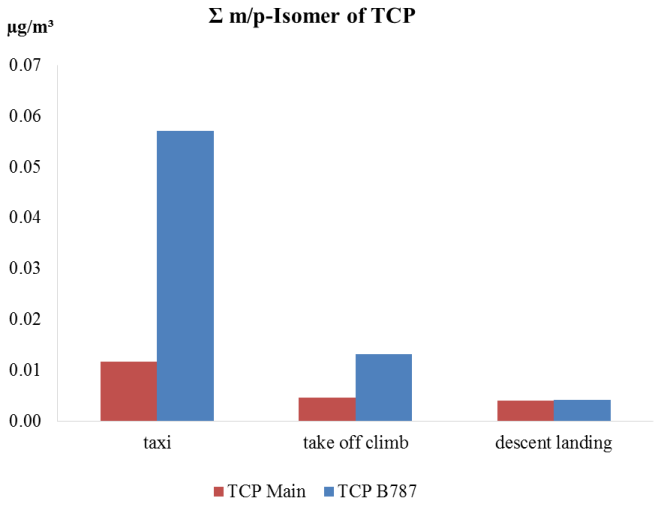


Figure 22 Mean values of TCP, comparison of flight phases for main study and B787 study.

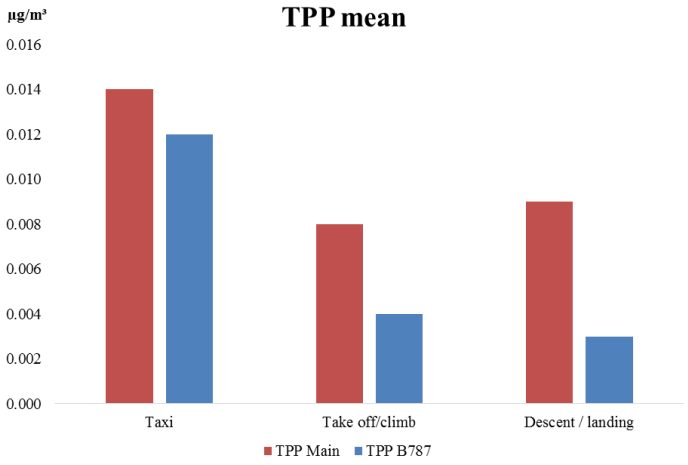


Figure 23 Mean values of TPP, comparison of flight phases for main study and B787 study.

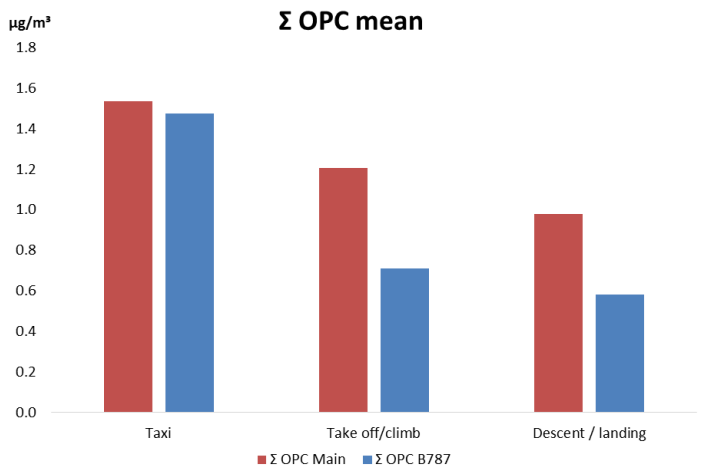


Figure 24 Mean values of all OPC, comparison of flight phases for main study and B787 study.

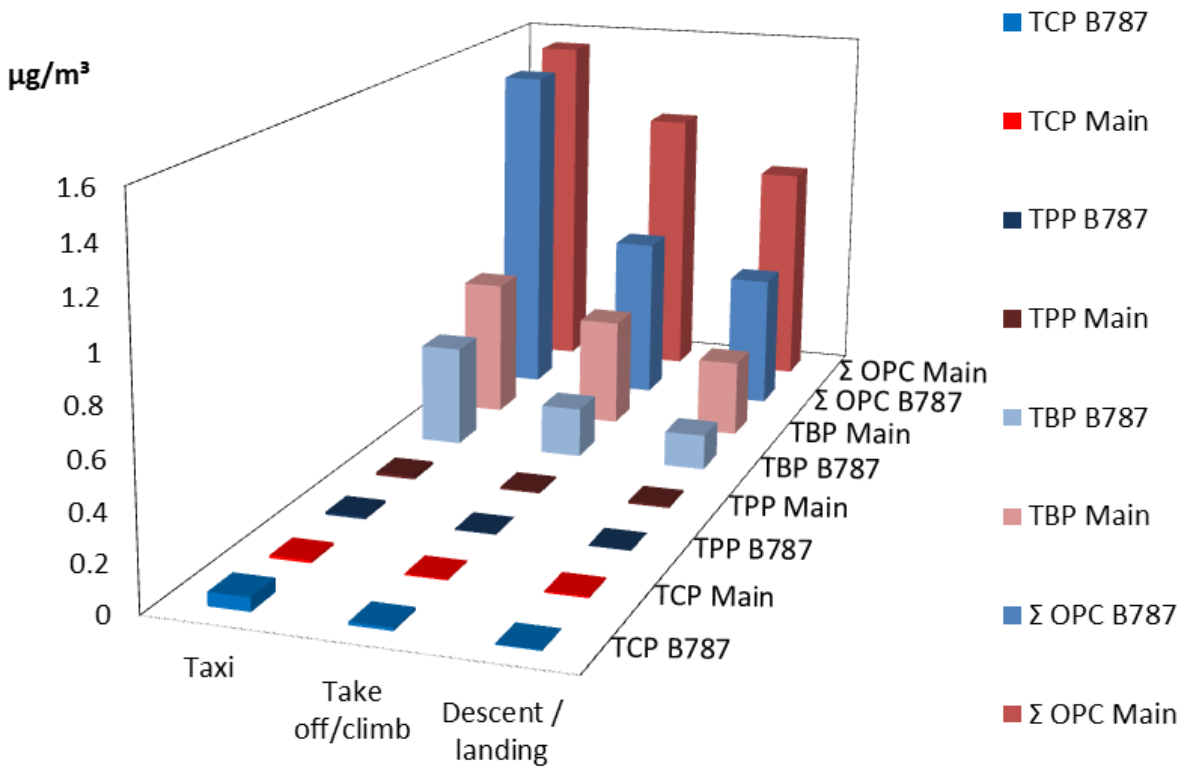


Figure 25 Comparative overview of the most significant OPC measured in the main study and the B787 study. TCP = Sum total-TCP (tricresyl phosphate); TPP = triphenyl phosphate; TBP = tributyl phosphate.

Table 19 Results of OPC measurements, comparison of results from different studies (Airbus A320, A380 and A321 studies conducted by MHH with LH and CFG)

Study	Main study	B787 study	B757-300*	A320	A380	A321
Sampling period	2015 – 2016	2016	2015	2011- 2012	2013 - 2015	2014 - 2015
Number of flights	60	8	2	4	64	44
Number of aircraft registrations	26	4	1	2	11	15
Number of samples	n = 461	n = 55	*n* = 10	*n* = 8	*n* = 196	*n* = 128
Compound	Median µg/m³	Median µg/m³	Median µg/m³	Median µg/m³	Median µg/m³	Median µg/m³
Triisobytyl phosphate (TiBP)	0.036	0.010	0.270	0.052	0.040	0.058
Tributyl phosphate (TBP)	0.279	0.153	0.341	0.85	0.66	0.85
Tris(2-chloro-ethyl) phosphate (TCEP)	0.006	0.004	0.022	0.041	0.044	0.067
Tris(chloro-isopropyl) phosphate (TCPP)	0.200	0.361	0.084	0.20	0.089	0.376
Tris(1.3-dichloro-isopropyl) phosphate (TDCPP)	0.005	0.003	0.003	0.006	0.006	0.010
Triphenyl phosphate (TPP)	0.006	0.003	0.003	0.024	0.011	0.010
Tris(butoxy-ethyl) phosphate (TBEP)	0.035	0.016	0.032	0.006	0.048	0.127
Diphenyl-2-ethylhexyl phosphate (DPHP)	0.010	0.004	0.004	0.008	0.019	0.019
Tris(ethyl-hexyl) phosphate (TEHP)	0.002	< LOD	0.001	0.005	0.006	0.005
Tri-o-cresyl phosphate (ToCP)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
omp-Tricresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
oom-Tricresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
oop/omm-Tricresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
opp-Tricresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-m-cresyl phosphate (TmCP)	0.001	0.002	0.002	0.014	0.003	0.004
mmp-Tricresyl phosphate	0.002	0.002	0.004	0.014	0.003	0.005
mpp-Tricresyl phosphate	0.001	0.002	0.003	0.017	0.003	0.004
Tri-p-cresyl phosphate (TpCP)	0.001	0.002	0.001	0.002	0.001	0.002
Trixylyl phosphate (TXP)	< LOD	< LOD	< LOD	< LOD	0.030**	< LOD

*****Additional flights in main study with CFG Boeing 757-300 (test flights after "smell event", ******TXP only in two samples

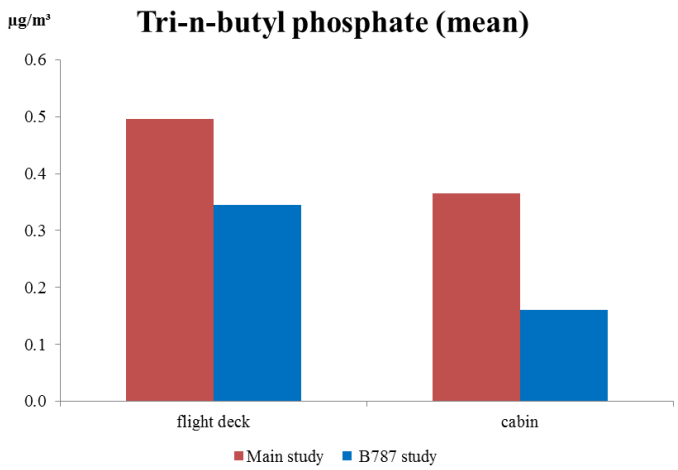


Figure 26 Tri-*n*-butyl phosphate, comparison of locations investigated, main study and B787 study (mean values)

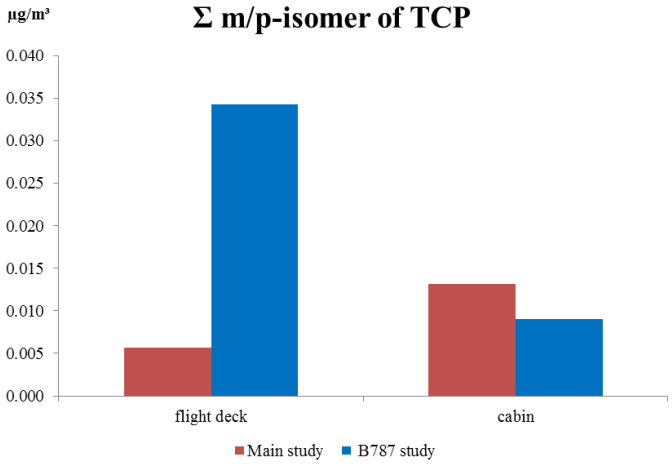


Figure 27 Sum of m/p-Isomer of TCP, comparison of locations investigated, main study and B787 study (mean values)

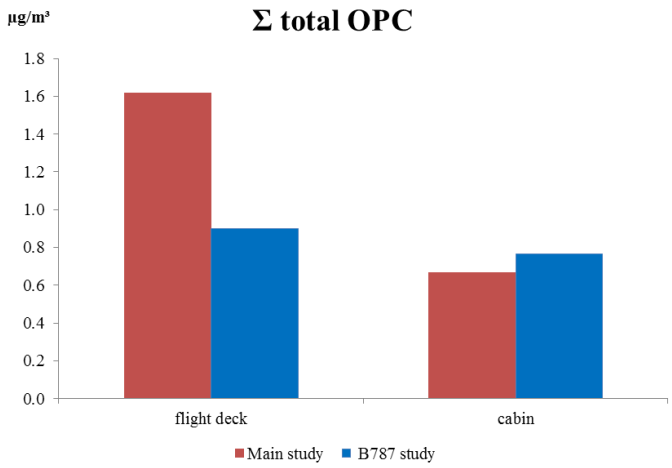


Figure 28 Sum of total OPC, comparison of locations investigated, main study and B787 study (mean values)

Comparison of types of aircraft, main study and B787 study, descriptive statistical data

Table 20 OPC results main study and B787 study, comparison of types of aircraft (mean concentration in µg/m³)

Type of aircraft	A320	A321	A340	B787-8	B747	B767 GE	B767 PW
Samples *n*	92	79	64	55	79	58	89
Concentration				µg/m³			
Triisobytyl phosphate	0.056	0.025	0.029	0.016	0.152	0.125	0.212
Tributyl phosphate	0.824	0.280	0.413	0.237	0.129	0.388	0.461
Tris(chloro-ethyl)phosphate	0.041	0.010	0.020	0.007	0.005	0.012	0.007
Tris(chloro-isopropyl)phosphate	0.429	1.485	0.146	0.502	0.406	0.296	0.202
Tris(1,3-dichloro-isopropyl)phosphate	0.007	0.008	0.004	0.005	0.009	0.008	0.009
Triphenyl phosphate	0.017	0.004	0.010	0.006	0.008	0.009	0.007
Tris(butoxy-ethyl)phosphate	0.085	0.044	0.063	0.035	0.139	0.043	0.070
Diphenyl-2-ethylhexylphosphate	0.019	0.015	0.016	0.013	0.018	0.011	0.008
Tris(ethyl-hexyl)phosphate	0.004	0.002	0.009	< LOD	0.008	0.002	0.005
Tri-o-cresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-omp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-oom-cresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-oop/omm-cresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-opp-cresyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Tri-m-cresyl phosphate	0.003	0.003	0.015	0.007	0.002	0.001	0.003
Tri-mmp-cresyl phosphate	0.005	0.003	0.020	0.010	0.002	0.002	0.004
Tri-mpp-cresyl phosphate	0.003	0.002	0.015	0.006	0.002	0.001	0.003
Tri-p-cresyl phosphate	0.001	0.001	0.008	0.003	0.001	0.000	0.002
Trixylyl phosphate	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sum m/p-Isomer	0.007	0.005	0.035	0.020	0.004	0.001	0.008
Sum o-Isomer	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Sum total-TCP	0.007	0.005	0.035	0.020	0.004	0.001	0.008
Sum all compounds	1.431	1.861	0.715	0.820	0.818	0.868	0.978
Sum of those contaminants which are restricted/have a threshold for indoor air concentrations	1.349	1.816	0.636	0.773	0.650	0.731	0.751

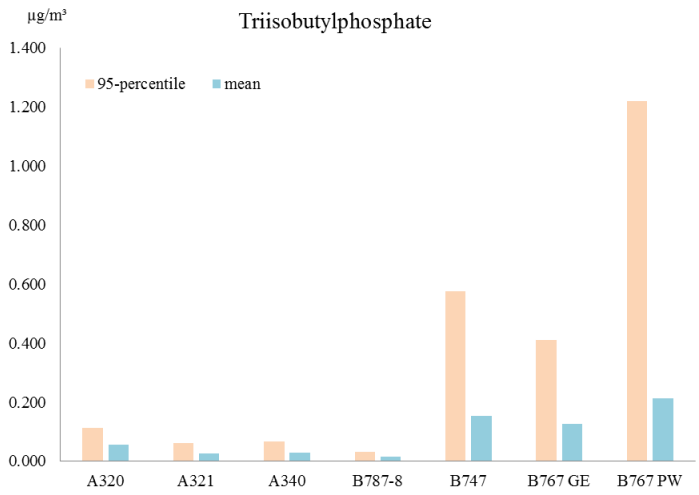


Figure 29 Triisobutyl phosphate detected with respect to the aircraft type investigated, (mean and 95th-percentile).

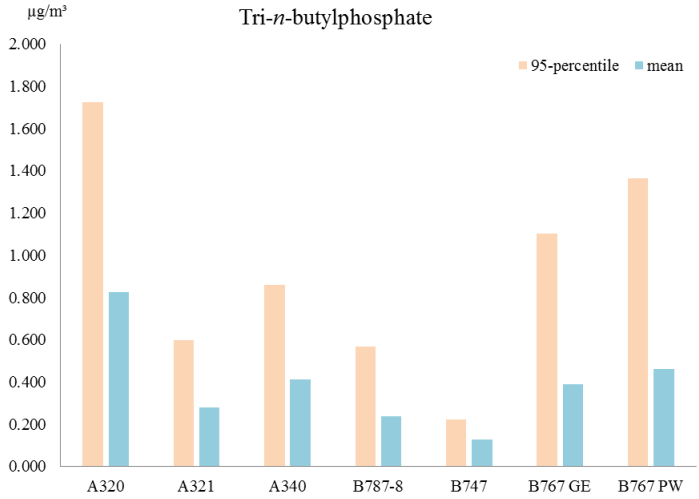


Figure 30 Tri-*n*-butyl phosphate detected with respect to the aircraft type investigated, (mean and 95th-percentile).

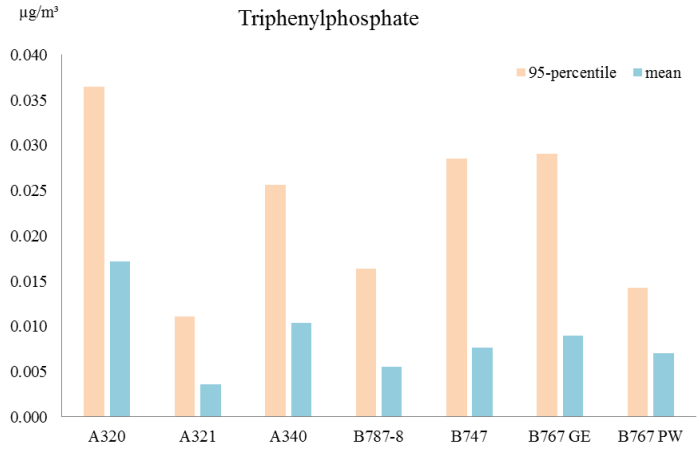


Figure 31 Triphenyl phosphate detected with respect to the aircraft type investigated, (mean and 95th-percentile).

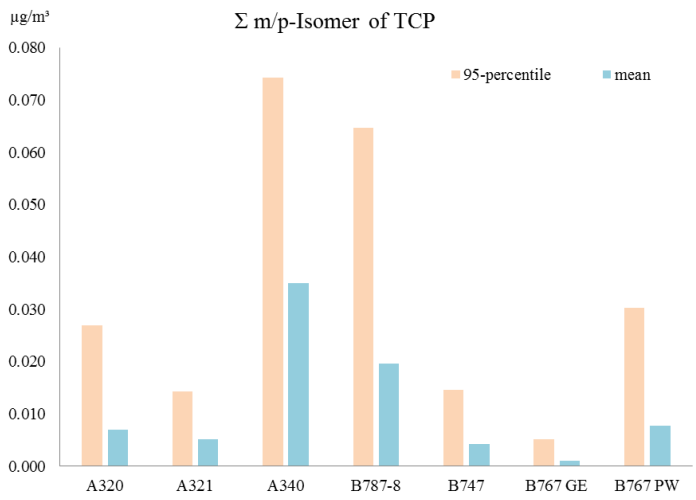


Figure 32 Sum of m/p-isomers of TCP detected with respect to the aircraft type investigated, (mean and 95th-percentile).

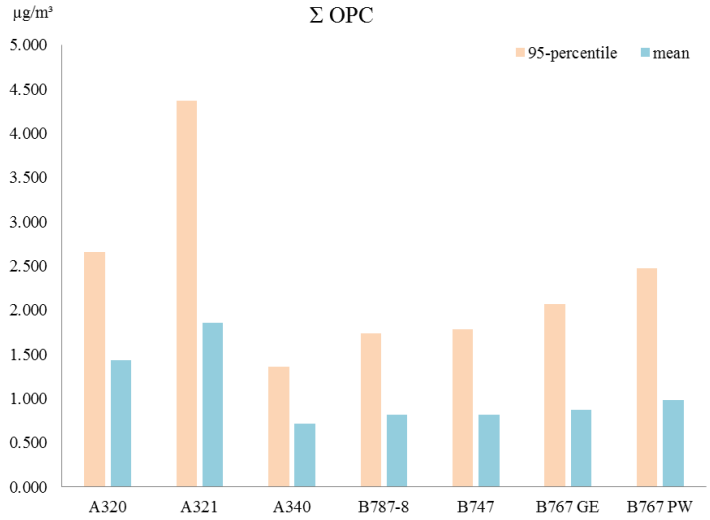


Figure 33 Sum of all OPC detected with respect to the aircraft type investigated, (mean and 95th-percentile).

6.4 Temperature, humidity and pressure

In Table 21 a comparison of all Dreamliner flights with 12 randomly selected flights from the main study (incl. every type of aircraft) in cruise is given. In Figure 34 - Figure 39 examples for climate data during exemplary flights are summarized.

Table 21 Climate data (only in cruise)

		Main study Cabin	Main study Cockpit	B787 study Cabin	B787 study Cockpit
Flights	n	12	12	8	8
Data points	n	4312	4264	2612	1948
Pressure Mean	[mbar]	816	816	811	811
Pressure Min	[mbar]	751	751	811	810
Pressure Max	[mbar]	870	870	838	838
Pressure Median	[mbar]	811	811	811	811
Pressure 95th-percentile	[mbar]	851	851	812	812
Humidity Mean	[%]	13	8	18	10
Humidity Min	[%]	5	2	10	3
Humidity Max	[%]	28	35	43	42
Humidity Median	[%]	13	7	18	8
Humidity 95th-percentile	[%]	20	17	24	24
Temperature Mean	[°C]	24	23	21	24
Temperature Min	[°C]	21	19	18	18
Temperature Max	[°C]	28	31	24	35
Temperature Median	[°C]	24	23	22	23
Temperature 95th-percentile	[°C]	27	25	24	31

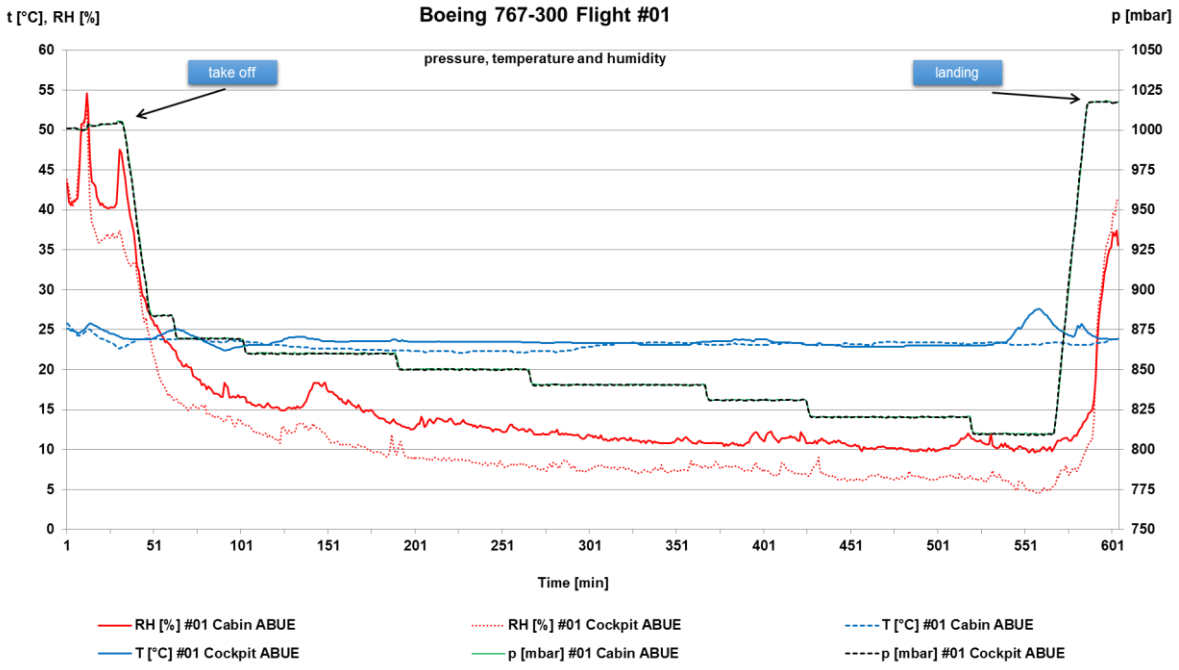


Figure 34 Climate data Boeing B767-300

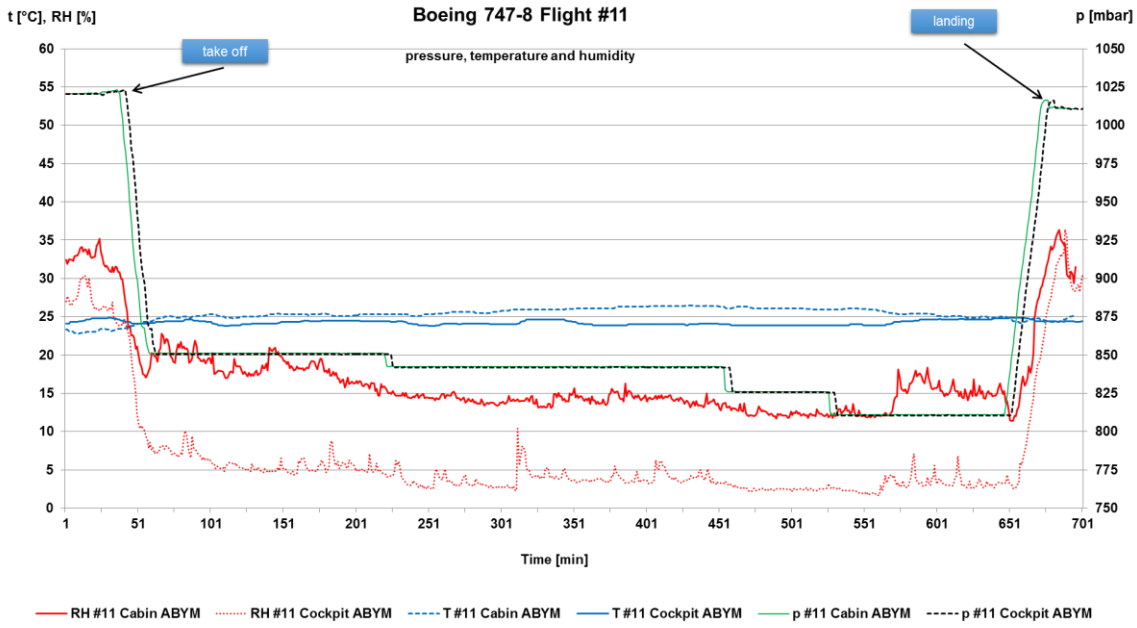


Figure 35 Climate data Boeing B747-8

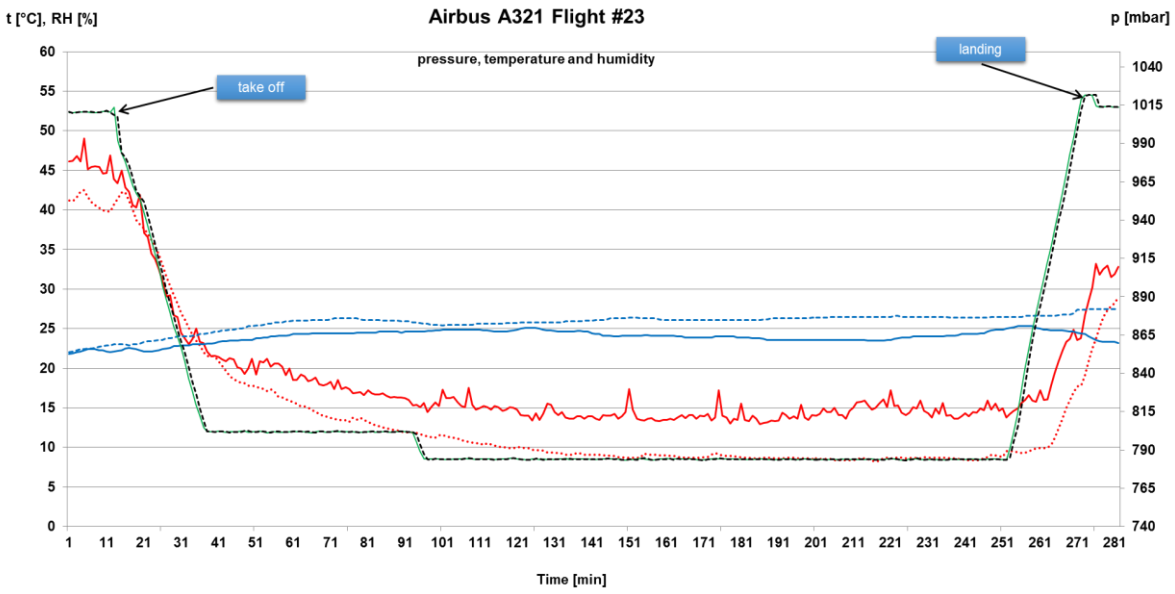


Figure 36 Climate data Airbus A320

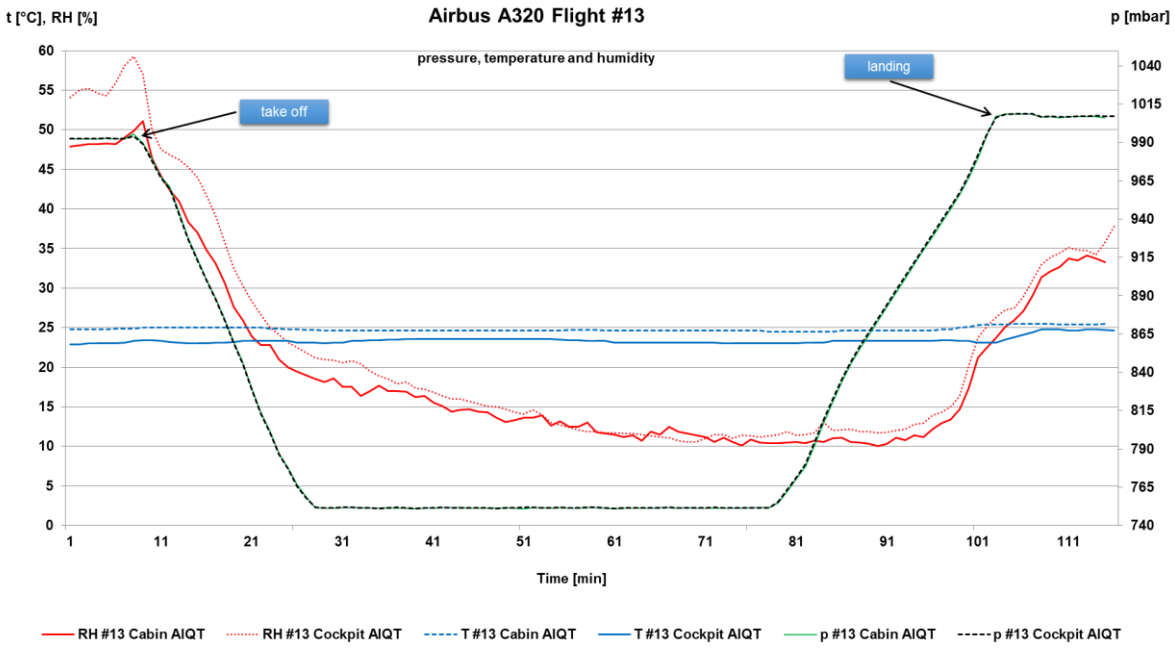


Figure 37 Climate data Airbus A321

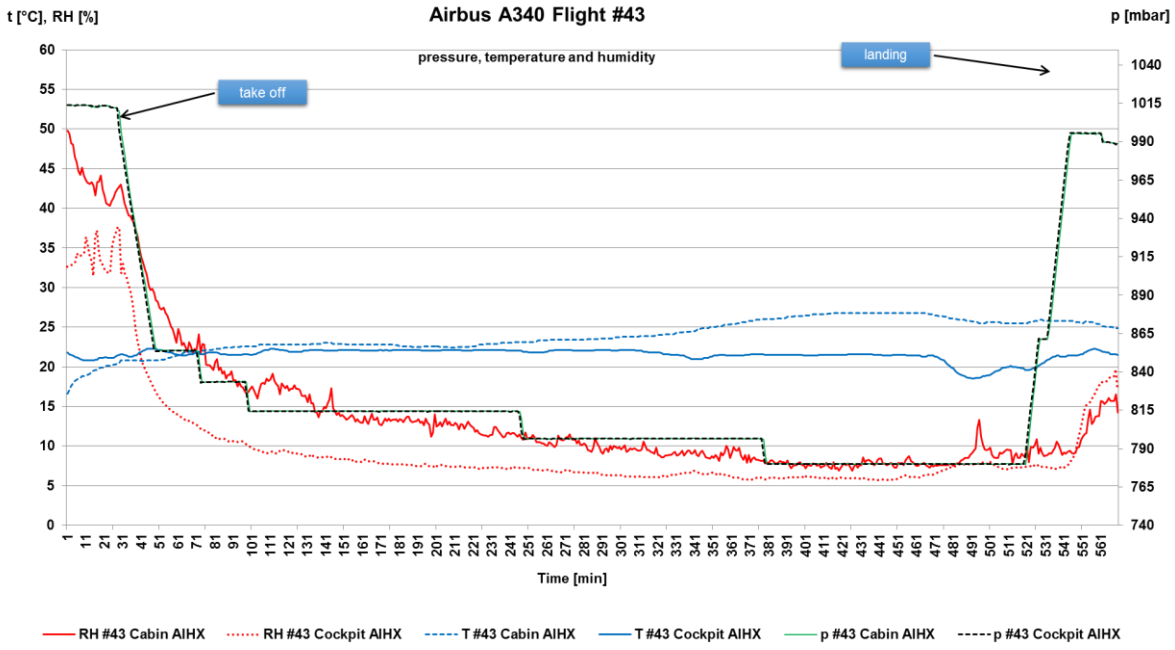


Figure 38 Climate data Airbus A340

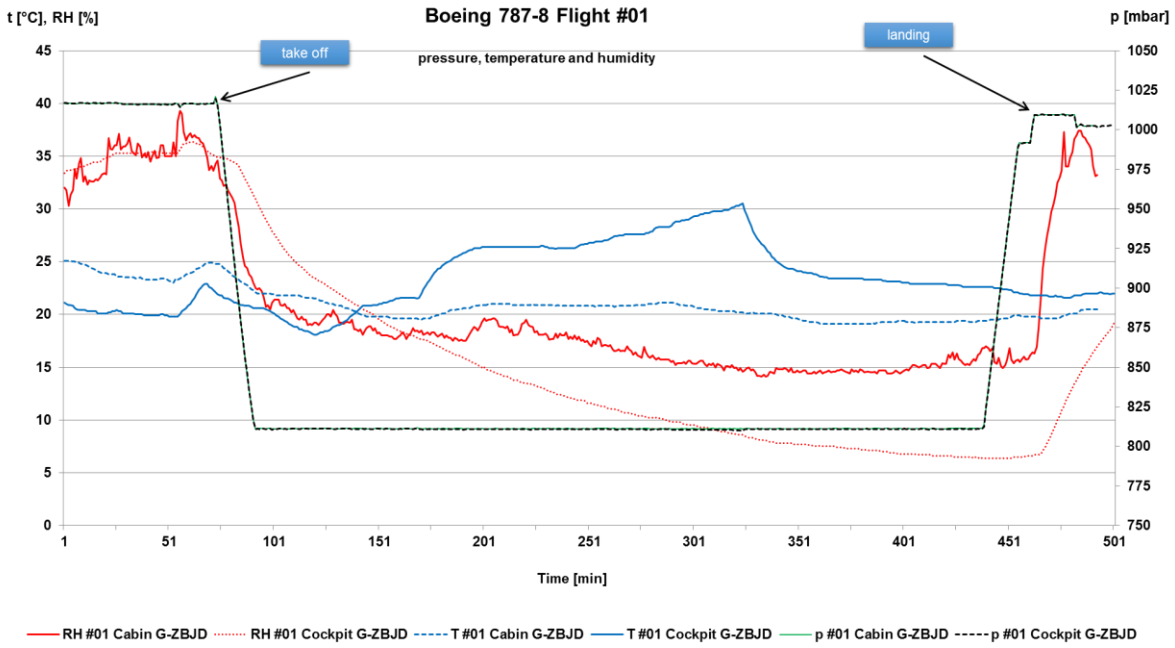


Figure 39 Climate data Boeing B787-8

6.5 Carbon dioxide (CO_2)

Carbon dioxide was detected continuously with NDIR-measurement at the flight deck and the cabin. Descriptive statistical data are presented in Table 22 (main study) and Table 24 (B787 study). In Figure 40 trend lines are given for all short- and long haul flights in the main study (mean values over all flights). Figure 41 shows a similar trend on B787 flights. Randomly emission of dry-ice in the galley was measured on one flight. Highest amounts of CO_2 (> 5000 ppm) were detected in the area of open galley boxes, containing dry-ice packages.

Table 22 CO_2 data from main study (bleed air aircraft)

Short haul aircraft	Mean Flight deck	Mean Cabin	Long haul aircraft	Mean Flight deck	Mean Cabin
	ppm	ppm		ppm	ppm
Mean	835	1417	Mean	753	1282
Min	629	1050	Min	594	955
Max	1918	2771	Max	1976	2674
Median	740	1298	Median	708	1230
95th-percentile	1408	2202	95th-percentile	1029	1712

In general, carbon dioxide serves as a common air quality parameter. According to work place atmosphere, a CO_2 concentration of 5000 ppm is typically considered as OEL, 8-h TWA. In this study, levels above 5000 ppm were observed occasionally during random measurements in aircraft galleys. Dry ice was identified as the potential emission source for increasing carbon dioxide amounts. More attention to this special issue is recommended.

Overall, CO_2 mean levels are medium according to DIN EN 13779 in the flight deck (~800 ppm) and (mostly) moderate in the cabin (~1300 ppm) (Table 23; IDA). However, CO_2 levels in aircraft cabin are predominantly affected by the number of passengers and air exchange rate applied. A detailed discussion of this relationship is given in chapter 7.1.

Table 23 Classification of CO_2 levels for indoor air quality according to DIN EN 13779: 2007–09 (DIN 2007–09); *based on outdoor CO_2 level of 400 ppm absolute

Indoor Air Level (IDA)	Description	CO_2 indoor air level [ppm]*
IDA 1	High Quality	≤ 800
IDA 2	Medium Quality	> 800–1000
IDA 3	Moderate Quality	> 1000–1400
IDA 4	Low Quality	> 1400

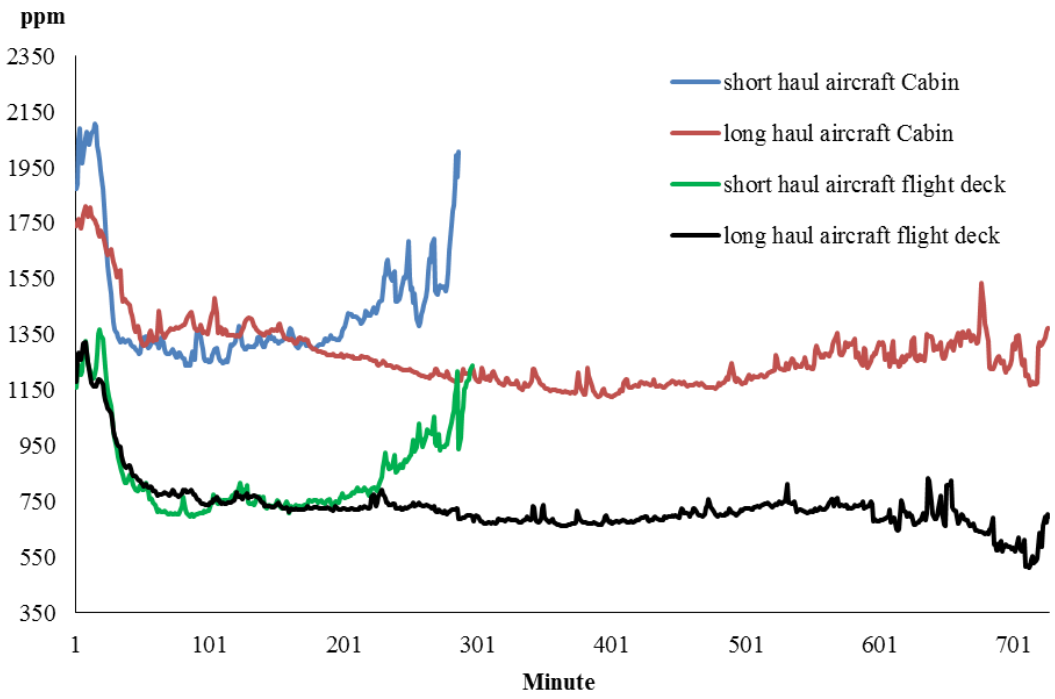


Figure 40 CO_2-graphs of mean concentrations for all flights in main study (bleed air aircraft)

Table 24 CO_2 data from B787 study

Flight deck	Mean ppm	Cabin	Mean ppm
Mean	603	Mean	1242
Min	473	Min	968
Max	1229	Max	2019
Median	561	Median	1213
95th-percentile	828	95th-percentile	1608

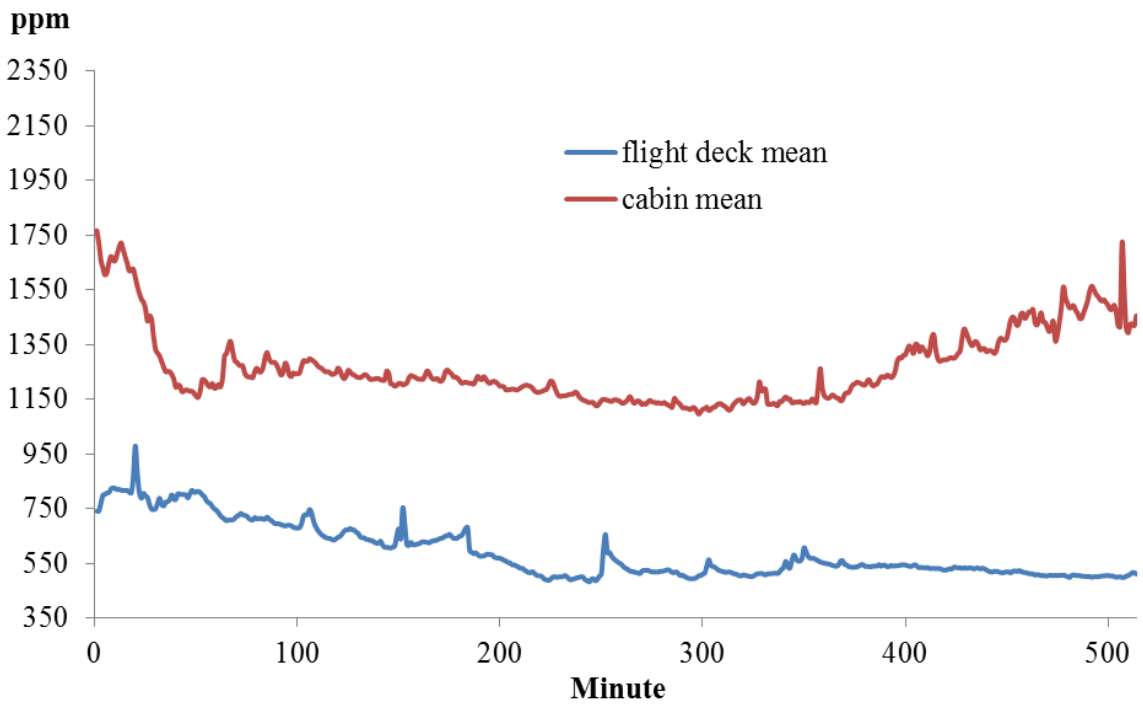


Figure 41 CO_2-graphs of mean concentrations for all flights on B787

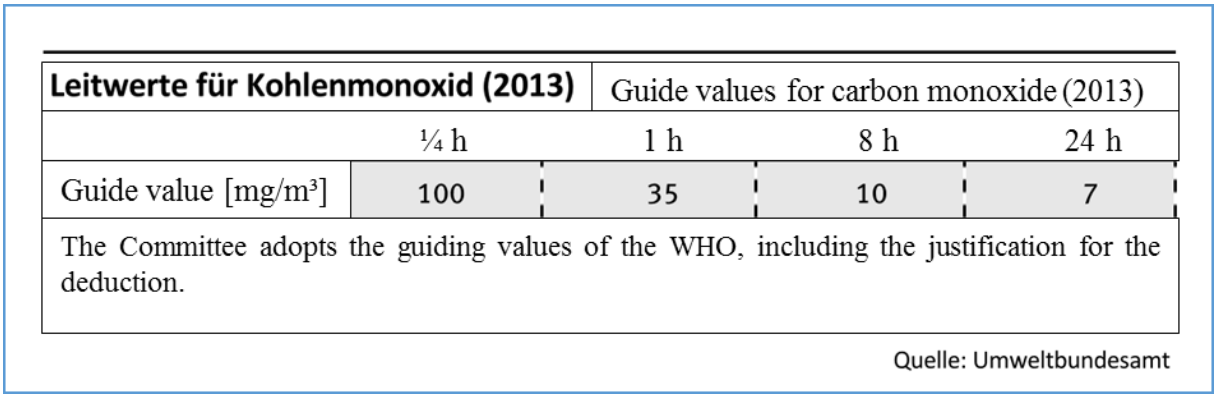
6.6 Carbon monoxide (CO)

Carbon monoxide was recorded online with electrochemical sensor-measurements at the flight deck and the cabin. As summarized in Table 25 and illustrated in Figure 43 CO was mostly not reliably detected due to the limit of detection (LOD) of 0.5 ppm in all flights. Solely for a few minutes, CO values were observed with a maximum of 4.8 ppm (Figure 44).

Table 25 CO measurement results overview of mean values, main study and B787 study (LOD = 0.5 ppm)

	Main study Flight deck ppm	Main study Cabin ppm	B787 study Flight deck ppm	B787 study Cabin ppm
Mean	< LOD	< LOD	< LOD	< LOD
Min	< LOD	< LOD	< LOD	< LOD
Max	4.8	3.0	0.6	1.6
Median	< LOD	< LOD	< LOD	< LOD
95th-percentile	< LOD	0.6	< LOD	1.06

The CO concentration observed in this study mostly amounted < LOD (0.5 ppm). In comparison to OEL (e.g., German AGW = 30 ppm, 8-h TWA) a high safety level was ensured for all measurement flights. Furthermore, both, the short-term and long-term indoor air guideline values for CO (e.g., WHO or German Environment Protection Agency, Figure 42) were not exceeded in any flight sampled.



Leitwerte für Kohlenmonoxid (2013)	Guide values for carbon monoxide (2013)			
	¼ h	1 h	8 h	24 h
Guide value [mg/m³]	100	35	10	7
The Committee adopts the guiding values of the WHO, including the justification for the deduction.				

Quelle: Umweltbundesamt

Figure 42 Guideline for CO, German Environment Protection Agency (consistent with WHO) 2013, 1 mg/m³ = 0.87 ppm (25°C), Source: German Environment Protection Agency (modified), https://www.umweltbundesamt.de/ themen/gesundheit/kommissionen-arbeitsgruppen/ausschuss-fuer-innenraumrichtwerte-vormals-ad-hoc

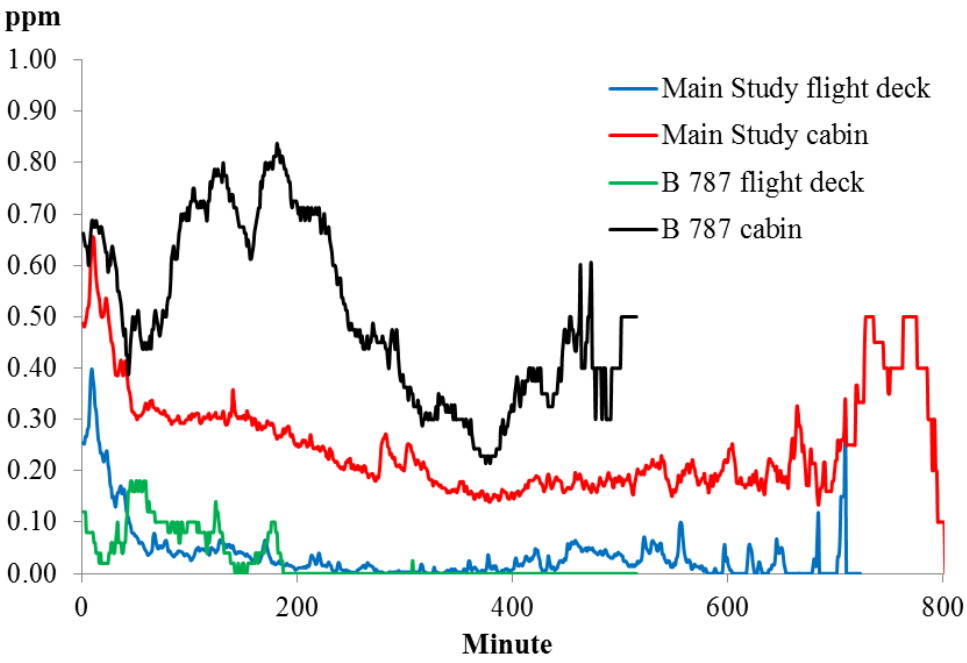


Figure 43 CO-graph as mean concentrations for all flights in main study and B787 study. Note signals below the limit of detection (LOD = 0.5 ppm) are not quantitatively reliable.

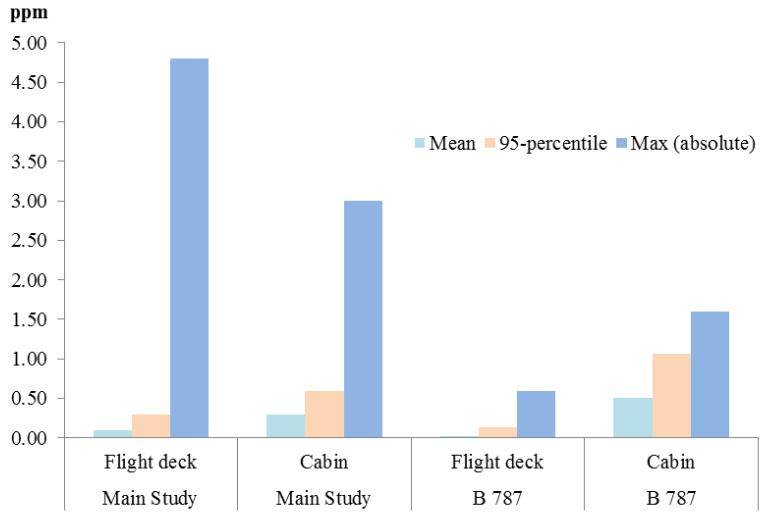


Figure 44 CO statistical data for all flights in main study and B787 study. Note signals below the limit of detection (LOD = 0.5 ppm) are not quantitatively reliable.

6.7 Ozone (O_3)

Ozone was measured with electrochemical sensor. Overall, O_3 was observed in a range from 1 to 294 ppb. The unusual high ozone levels during B787-flight number 08 were rejected as incorrect measurement (see explanation in Table 26). Lower O_3 levels in cabin air as in flight

deck air may be caused by faster decomposition due to more available surface and/or different air flow rates.

Table 26 Ozone measurement overview of mean values, main study and B787 study

	Main study Flight deck Mean ppb	Main study Cabin Mean ppb	B787 study Flight deck Mean ppb	B787 study Cabin Mean ppb	B787 study Cabin Mean ppb
Mean	28	6	14	21	3
Min	7	2	2	1	1
Max	62	18	28	529	11
Median	25	5	15	3	3
95th-percentile	53	14	25	172	7

Grey highlighted: High Ozone levels during taxi-out on flight #08 for 22 minutes are unusual and not consistent with flight deck data. Most likely, this was incorrect measurement. Discard this values leads to expected values in comparison to main study (right column).

Natural ozone, primarily formed above the tropopause, can affect negatively the cabin air quality. Frequency and level of O_3-contamination depends on various factors, e.g. flight-level and flight-route. Several different recommendations are existing in parallel to evaluate O_3-contaminations in various environments.

- EASA: 0.25 ppm (250 ppb) sea level equivalent, at any time above flight level 320
- EASA: 0.1 ppm (100 ppb) sea level equivalent, time-weighted average during any 3-hour interval above flight level 270
- ASHRAE: 0.05 ppm
- OSHA PEL 0.1ppm
- EPA NAAQS 0.12 ppm (1 h) and 0.08 ppm (8 hr)
- ACGIH TWA: 0.05; 0.08; 0.1 ppm (heavy, moderate and light work)
- NIOSH: 0.10 ppm
- WHO: 0.06 ppm for 8 h

In this study, O_3 amounts were observed above 250 ppb in one aircraft (B747-8; flight 49) for three short time periods (in total 15 minutes). Otherwise, the O_3-levels were remarkably low. Normally technical devices are installed in modern aircraft to minimize ozone input (ozone-converter).

6.8 Aerosol sensing system - feasibility and exploratory data

Basic considerations: Leak oil components evapourated in the compressor stage of the jet engine (at 200°C) may possibly form an aerosol by gas to particle conversion upon cooling in the bleed air ducts and air conditioning system either before or in the mixer unit. If the local oil vapour concentrations are high enough the vapours are likely to condense by homogenous nucleation i.e. formation of new particles as opposed to heterogeneous condensation on existing particles. At cruising altitude the aerosol concentration of the jet intake air is very low and the recirculated air passes through HEPA filters before entering the mixer unit. This low concentration also favours nucleation as a pathway of oil aerosol formation. Homogeneous nucleation will result in an oil aerosol size distribution in the ultrafine particle size range smaller than a few hundred nanometres. Detection of concentration peaks of submicron aerosols in the bleed air could therefore be a hint on oil leaks in the engine.

Since the oil leak related smell events (associated with aerosol formation) rare and of short duration their detection requires continuous measurements with high time resolution.

The rationale for incorporation of aerosol measurements in this pre-study was.

- Feasibility testing of an available sensor unit
- Qualitative characterization of aerosol events in the air supply of the cockpit
- Gathering knowledge for the design of a future study on cabin air quality

An example of the raw data of the aerosol sensor during a flight from Punta Cana to Frankfurt is shown in Figure 45. The photometer signals are characterized by a long term pattern and with superimposed distinct concentration peaks. The zero point of the time scale is the start of the aerosol sensor. The decrease in relative humidity indicates the beginning of the flight phase.

The long term variation suggesting a continuous increase in aerosol concentration during the flight is unrealistic. The signal pattern is rather caused by a temperature increase in the sampling box due to the heat production by the sampling pumps. This leads to a drift in the electrical off-set related to influences of temperature on the characteristics of electronic components. This effect is more pronounced in the channel using perpendicularly polarized light compared to the sensor with parallel polarization since the electrical offset of the latter one is considerably lower. This conclusion was drawn from temperature measurements in the sampling box and simulations in a climate chamber carried out during the break of the campaign end of 2015. Measures were subsequently undertaken to reduce the temperature influence on the sensor signal (see example in Figure 45). However, the problem could not be completely remedied.

The short events however can be quantified by subtracting the voltage value of the local base line signal from the peak voltage. On this flight 8 signal peaks with different heights could be identified during the final period of the flight: peaks number 1- 4 at cruising altitude, peak number 5 on the descent and peaks number 6-8 at ground level.

Except for peak number 5, the peak heights for the perpendicular polarization are larger than those for the parallel polarization indicating the presence of submicron aerosols during the peak events. The peaks occuring during the flights last 1-2 minutes, those on the ground up to 5 minutes.

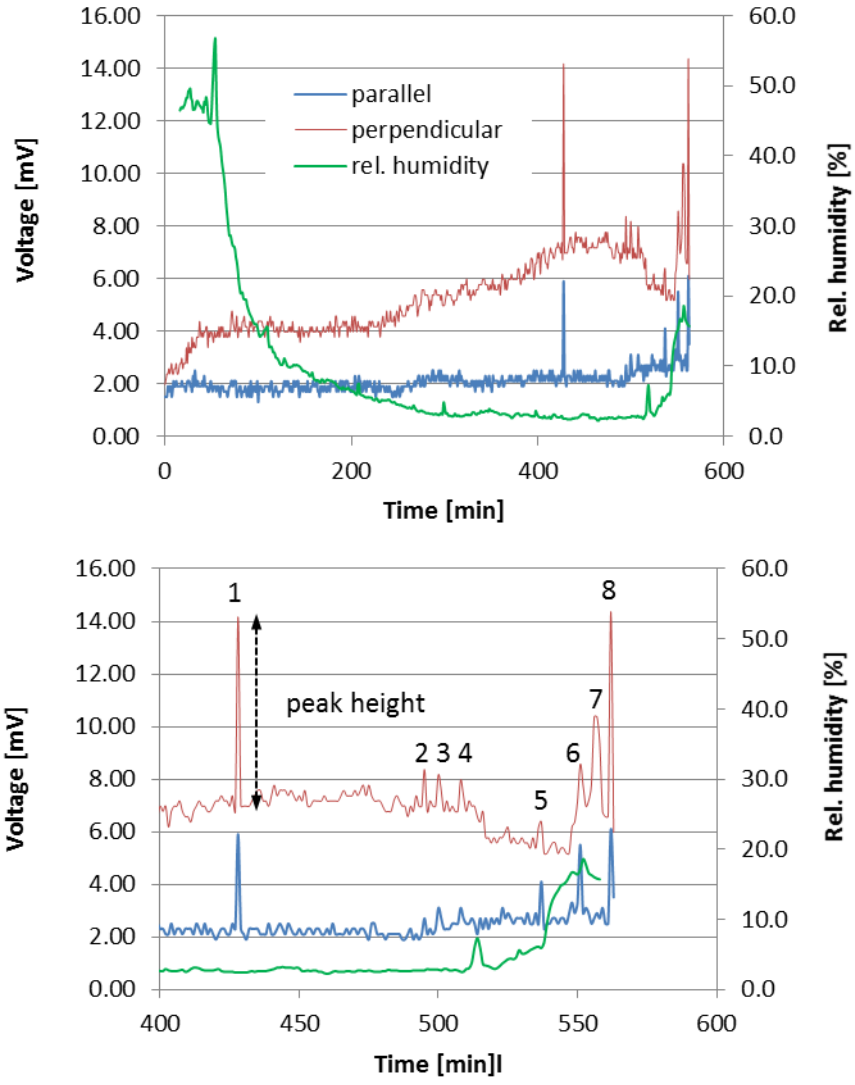


Figure 45 Signal pattern of the two light scattering sensors probing the air entering the cockpit at the ventilation nozzle during a long haul flight (Punta Cana->Frankfurt). Green line: relative humidity as recorded by the Graywolf detector sampling the air in the cockpit (jump seat). The bottom picture zooms into the final two flight hours. Long term trend caused by influence of temperature on electrical offset of the sensors. A voltage signal of 1 mV corresponds to a concentration of 2 µg/m³.

The photometric sensitivity is around 2 µg/m³/mV (perpendicular polarization) corresponding to an increase in concentration of 14 µg/m³ at the first peak (peak height 7 mV). These are

approximate values since the calibration factor depends on particle size and the optical properties of the aerosol which are not exactly known.

An example for a roundtrip aerosol monitoring (Frankfurt->Oslo->Frankfurt) is shown in Figure 46. On this flight, aerosol concentration peaks occur in the middle of the trip: on the descent into Oslo and during stopover on the ground.

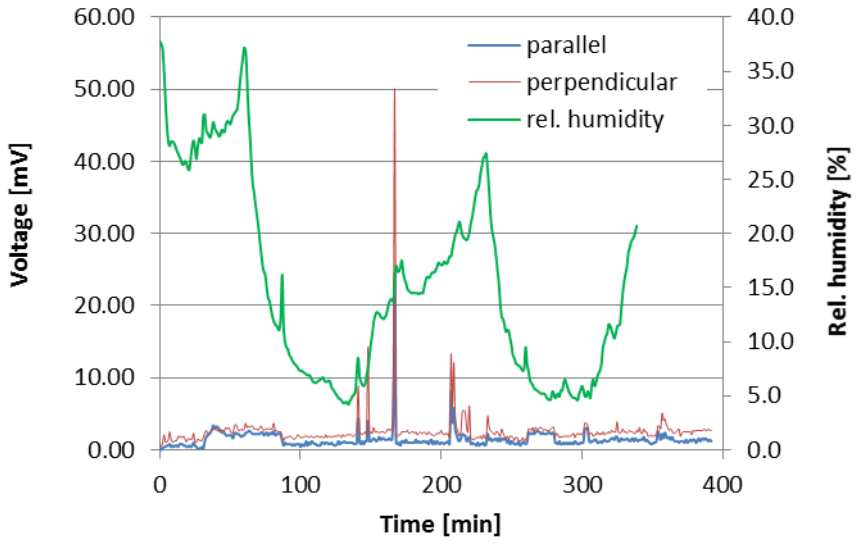


Figure 46 Signal pattern of the two light scattering sensors probing the air entering the cockpit at the ventilation nozzle during a round trip (Frankfurt->Oslo->Frankfurt, A320). Green line: relative humidity as recorded by the Graywolf detector sampling the air in the cockpit (jump seat). A voltage signal of 1 mV corresponds to a concentration of 2 µg/m³.

The aerosol sensor delivered data for all flights carried out. Each individual data set was evaluated with respect to the occurrence of peaks in the signal pattern. Peaks were identified if the voltage increased by more than 1 mV above local baseline signal.

The results of this evaluation are summarized in Figure 47 to Figure 51. The ordering is with respect to the type of the aeroplane. Whereas B767, B748, A340 and B787 performed long haul flights, A321 was used on medium haul destinations. The time scale is the elapsed aerosol sensor time (in hours) and covers one flight direction for the long haul destinations, respectively the time required for return-flights for the medium distances. The peak height of the perpendicular polarization (blue dots) are quantified on the primary axes. The ratio of the peak heights (parallel/perpendicular) are indicated as open triangles and are plotted on the secondary axes.

The number of flights carried out with each aeroplane type are: 14 for B767, 12 for B747, 6 for A340, 6 for B787 (all long haul flights) and 9 for the A320 (return flights).

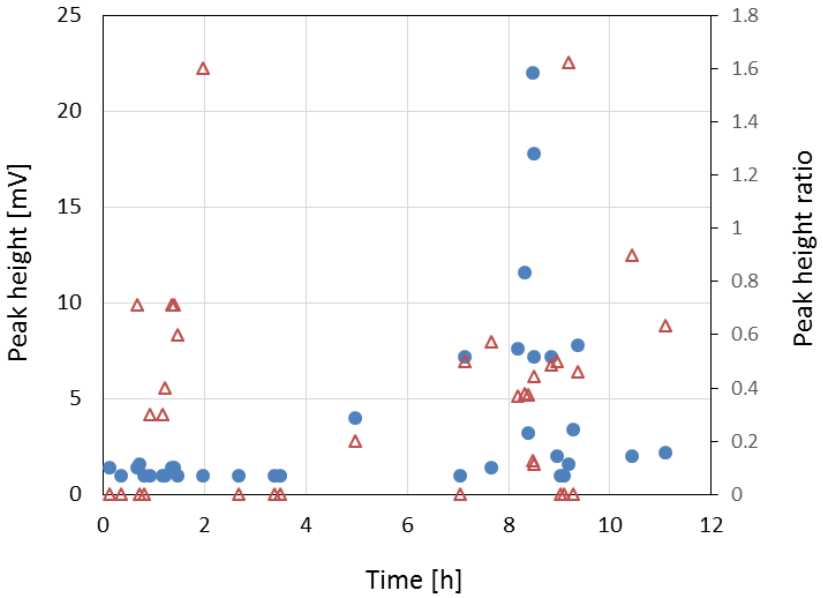


Figure 47 Analysis of the peaks of the aerosol sensor. Type of aeroplane: B767

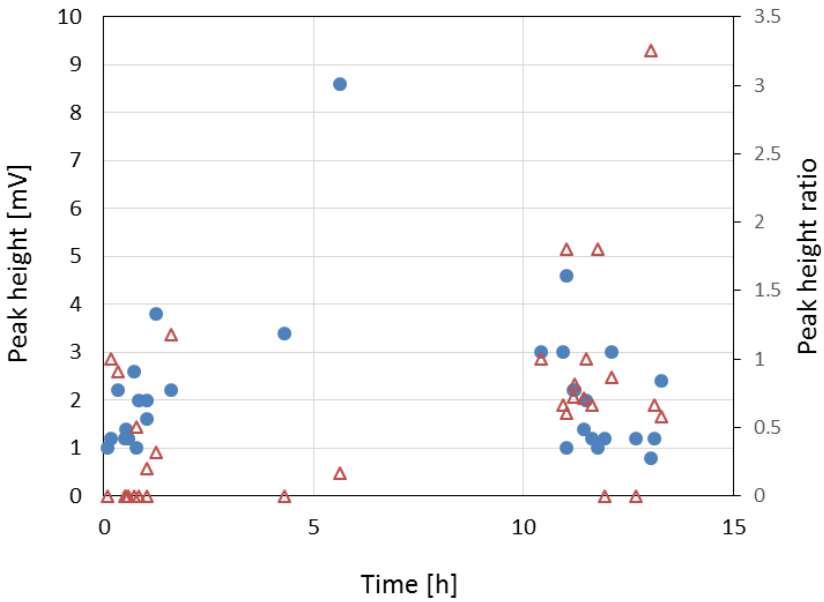


Figure 48 Analysis of the peaks of the aerosol sensor. Type of aeroplane: B747

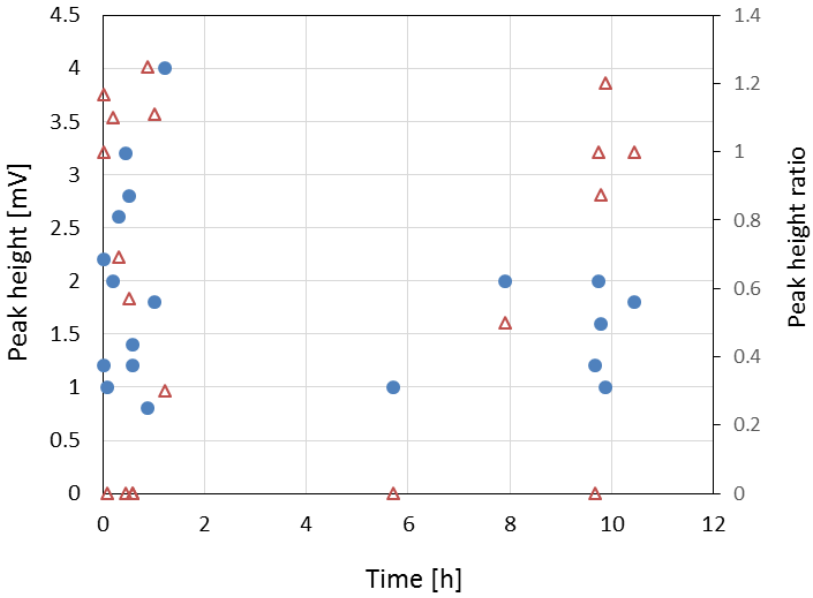


Figure 49 Analysis of the peaks of the aerosol sensor. Type of aeroplane: A340

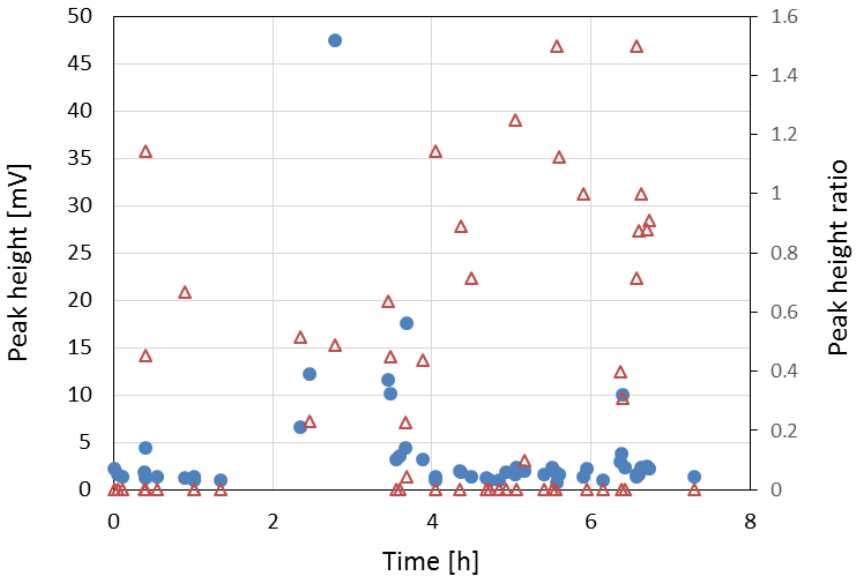


Figure 50 Analysis of the peaks of the aerosol sensor. Type of aeroplane: A320

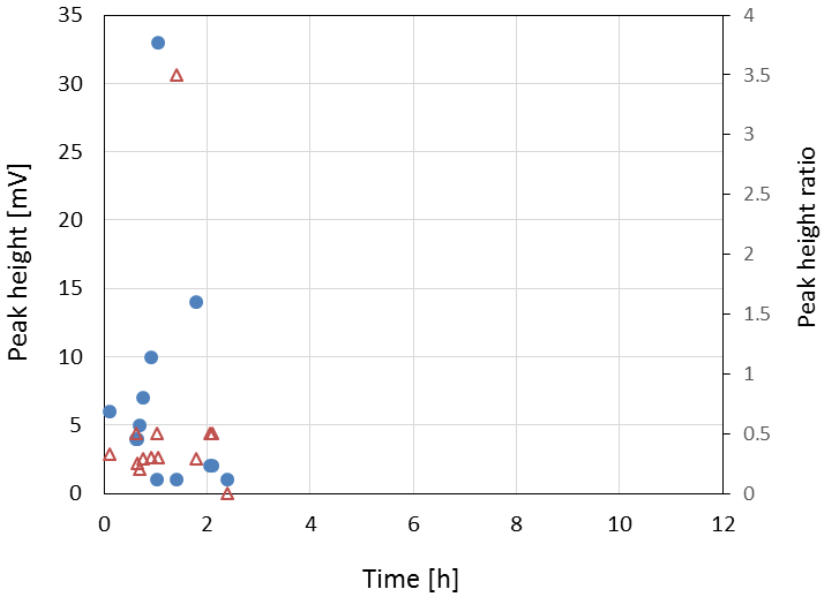


Figure 51 Analysis of the peaks of the aerosol sensor. Type of aeroplane: B787

All B767 flights were Frankfurt to Punta Cana or Malé and return flights. Most of the concentration peaks were measured at elapsed times larger than 8 h (Figure 47). They occurred during the approach to Frankfurt, during taxiing and at the gate position. There are few elevated events during the cruising phase (4 mV at 5 h, and 7 mV at 7 h). All peaks detected during the early phase of data recording were smaller than 2 mV in height. The peak height ratios for the elevated peaks are 0.2 and 0.5, respectively indicating aerosols in the ultrafine size range.

For the B747 most of the peaks were measured at the beginning and at the end of the laps with two peaks of 3.4 and 8.6 mV during the cruising period and peak height ratios of 0 and 0.16, respectively.

For the A340 peaks are again abundant at begin and end of the measurements, with some small peaks again during cruising (Figure 49). The peak height level is generally smaller compared to what is seen in Figure 47 and Figure 48.
Figure 50 shows the peaks identified on the medium distance round trip flights carried out with the A320. The peaks in the time slot between 2 and 4 hours result mainly from a single flight to Oslo (Figure 46). This time period covers mainly the stop over at the airport.

Finally, the B787 shows peaks only during the first two hours. No peaks were detected thereafter (Figure 51).

Discussion: The optical sensor allows for detection of transient aerosol influx into the cockpit via the ventilation duct. Data were collected from various aeroplanes on a limited number of flights. During the flights the detected aerosol events were of short duration (< 2 min) and peak concentrations were maximum of the order of 20 µg/m³ (approximate value) for events during cruising and 100 µg/m³ for aerosol peaks occurring when the plane is at the gate position.

The origin of the aerosol entry into the cockpit air cannot be definitely clarified. At the gate and during taxiing the most likely source is the outside air polluted with exhaust particles stemming from the ground traffic of aeroplanes and vehicles and sucked in either by the APU or the engines providing the air supply of the cockpit.

Events detected during the approach to Frankfurt (peaks number 2-5 in Figure 45, for example) could be associated with the passage of the aeroplane through polluted air masses or through exhaust plumes in the low atmospheric boundary layer.

The same could also be true for the peaks occurring during cruising when the flight path accidentally enters the exhaust plume of a preceding aeroplane. On the other hand, internal aerosol sources cannot be ruled out. A more detailed analysis of the cockpit air supply such as bleed air fraction etc. will be necessary to get further insights. Smell events have not been reported on the flights where the peaks occurred.

7 General discussion on cabin air contamination release and detection

The investigation of the flight phases has been implemented based on the assumption that pollutant input through the bleed air system is caused by changes in engine power, with sudden changes (e.g., during take-off or descent/landing) leading to a measurable increase in oil leakage The seals of the engine shafts running at different speeds are considered as the main source of possible oil spillage. As outside air enters the compressor stages of the engine core, it is compressed along with atomised oil. Some of this compressed air is then extracted through one of two bleed port openings inside the engine.

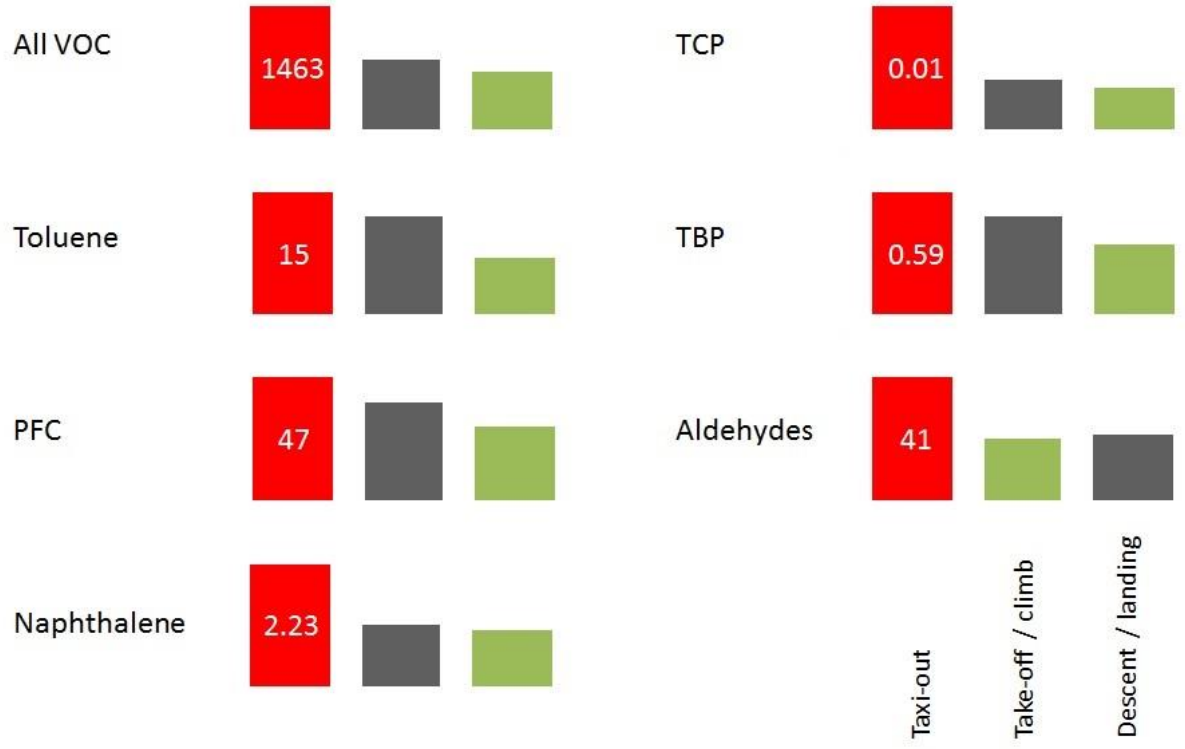


Figure 52 Observed uniform course of the quantitative contaminant data from the Main study (bleed air supply) with respect to the investigated flight phases. The individual concentrations in the pictograms are given in a colour code (high = red, medium = grey, low = green). For the take-off values the concentrations in µg/m^3 are additionally given (median values in white numbers) for comparability reasons. Note that the outcome is totally consistent although different methodologies were used for VOC, OPC and aldehyde detection. The compound selection focuses, with exception of TCP (normally detected in concentrations far below 0.01 µg/m^3), on contaminants representative for the aircraft cabins. However, almost all detected cabin VOC follow this concentration course. An opposing trend was found for discontinuous release only. The white number given in the bar for all VOC represent the sum of all VOC (µg/m^3) measured during the taxi-out flight phase. These values are also given for all other presented contaminants. In case of toluene (commonly known indoor contaminant), perfluorinated compounds (PFC; air condition), naphthalene (mothballs), TBP (aircraft hydraulic oil) and short-chain aldehydes (interior, adhesive, etc.) an origin from engines are not considered to be very likely. Solely TCP is supposed to be related to undesired engine oil entry and serves, therefore, as a marker for bleed air contaminations.

The engine bleed port used for air extraction (high or low pressure port) is dependent on the engine thrust setting. The bleed air system is a fully automated system, serving energy conservation. Modern aircraft provide about 8.5 to 17 m^3 conditioned air per hour for each passenger, which can only be achieved with considerable engine power. However, numerous CAC-events have been reported at precisely these times of change in engine thrust setting. Characteristic substances for oil leakage should therefore be detectable depending on the flight phase.

This assumption has not been fully confirmed yet. All data show a uniform course regarding the concentration levels of cabin air contaminants instead: starting with a high amount of contaminants during taxi-out, followed by a decline during take-off/climb and even lower contaminant concentration levels during descent/landing (Figure 52). Most of the VOC, OPC, aldehydes and TVOC concentration data showed this uniform course within the investigated flight phases. Overall, similar VOC contribution and quantities were observed in both studies (main study and B787 study). Slightly higher amounts of VOC were, however, measured in the main study. This observation might be explained by the use of an activated charcoal filter in the recirculation system of B787 aircraft, which retains preferably some of the higher boiling VOCs. But how can the generally observed decrease in contaminant concentration over the flight phases be explained? A simple model consideration is proposed below to characterise this assumed "contaminant thinning effect".

"Contaminant thinning effect forced by the high air exchange rate in aircraft"

The total air exchange rate in aircraft is usually greater than 25 per hour, in which some of the cabin air is being recycled on several types of aircraft. However, the high air exchange rate has a significant impact on all measurable volatile compounds in the cabin air. If this forced "thinning effect" is taken into account, many conclusions can be drawn from cabin air measurements. Taking into consideration the simplest spatial situation for a given ventilated indoor situation: a box-shaped space (box model) without any sinks and interfering objects (furnishing). In the box there ought to be various emission sources (S_i) with a defined source strength as well as a given air exchange rate (Figure 53).

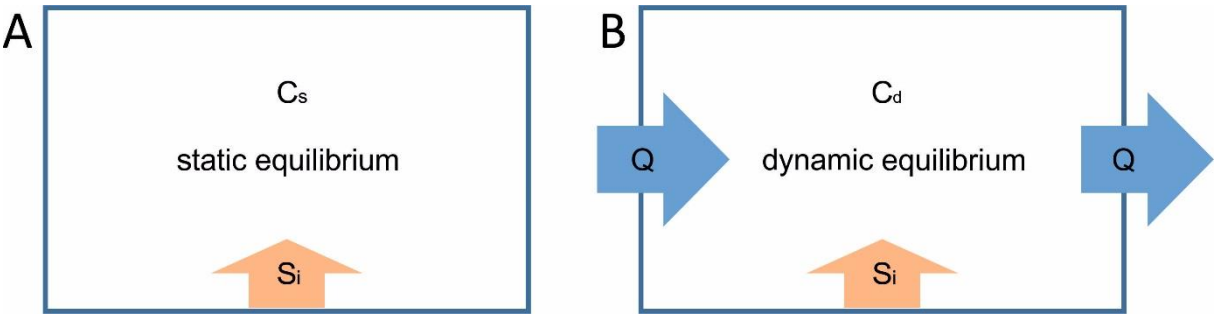


Figure 53 Equilibrium conditions for measurable VOC concentrations illustrated by a box model for the non-ventilated state (A) and ventilated state (B). The arrow labelled S_i quantifies the source strength [mass/time] of various internal (i) volatile compounds while the arrows labelled Q indicate the mass flow [mass/time] related to the defined air exchange. Note, static equilibrium (C_s) is never achieved for real indoor situations, since air supply is vital for the occupants. However, for situations with very low air exchange unusual high VOC concentrations can be observed for given S_i. State B is therefore the rule, with exceptional high air exchange rates (>20 h^{-1}) being maintained in the aircraft. The high air exchange has important consequences on the measurable VOC concentrations (C_d) in the aircraft cabin (further explanations in the text).

The air exchange is given by the mass flow (Q). Figure 53B describes very roughly the situation in aircraft, which likewise represents a ventilated defined volume. At nearly constant conditions, an equilibrium concentration is soon established for each volatile substance with a constant source strength. For the considerations introduced here the outside air is initially regarded as free of pollutants (pure). In the box model, most of the VOC dilutes within a few minutes below detectable limits due to the applied high air exchange rates. This is obviously not the case for most of the monitored VOC during flight operation, since:

a) the outside air is not free of volatile pollutants at the airport.
b) the thinning of VOC is delayed or hindered by sinks within the cabin (delayed "thinning effect").

The latter is mainly caused by the complex geometry of the furnishing such as seats, galley or wash rooms and the type of airflow control in aircraft. Furthermore these interiors and the passengers themselves are potential sources for VOC. For the ideal case of a constant emission and air exchange, the physical parameters in the cabin can now easily be determined. With mass (m) replaced by concentration (C) times volume (V) the concentration can be used for calculation. The rate of change of the VOC concentrations (C_{VOC}) inside the box model or any similar volume is given by the balance between the strengths of the source and the sinks:

$$\frac{d}{dt}C_{VOC} = \frac{S_{i+e}}{V} - \Lambda * C_{VOC} \qquad \text{Eq. 1}$$

The strength of the source (S) is the sum of internal and external sources (i+e), even if differentiation between the two is hardly possible in reality. The air exchange rate (Λ) is specified in the number of air changes per hour. Furthermore, the VOC sources in indoor spaces are frequently unknown, low concentrated or discontinuous in their emission behaviour, which

makes VOC an unsuitable parameter in a simple model for explanation. However, this is not the case for the higher concentrated carbon dioxide (CO_2) as this gas is continuously exhaled by all passengers and crew members at similar rates. The sum of all passengers and crew members can be defined as one permanent source (S) with a known (easy to estimate) emission rate. Based on the CO_2 example, the plausibility of the above box model for aircraft cabins can be well demonstrated (Figure 53).

7.1 Observations and considerations on permanent contaminant release

As already stated above the high air exchange rate in aircraft serves the wellbeing of the passengers and crew members (Section 1). The high air exchange rate guarantees the removal or sufficient dilution of harmful gases and vapours in the aircraft cabin. This safety consideration is also valid for CO_2 and CO which should not exceed 5,000 ppm and 50 ppm respectively.

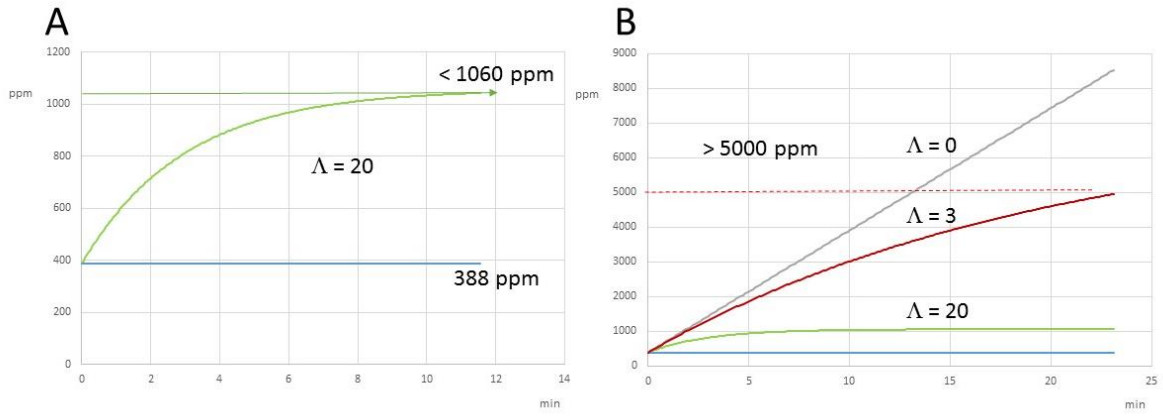


Figure 54 Calculated carbon dioxide (CO_2) concentrations (Equation 1) in a fully occupied aircraft with consideration of typical flight parameters. The green curves give the concentration course of CO_2 for a hypothetical aircraft with 470 m^3 ventilated cabin volume (well mixed box) and an air exchange rate of 20 h^{-1}. The hypothetical aircraft is occupied by 345 passengers who start breathing at t_0. Each passenger releases 0.44 g CO_2 per minute and the ambient air contains 388 ppm CO_2. These conditions are very similar to an A340-6 aircraft. (A) In less than 10 min a dynamic equilibrium is established which is close to 1060 ppm, a commonly accepted value for appropriate air quality in indoor environments. Without passengers the CO_2 concentration would remain at 388 ppm (blue curves) according to the box model, since the outdoor air is, as the cabin air, "contaminated" with CO_2. This example shows that the simple box model can provide good predictions regarding the concentration profile of contaminants which are continuously fed into cabin air by external sources such as bleed air oil leakage (Further explanations in the text). (B) Again, the importance of the high air exchange rate (Λ) in aircraft is pointed out here. Without air exchange, toxic CO_2 concentrations (~ 8000 ppm) would be reached within 25 minutes (grey curve). The use of typical indoor air exchange rates (Λ ~ 3) would also lead to undesired CO_2 concentrations above 5000 ppm within 25 minutes (red curve).

For cabin concentration calculations the same principle applies to carbon dioxide as postulated for VOC (Equation 1 Carbon dioxide is always present in the ambient air at a concentration of approx. 388 ppm. Each passenger generates on average about 0.44 g CO_2 per minute according

to considerations for the in-flight situation by Spengler et al. [27]. With these basic data, the theoretical CO_2 concentration in any aircraft can be calculated using the introduced box model (Figure 54). For the example of CO_2, the concentrations or mass flows were in a reliably measurable range, with average values above 1000 ppm in both measurement campaigns (69 flights). These results confirm the outcome of the box model, which predicts an equilibrium CO_2 concentration of approx. 1060 ppm within 10 min at an air exchange rate of 20 h^{-1}.

After the box model has been proven to provide results which are in agreement with the observed CO_2 content in aircraft, its transferability to other volatile contaminants should be discussed. The emission of pollutants from aircraft furnishing is somewhat more complex and cannot be described by the above introduced box model. In fact, a longer or delayed release may occur, since cabin furnishing itself can interfere with the volatiles in a complex manner (e.g., pollutant sink/source). The emission of pollutants are considered to be delayed by several dynamic adsorption and desorption processes and by the targeted airflow management in aircraft. For such hindered VOC releases box in box models (Figure 57A) are available, which, however, are not considered being beneficial for describing the quantitative course of bleed air contaminations. Normally any contamination ought to be quickly diluted close to zero by the applied high air exchange rates in aircraft. The black curve in Figure 55 depicts the measured course of the CO_2 concentration in aircraft which reaches typical cabin air levels of 1380 ppm within approx. 30 min after closing of the cabin doors. In fact, the course is significantly delayed (arrow) compared to the calculated CO_2 concentration curve (green). Such an extent of delayed CO_2 thinning cannot be caused by geometric influences of the cabin furnishings alone since the occupants of the aircraft exhaled directly into the cabin air. It is assumed that significant changes in the air exchange rate could be the cause for the observed discrepancy between the model approach and the measurements. Apparently the envisaged air exchange rates are not reached after engines start and during taxi operation. This can cause the CO_2 content to even rise after the cabin doors are closed as indicated in Figure 55. As soon as the engines run at sufficiently high thrust (take-off and cruise), the desired air exchange rate for the cabin can be achieved at full extent. A very similar observation was made in the study by Spengler et al. [27]. The assumption of an engine-performance-dependent air exchange rate was finally confirmed by the observed increase in CO_2 after leaving the cruise altitude for the landing (Figure 55). Again, a reduced air exchange (engine idle) could be the probable cause of the CO_2 increase.

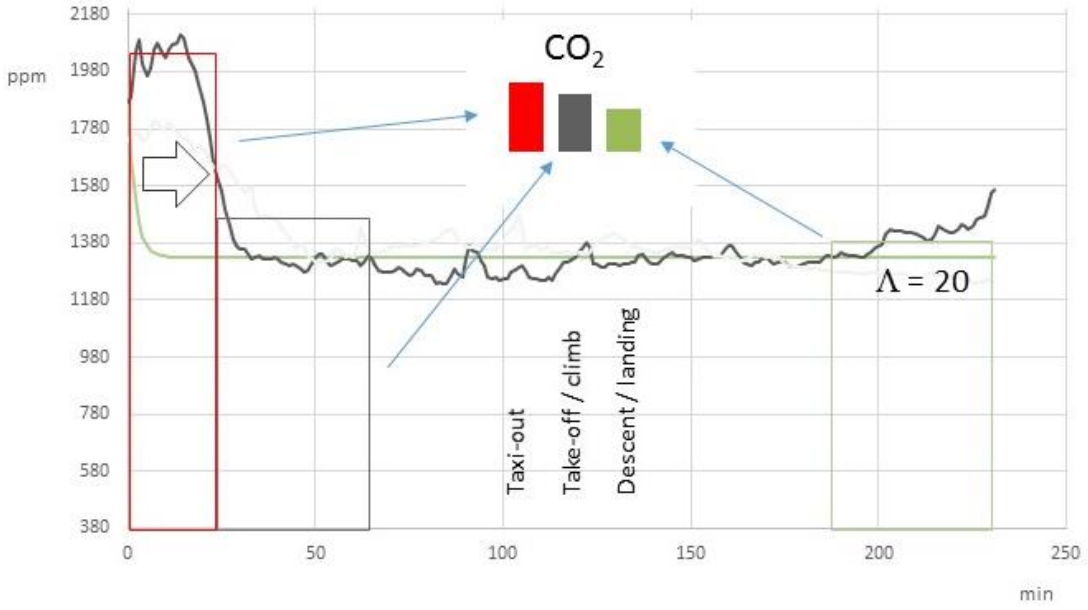


Figure 55 Illustration of measured CO_2 concentration curves (cabin) and the therefrom derived air exchange rate dependent "thinning effect". The black curve represent the average CO_2 concentration measured during short distance flights of the main study, whereas the green curve gives the calculated CO_2 concentrations if a constant air exchange rate of 20 per hour is assumed. The observed delay in CO_2 thinning (big arrow) may result from a possibly reduced air exchange rate during taxi operations. If the average measurement time of the flight phases (coloured boxes) is taken for a theoretical discontinuous CO_2 measurement (similar to the VOC/OPC measurements), the typical pictogram for the postulated dilution effect is obtained also for CO_2.

If the CO_2 contents of the investigated flight phases are summed up, a similar concentration curve as shown above for VOC in Figure 52 can be obtained as pictogram. This is not surprising since this air exchange rate dependent principle applies to all constant emission sources in aircraft cabins. This fact can be substantiated by considering an ubiquitous representative for indoor air contamination: toluene. For toluene, a nearly constant source strength can be assumed in the aircraft cabin, whereas an engine-dependent contamination is very unlikely. Therefore, for toluene the expected dilution effect can be represented by the known pictogram (Figure 56A). Fortunately, toluene has been already studied in much finer divided flight phases [1]. Using these data, the postulated air exchange rate dependent "thinning effect" can be confirmed. For this consideration, only the corresponding flight phases have to be combined and transferred into the pictogram as shown in Figure 56B. The result is in good agreement with our study. This indicates that the ventilation conditions in the examined aircraft in both studies must also have been highly comparable. This, however, has consequences for the interpretation of all flight-dependent quantitative cabin air contamination data.

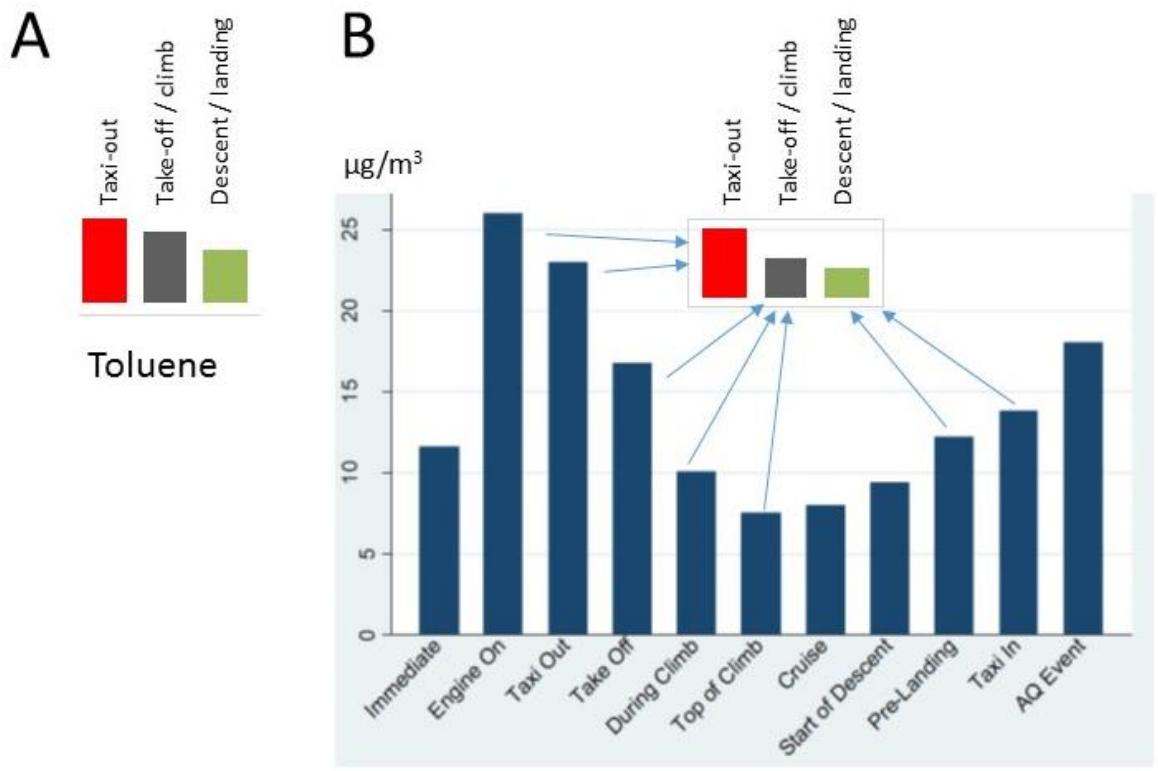


Figure 56 Observed concentration course of quantitative toluene data from the main study (A) and the Cranfield study (B) [1] with respect to the investigated flight phases. For the more extensive sampled (regarding the tested flight phases) Cranfield study (B) the generation of the pictogram is illustrated (blue arrows). The individual concentrations in the pictograms which represent the sum values from the bar chart are given in a colour code (high = red, medium = grey, low = green).

The concentration shown in the column diagram (Figure 56B) does not reflect a varying source strength in the toluene emission. Solely the reduced air exchange rate occurring most likely during landing and taxi operation is documented by the pictogram. A further indication for this assumption is given by the likewise performed immediate measurement without main engines running. At this time, the auxiliary power unit (APU) ensures the necessary air exchange in the aircraft. The APU in aircraft usually have a similar capacity regarding air supply as the bleed air during flight operation. Therefore, similar equilibrium concentrations for toluene are expected and achieved for these flight phases (Figure 56B). It therefore makes also little sense to use toluene as a quantitative indicator for cabin air quality (CAQ) events.

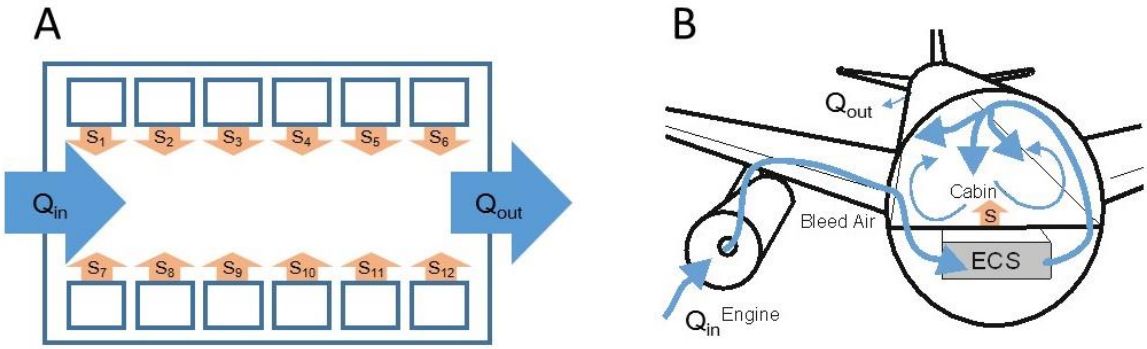


Figure 57 The differentiation between external (e.g., engine oil leakage, contaminated airport air, etc.) and internal (e.g., interior, passengers, food, etc.) emission sources is hardly possible by indoor (cabin) measurements alone. (A) The often observed contaminant persistence may be explained by internal sinks or little aerated niches, which can be calculated with box in box models (not used here). (B) A delayed contaminant decrease (delayed equilibration) should not be observed for contaminants introduced by the air supply (Q_{in} = bleed air). Here, all contaminant concentrations must follow directly the concentration given by the constant source strengths (e.g., S_e = external leaking rate of the engine and/or the ECS).

How can bleed air contaminations be distinguished from other contaminants? In principle, the nature (external or internal) and extent of the pollutant sources cannot be precisely determined by indoor measurements. In aircraft, however, the situation is unique in comparison to other indoor environments. High air exchange rates and the introduction of mostly high-purity stratosphere air create an exceptional situation, which has a characteristic effect on the measurable concentrations of pollutants. Just as the constant carbon dioxide content of the atmosphere (approx. 380 ppm CO_2 = constant external source S_e) does not lead to a change in concentration in the cabin (if humans or other CO_2 sources are assumed not to be present; Figure 54A), every other constant pollutant input through the bleed air must result in a constant contaminant concentration in cabin air as well. Therefore, the detection of bleed air impurities is generally favoured since the cabin air is normally flushed 20 to 25 times per hour with the possibly polluted bleed air. Although this does not lead to a continuous increase in cabin air impurities for the reasons indicated, other non-bleed air pollutant sources (cabin) should clearly be discriminated against. In other words: a steady bleed air contamination should generate a constant measurable value, while for specific initial concentration of cabin air contaminants the "thinning effect" will establish a decrease in concentration until an equilibrium concentration is reached. This is exactly the case with almost all air contaminants detected for the different flight-phases: high contaminant concentrations during taxi-out, lower contaminant concentrations during take-off/climb and even lower contaminant concentrations during descent/landing. A continuous oil entry into the bleed air should therefore lead to an almost

constant TCP[1] concentration in the cabin air, whereas discontinuous oil entry should reveal a significant deviation from the observed "thinning effect". Moreover, with the help of the box model, the minimum detectable engine oil leak rate can be calculated. With given constant air exchange and constant oil leak rate the resulting cabin air concentration of TCP (or any other contaminant) is independent on cabin size or aircraft type (Figure 59A).

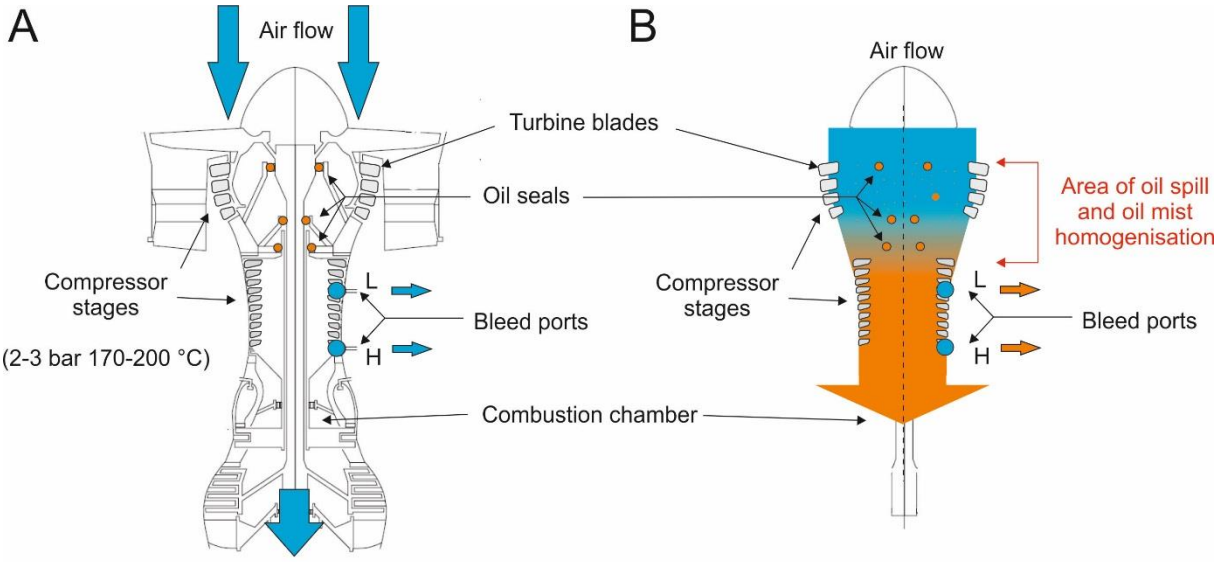


Figure 58 Illustration of the air flow in the engine core of typical modern commercial jet engines. Note, only about onetenth to one-fifth of the air drawn into the engine enters the core and is therefore relevant for possible bleed air contaminations. (A) Oil seals which are considered relevant for contamination are shown with orange dots and typical bleed port openings in the different compressor stages of the engine core are shown with blue dots. The bleed air system switches automatically between the low (L) and high (H) stage port openings taking different engine power conditions (e.g., take-off, cruise and landing) into account. (B) Possible oil losses from the turbine shaft will be atomized by the high rotation of the turbine blades. Thus, at the height of port openings a homogeneous distribution of the oil mist can be expected (orange air flow). However, only a fraction from this homogenized air is supplied to the bleed air, while the majority of the contaminated air must pass through the combustion chamber to the environment. Furthermore, due to orthogonal deflection at the port openings, aerosols should follow the main air stream in direction of the combustion chamber, resulting in a further reduction of possible cabin air contaminants.

Under the assumption that the oil entry into the cabin suffers no losses on its way through the ECS (including the bleed air system) less than 1 mg oil leaking per minute can be detected with the applied TCP detection methodology (LOD = approx. 2 ng TCP/m^3; Section 4.2.3). A low LOD for OPC detection is generally considered a substantial prerequisite for tracking oil leaks in engine seals. However, the actual leakage rate must certainly be significantly higher, since only a fraction of the oil is believed to enter the cabin. This loss can simply be explained by the given geometry and the physical conditions at the bleed ports in the engine core of modern commercial jet engines.

[1] With a content of about 3%, TCP is considered to be well suited as marker compound for engine oil leakage. However, a high-sensitivity TCP analysis is a prerequisite for this approach.

Main air mass flow direction, homogenization in the compressor states and orthogonal deflection at the bleed ports should lead to a significant reduction in the amount of engine oil that can enter into the bleed air system (Figure 58). There is uncertainty about the actual amount of oil migrating into the bleed air, however it is likely that more than 95% of the mass flow (Q) will leave the engine through the combustion chamber. There is a real need for research as this oil drain can have a dramatic impact on the cabin air quality. The situation is made even more complicated by the complexity of the ECS. Pre-coolers, ozone catalytic converters and the air conditioning packs are further sinks (e.g., condensation, surface absorption, hydrolysis or pyrolysis of OPC, etc.) for the turbine oil compounds and pyrolysis products [39, 40]. These are all important aspects that could and should be addressed in a follow-up project. Most important remains the fact that only a small percentage of the engine oil may actually enter the cabin.

Table 27 Estimated cabin air concentrations of TCP and ToCP for several theoretical engine oil leaking rates (source strengths). Calculated values below the LOD of 2 ng/m^3 are highlighted in red. The oil partition in percent hypothetically entering the cabin is shown in the first column. The 5% calculation is assumed to be the most accurate (see text). At a leak rate of 0.1 g oil per min, both TCP (content 3%) and ToCP (0.003%) can be detected by the method used. The calculation is based on the aircraft model introduced in Figure 54. According to this model approx. 157 m^3 bleed air enters the cabin per minute. The mean value of TCP in this study was 9 ng/m^3 for bleed air aircraft and 20 ng/m^3 for the B787 aircraft (no bleed air system). ToCP were not detected in any investigated aircraft type.

see Figure 58B calculated theoretical cabin entry	Cabin air concentration	Engine oil leakage rate [g/min]				
		10	1	0.1	0.001	0.0001
100%	TCP [ng/m^3]	1914894	191489	19149	191.5	19.15
	ToCP [ng/m^3]	1915	191	19	0.2	0.02
50%	TCP [ng/m^3]	957447	95745	9574	95.7	9.57
	ToCP [ng/m^3]	957	96	10	0.1	0.01
5%	TCP [ng/m^3]	95745	9574	957	9.6	0.96
	ToCP [ng/m^3]	96	10	1	0.0	0.00

With these facts, the source strengths of oil leaks (given in gram oil per min) in engines can be estimated in a more realistic manner. The detected mean value (LOD for TCP approx. 2 ng/m^3) of 9 ng TCP/m^3 (0.0006 ppb) during the main study suggest very small leaking rates below 0.001 g oil/min (Table 27). These quantitative considerations also apply to all conceivable oil pyrolysis products which can only be present at even lower concentrations. Therefore, the use of low level oil decomposition products such as pentanoic acid, heptanoic acid, degraded OPC, etc. as alternative indicators for bleed air contamination must be put into question. Moreover, a health hazard from such low contaminant concentrations does not appear plausible.

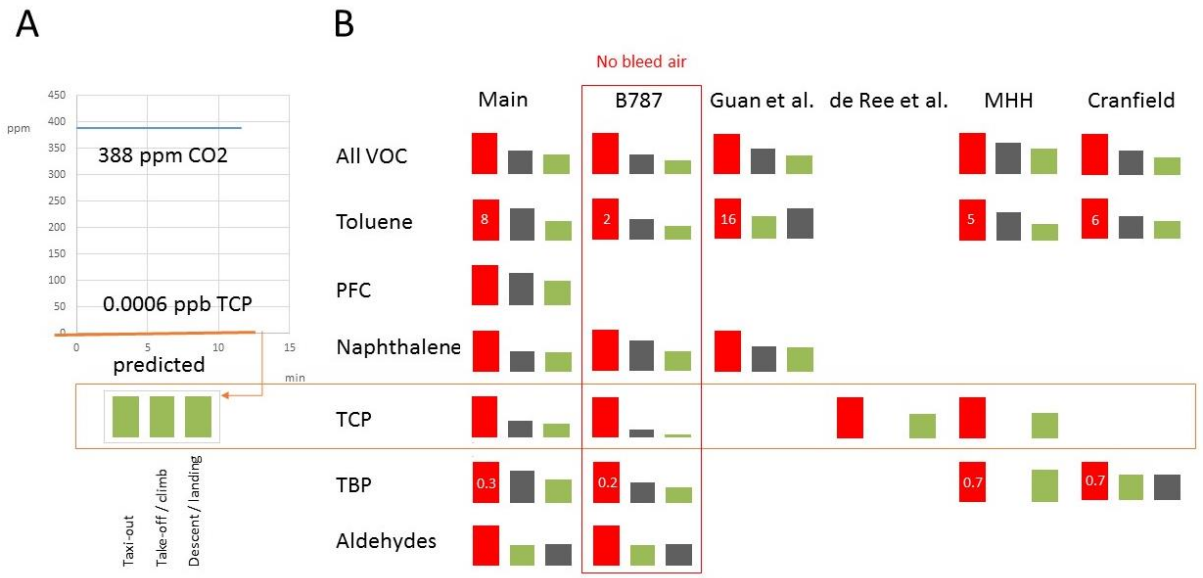


Figure 59 (A) The graph shows the predicted TCP-concentration course in case of continuous bleed air contamination caused by constant leaking of engine oil seals. The constant concentration hypothesis is introduced in more detail with help of the given atmospheric carbon dioxide content (388 ppm) in the text. The bars in the pictogram below the graph and in all other pictograms represent relative predicted or measured flight phase VOC concentration. The investigated flight phases are from left to right: taxi-out; take-off/climb and descent/landing. (B) Available measured aircraft VOC data (as sum values) in main study and B787 study = current study; Guan et al. = [2]; de Ree et al. [41]; MHH = Lufthansa Study [42]; Cranfield = Cranfield Study [1]. Here, measured sum values of all VOC = sum of all VOC measured during the corresponding flight phase; toluene = most common cabin VOC measured in higher concentrations in all campaigns; PFC = perfluorinated compounds as confirmed cabin VOC from air condition leakages; naphthalene = additional confirmed cabin VOC often used in mothballs; TCP = as possible external contamination from bleed air (the data shown is the TCP sum with two abnormal A340-6 flights excluded, explanation is given at the end of chapter); TBP = as widely detected cabin VOC used in aircraft hydraulic systems; aldehydes = as another additional VOC example measured with a different detection method. Note the bars in the pictograms allow no quantitative comparison. Only the relative distribution during the individual flight phases are depicted. Furthermore, the measured toluene concentrations (white numbers) are given in µg/m^3, whereas TCP concentration are given in ng/m^3. A more detailed explanation is given in the text.

The assumption of an observable low leak rate cannot be confirmed by the data of this and other studies. Hence the low concentrations of cabin air contamination caused by oil leaks in engines should, therefore, not be cause for major concerns. According to the findings introduced above the TCP concentrations in the cabin, if introduced as continuous bleed air contamination, ought to be constant or in significant deviation from the generally observed concentration course ("thinning effect"). This is for the vast number of investigated individual aircraft not the case (Figure 59). Moreover, in comparison with other flight phase differentiating studies the general validity of the air exchange rate depending "thinning effect" during the flight phases can be demonstrated (see also Figure 56).

The most astonishing fact is the occurrence of TCP with detected mean values of 20 ng TCP/m^3 (0.0013 ppb) in the non-bleed air driven aircraft B787. Here again TCP displays the

characteristic concentration course of typical cabin contaminants (e.g., toluene, PFC, naphthalene, etc.). The hypothesis that TCP in the cabin air of aircraft derives from the bleed air contamination must, therefore, be questioned. Results of investigated HEPA filter systems by Eckels SJ et al. [9] showed for example, that only in 3 % (filter type one) respectively 30 % (filter type 2) a mixture of TCP and engine oil stock base was measured. This leads to the assumption that also in other cases not every TCP contamination on aircraft HEPA filter is linked to engine oil. Based on this comprehensive knowledge, careful interpretation of data provided by wipe samples from aircraft cabin surfaces or air samples is recommended.

The often observed lack of TCP measurements in the other studies requires an explanation (Figure 59). A closer look on the detected TCP concentrations suggests that the other studies might not have had the analytical capacities to capture such a low level contaminant as state of the art equipment is required to do so. Higher concentrated TBP (0.5-1 µg/m^3) from the hydraulic system is, therefore, detected more often in cabin air studies. According to the current findings, however, the ubiquity of low TCP (< 10 ng/m^3) concentrations in aircraft cabins must be postulated.

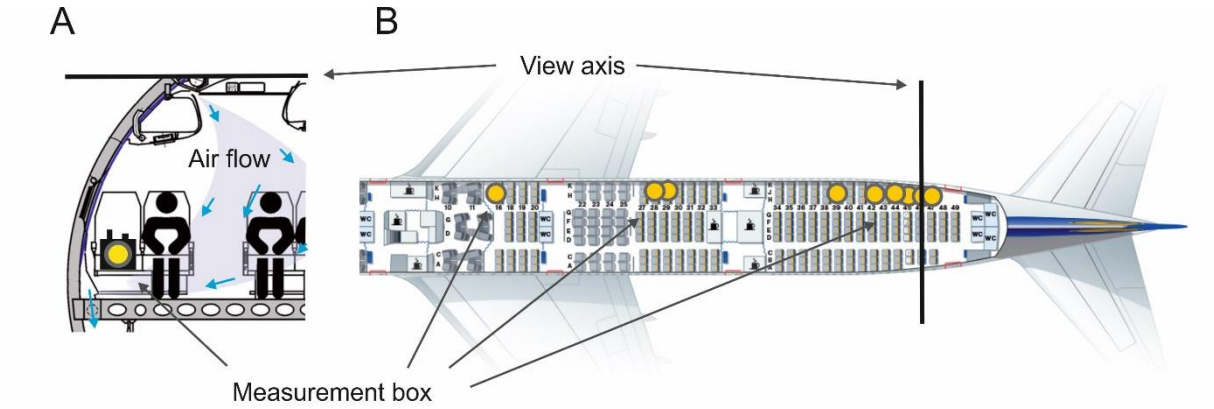


Figure 60 Illustration of the different measuring points positions taken at several B747-8 long-haul flights. (A) Permanently selected seat position of the measurement box (yellow dot). This lateral position is widely believed to be potentially less aerated (blue arrows), which has turned out to be wrong. (B) Exemplary indication of different location of the measurement box within the B747-8 cabin during several measurement flights. Here again the air measurements showed no local discrepancies.

In addition other peculiarities related to cabin measurements need to be discussed. It was planned to position the measuring equipment in the wall area of the cabin in order to reduce disturbances in the flight operation. A possible lower fresh air flow was therefore accepted (Figure 60A). An influence of this lateral measuring position as well as the different measuring positions within the cabin was, however, not confirmed (Figure 60B). The ventilation conditions in aircraft are apparently so powerful that even very different measurement locations (seating positions) remain comparable with respect to the measured results. This fact is not surprising since the strong ventilation guaranties sufficient air exchange for every passenger in

regard to remove exhaled CO_2. In addition all other pollutants in cabin air are removed with the same efficiency. More efforts in future cabin air in-flight measurements are therefore considered to be of little use. The strict requirements for the air supply obviously also apply to the newly designed B787. Quantitative comparison between B787 and bleed air-supplied aircraft in regard to the other contaminants (Figure 59B) revealed identical patterns which is due to the identical air exchange conditions in the investigated aircraft. This observation and the perfect agreement with the other flight phase resolved studies underline the correctness of the above made assumptions (aircraft type independent "thinning effect").

Conclusion: Overall the concentration measurements in cabin air during flight operation require a more sophisticated approach due to the observed changes in the air exchange rate. Especially during taxi-out a reduced air exchange is assumed. During flight operation the air exchange rate turns back to the standard condition what then directly causes the observed "thinning effect". For this reason contaminant concentrations from different flight phases cannot be compared directly with each other.

7.2 Observations and considerations on non-permanent contaminant release

Notably, not all of the 104 quantified VOC comply with the scheme. The exceptions have to be discussed because a deviation from the "thinning effect" is a clear indication of a discontinuous additional emission source in the cabin or an external pollutant input during flight operation. Figure 61 gives an overview of the number and quantitative extent of the observed "unusual" VOC release. The shown volatile cosmetic products and food ingredients are related to specific actions or behaviours which are known to be representative for time-related emission events. It becomes apparent once again that the discontinuous or sporadic VOC emissions can be distinguished from the continuous ones due to the high air exchange rates applied in aircraft cabins. The known relationships of time- or event-related emission have been, however, already sufficiently reported [2] and are not considered to be a cause for concern. The observed isoalkane fraction (estimated chain length of carbon atoms C_{14}-C_{20}, see Figure 61C), which occurs sporadically in many flights during the take-off/climb phase is, however, a new finding. The composition of the isoalkane fraction is chemically different from TCP-containing engine oil. Accordingly, there is also no correlation between the occurrence of the isoalkane fraction and TCP. Also no correlation to other recorded parameters such as aircraft type, age, destination, etc. could be established. The appearance of the isoalkane fraction in the mass spectrometric total ion chromatogram (MS-TIC) is shown exemplary for three flights in Figure 62.

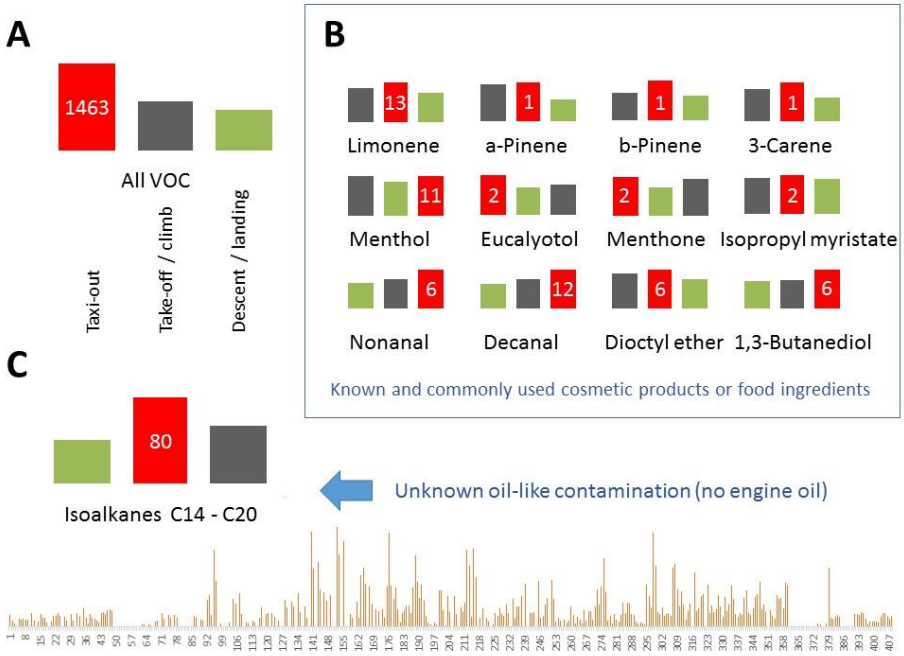


Figure 61 Compilation of flight phase pictograms of measured volatile compounds which reveal a deviation in their release behaviour with respect to the postulated air exchange rate depending "thinning effect". For highest values the concentrations in µg/m^3 are additionally given (median values in white numbers) for comparability reasons. (A) Postulated thinning effect documented in the sum of all VOC detected. (B) Pictograms of commonly used volatile consumption products with known discontinuous but over time regular use during flight (body care and food) leading to air concentrations independent from the actual flight phase. (C) Unknown fraction of isoalkanes with significantly increased release during take-off/climb. The graph gives an overview on intensity and occurrence during the investigated 408 flight phases of this fraction. The isoalkane fraction is proven to be no engine oil but can eventually be related to other lubrication material heated up during the full power take-off/climb phase.

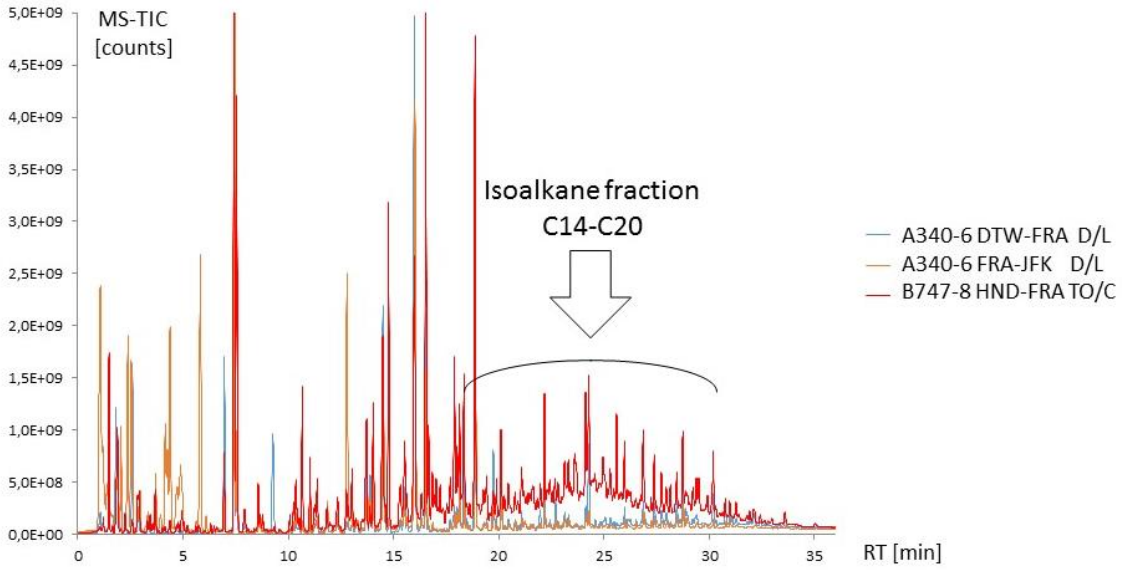
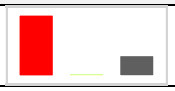
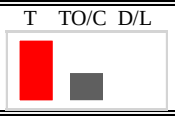
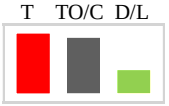
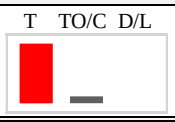
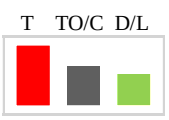
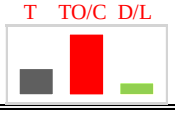
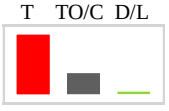


Figure 62: Exemplary MS total ion chromatograms (TIC) of two selected flights (both A340-6) without and one flight (B787-8; red) with heavy isoalkane release (in total, about 220 µg). The complex isoalkane fraction appears as an unobtrusive increase in the chromatogram at 24 minutes and can therefore easily overlooked. D/L = **d**escent/**l**anding and TO/C = **t**ake-**o**ff/**c**limb.

Another important observation is the seldom observed intermittent release of TCP in terms of quantity which manifests itself as a deviation in the flight phase-dependent pictograms. In 67 percent of over 500 investigated flight phases (main study and B787 study) the TCP contamination occur only sporadically regardless of the investigated type of aircraft and most of the TCP occurrence can be attributed to a few flight phases (Table 28). Furthermore, these notable flight phases belong without exception to aircraft with bleed-air supply investigated in the main study. In total 4.33 µg TCP were detected in all flights of the main study of which 43 percent were attributable to two A340-6 and one A320 flight phases (red highlighted flight phases in Table 28) alone. This is why the atypical TCP amounts of these flight phases were excluded in the considerations of the "thinning effect" in Figure 59. The TCP concentration patterns displayed in the flight phase pictograms deviate significantly from the profile characteristic for a "thinning effect". For both A340-6 aircraft in question significantly increased TCP concentrations in the descent/landing (D/L) phase were observed, whereas the A320 showed the highest TCP release during take-off and climb (TO/C). During the displayed flight phases of the highlighted A340-6 and A320 aircraft an increased entry of TCP must have taken place. In the case of all other presented aircraft, a high initial value of TCP during taxi-out is rapidly diluted by the high air exchange as predicted by box model describing the "thinning effect" (see corresponding pictograms in Table 28). The MS-TIC of the samples collected during the two TCP affected A340-6 flights are displayed in Figure 62 to eliminate any conceivable connection with the so far unknown isoalkane release discussed above. It should be noted that the occurrence of TCP was never accompanied by increased amounts of pentanoic acid and heptanoic acid (data not shown). Also the increased TCP entry of the here reported incidents remained unrecognized by the occupants of the affected aircraft. Typical oil odours sensations in other cases, however, had no concrete analytical outcome (data not shown).

Table 28 Flight phase dependent compilation of the most prominent occurrence of TCP. The red highlighted flights differ from the usual concentration profile caused by the "thinning effect". (see flight phase pictograms; T = **t**axi-out; TO/C = **t**ake **o**ff/**c**limb; D/L = **d**escent/**l**anding). The pictograms help to identify the flight phases, which points to an additional strong external TCP source. Here, oil entry by engine-leaking (CAC-event) is likely the cause. The B787 (last three flights), on the other hand, shows the typical "thinning effect" as an indication for a normal cabin contamination.

Aircraft type	Age [yr]	Engine	Dest.	Phase	Location	mmm-TCP	mmp-TCP	mpp-TCP	ppp-TCP	Σm/p-TCP	Flight phases pictogram
						[ng/m³]					
B767	24	PW 4062	FRA-PUI	T	Cockpit	6	7	6	3	21	
B767	24	PW 4062	FRA-PUI	TO/C	Cockpit	1	2	1	0	4	T TO/C D/L
B767	24	PW 4062	FRA-PUI	D/L	Cockpit	1	1	1	0	3	
B767	24	PW 4062	PUI-FRA	T	Cockpit	6	8	9	3	26	
B767	24	PW 4062	FRA-PUI	T	Cabin	17	28	35	13	94	
B767	24	PW 4062	FRA-PUI	TO/C	Cabin	1	1	1	0	3	
B767	24	PW 4062	FRA-PUI	D/L	Cabin	6	10	11	4	31	T TO/C D/L

Aircraft type	Age [yr]	Engine	Dest.	Phase	Location	mmm-TCP	mmp-TCP	mpp-TCP	ppp-TCP	Σm/p-TCP	Flight phases pictogram
						[ng/m³]					
											
B767	24	PW 4062	PUI-FRA	T	Cabin	1	1	2	0	5	
B747-800	2	GEnx-2B67	FRA-HND	T	Cockpit	5	13	13	6	37	
B747-800	2	GEnx-2B67	FRA-HND	TO/C	Cockpit	3	7	5	2	17	
A340	10	RR Trent 556-61	JFK-FRA	T	Cabin	14	37	23	8	82	
A340	10	RR Trent 556-61	JFK-FRA	TO/C	Cabin	23	4	38	13	78	
A340	10	RR Trent 556-61	JFK-FRA	D/L	Cabin	7	13	10	3	33	
A321	1	CFM56-5B3/3	TFS-FRA	T	Cabin	39	53	30	6	128	
A321	1	CFM56-5B3/3	TFS-FRA	TO/C	Cabin	3	6	5	2	16	
A340-6	8	RR Trent 556-61	FRA-DTW	T	Cockpit	2	2	2	0	6	
A340-6	8	RR Trent 556-61	FRA-DTW	TO/C	Cockpit	1	2	1	0	4	
A340-6	8	RR Trent 556-61	FRA-DTW	D/L	Cockpit	1	1	1	0	3	
A340-6	8	RR Trent 556-61	DTW-FRA	T	Cabin	1	2	1	0	4	
A340-6	8	RR Trent 556-61	DTW-FRA	TO/C	Cabin	1	1	0	0	2	
A340-6	8	RR Trent 556-61	DTW-FRA	D/L	Cabin	428	691	339	57	1515	
A320	26	CFM56-5A1	FRA-OSL	T	Cabin	15	26	12	0	53	
A320	26	CFM56-5A1	FRA-OSL	TO/C	Cabin	32	59	26	2	119	
A320	26	CFM56-5A1	FRA-OSL	D/L	Cabin	6	12	5	0	23	
A340-6	10	RR Trent 556-61	FRA-JFK	T	Cockpit	2	3	2	0	7	
A340-6	10	RR Trent 556-61	FRA-JFK	TO/C	Cockpit	1	2	1	0	5	
A340-6	10	RR Trent 556-61	FRA-JFK	D/L	Cockpit	63	97	46	8	214	
B787-8	3	RR Trent 1000	LHR-EWR	T	Cockpit	119	205	75	4	403	
B787-8	3	RR Trent 1000	LHR-EWR	TO/C	Cockpit	14	29	12	2	57	
B787-8	3	RR Trent 1000	LHR-EWR	D/L	Cockpit	3	5	2	0	10	
B787-8	3	RR Trent 1000	LHR-EWR	T	Cockpit	10	26	24	8	68	
B787-8	3	RR Trent 1000	LHR-EWR	TO/C	Cockpit	2	6	5	1	15	
B787-8	3	RR Trent 1000	LHR-EWR	D/L	Cockpit	4	6	4	1	14	
B787-8	2	RR Trent 1000	LHR-EWR	T	Cabin	13	27	21	8	68	
B787-8	2	RR Trent 1000	LHR-EWR	TO/C	Cabin	3	9	8	4	24	
B787-8	2	RR Trent 1000	LHR-EWR	D/L	Cabin	1	2	2	1	6	

In summary, it can be stated that TCP and isoalkane releases can occur in almost all types of aircraft investigated in the study. The age of the aircraft does not seem to affect the type and extent of contamination. The introduced forced “thinning effect” together with the flight phase

related sampling strategy (quantitatively displayed as pictograms) help to differentiate between complex continuous and discontinuous contaminant release. Bleed air contaminants are easier to track down than other contaminants even when an external source cannot be conclusively proven. TCP was also found in larger quantity in the investigated B787-8 aircraft. This makes the search for bleed air related contamination more difficult since there are obviously other sources than bleed air for TCP in aircraft cabins. These sources, however, are well known for indoor environments [12–14, 43–45]. Thus for technical environments such as office buildings, industrial work places and aircraft cabins a permanent low concentrated TCP occurrence has to be considered as an ubiquitous burden. The measured low background levels are, however, not critical from a toxicological point of view (Table 2). This also applies for the here presented non-event cases, which can be considered as permanent TCP burden in aircraft cabins. Nevertheless, each future study should have sufficient analytical sensitivity regarding the detection of OPC and should also be able to address possible alternative sources for TCP entry into the cabin air of the B787 or other aircraft. Since it has been shown that a permanent entry of TCP by engine caused oil leakage can be considered unlikely, the use of analytical methods with low sensitivity (e.g., online MS or TVOC measurement during flight operations) are not recommended for these kind of investigations.

However, this does not apply for oil-triggered CAC-events during flight operation. Here, too, the above introduced box model provides more clarity.

The box model also allows a more detailed examination of possible CAC-events (highlighted red in Table 28). With the assumptions made in the previous section, it is possible to estimate the oil quantity which causes such an event. The calculations need only to be adapted for these special cases. The following parameters are used for a model calculation of the most serious TCP incident (A340-6 flight DTW-FRA):

Volume A340-6 (V_{cabin} + $V_{cockpit}$):	V_{A340} = 470 m^3
Fresh air cabin exchange rate:	Λ= 20 h^{-1} (2 packs norm operation)
TCP concentration detected during descent/landing:	$C_{D/L}$ = 1.5 µg/m^3
Mass flow per minute ($Q = \Lambda_{min} \cdot V_{A340}$):	Q = 156.66 m^3/min
Duration of descent/landing phase:	$T_{D/L}$= 37 min

Total amount of TCP entering the cabin volume can be calculated as follows:

$$Mass_{TCP} = T_{D/L} * C_{D/L} * \Lambda_{min} * V_{A340} = 8695 \mu g \qquad \text{Eq. 2}$$

According to this calculation a total of 8695 µg (8.695 mg) TCP enters the A340 cabin during the 37 minutes lasting descent/landing (D/L) phase. This refers to approx. 290 mg engine oil in total considering a 3% (w/w) content of TCP. The oil amount released by the engine can, of course, be considerably higher if we take the assumptions concerning the mass flow (Q) in engines into consideration (Table 27). If only 5% of the oil reaches the cabin, the actual leak rate of 7.84 mg oil/min (= 290 mg/37 min) would increase to 156.8 mg oil/min. However, these simple assumptions apply only to a uniform leaking rate over the measured landing phase, which is very unlikely. An intermittent emission is more likely to happen since the typical reported acute CAC-event last only a few minutes and the alternative of a conceivable permanent oil leaking has not been detected in any study so far. In Figure 63 a hypothetical acute CAC-event is simulated for the rare case that 100 g engine oil are lost at the main engine and distributed in the aircraft cabin within 10 min. The emission profile is for reasons of simplification linearly up- and down-modulated because instantaneous contaminant entry into the cabin is not considered possible due to retention effects occurring while passing the ECS.

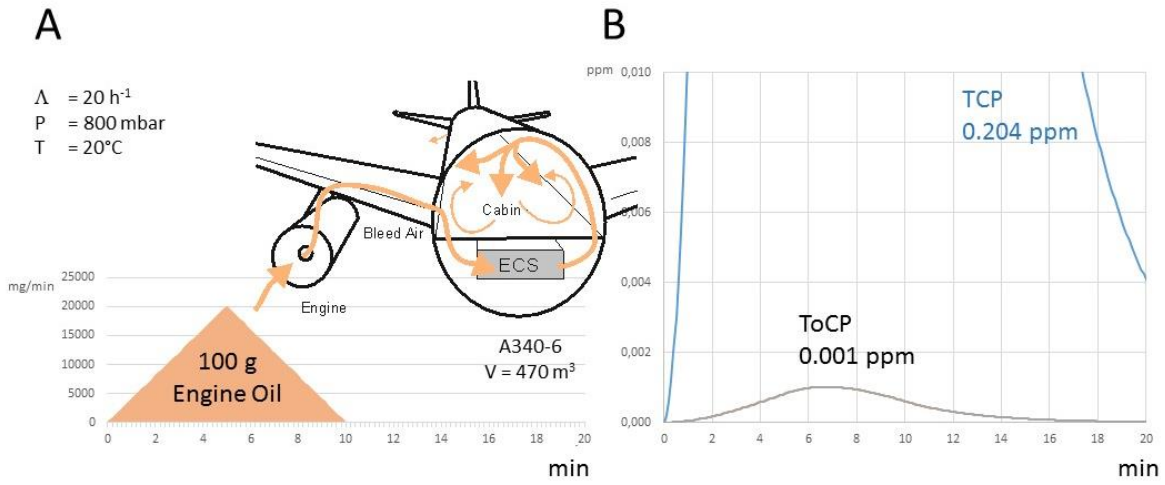


Figure 63 Calculated TCP and ToCP concentration curves (Equations 1 and 2) for a 10 min lasting oil-triggered CAC-event in a hypothetical aircraft with consideration of conditions given in an A340-6. (A) Simplified release model for 100 g engine oil release (mean 10 g/min) representing the change in the source strength of the oil leakage which is not considered to start instantaneous with maximum concentration. Note, for this modelling a 100% oil transfer from the engine into the cabin is assumed, which is considered as highly unlikely (Table 27). (B) Maximum peak values of TCP/ToCP concentrations in the aircraft cabin according to the calculated event. Note the high air exchange applied in aircraft ensures that the maximum concentrations given here will last only a few minutes. The modelled peak value of 0.001 ppm (12 µg/m^3) ToCP (if a 0.5% ToCP content in TCP is assumed) is not of significance from toxicological point of view.

Noteworthy is the fact, that a 100% oil entry into the cabin is assumed, which is considered unlikely taking the considerations above into account. Even this hypothetical worst-case scenario does not lead to contaminant concentrations of concern. The actual observable levels

should be even an order of magnitude lower. Such strictly mathematical considerations on CAC-events have already been made [46]. However, also for the other two observed TCP incidents (A340-6 FRA-JFK and A320 FRA-OSL) the oil entry must have been considerably lower, given the observed TCP levels of max. 214 ng/m^3. A health hazard should therefore not have occurred.

Finally, it should be pointed out that the observed higher TCP release during these highlighted flight phases does not reveal the real origin of the engine oil. It is just known for sure that there must have been additional sources during these flight phases. Thus the TCP containing oil may stem from any part of the affected aircraft (e.g., engine, APU, ECS, unknown deposits). Since TCP does not appear at the same time in the cockpit and cabin for the reported incidents, doubts about the engine as solely source are appropriate. Therefore caution is required until investigation on the actual air flow of the affected aircraft may explain these findings. However, until these facts have been clarified, an engine oil triggered CAC-event has not been analytical confirmed yet.

Conclusion: Based on the here introduced "thinning effect", non-permanent contaminant release can be well distinguished from typical background contamination in aircraft cabins.

7.3 Classification of cause and occurrence of technical CAC-events

As stated in the results so far, persistent entries of TCP-containing oils appear to play a subordinate role in the occurrence of CAC-events. The OPC frequently detected in aircraft cabins originated most likely from different sources, which should be distinguished from technically caused CAC-events. It is therefore important to clearly distinguish the possible routes of technically caused contamination from permanent cabin contamination sources in aircraft. As shown, unusual TCP emissions in the aircraft cabin can be identified by phase-dependent sampling using the "thinning effect". These intermittent TCP emissions probably have their origin in the engine (in flight) or APU (on the ground) operation. Hereinafter, these oil-triggered CAC-events are referred to as technical CAC-event (TCAC-event) and must be distinguished from the ubiquitous contaminant burden in aircraft cabins. For the TCAC, two entry constellations can generally be differentiated, whereby a possible permanent contaminant entry should play a subordinate role due to the available data:

a) permanent engine oil (contaminant) entry into the cabin
b) event triggered engine oil (contaminant) entry into the cabin

Based on reports and technical considerations, most engines might have a certain turbine oil leak rate. These obvious permanent oil entries were not detectable even with the here applied trace analysis tools. How are these findings to be interpreted? According to the calculations in

Table 27 engine oil leak rates of 0.001 g/min and above should ultimately be detectable with the applied analytical method. However, this has not been achieved in any of the over 200 investigated flight phases. It has therefore to be assumed that the oil or oil components fed by the bleed-air ports did not reach the aircraft cabin or if so they were below the detection limit (<LOD). This assumption is supported by numerous and well-documented reports [1, 2, 42]. It can be conjectured, however, that these oil contaminations are deposited on the route to the cabin. Individual deposits with not defined contaminant load but also large surface areas in the ducts of the ECS are conceivable sinks [19].

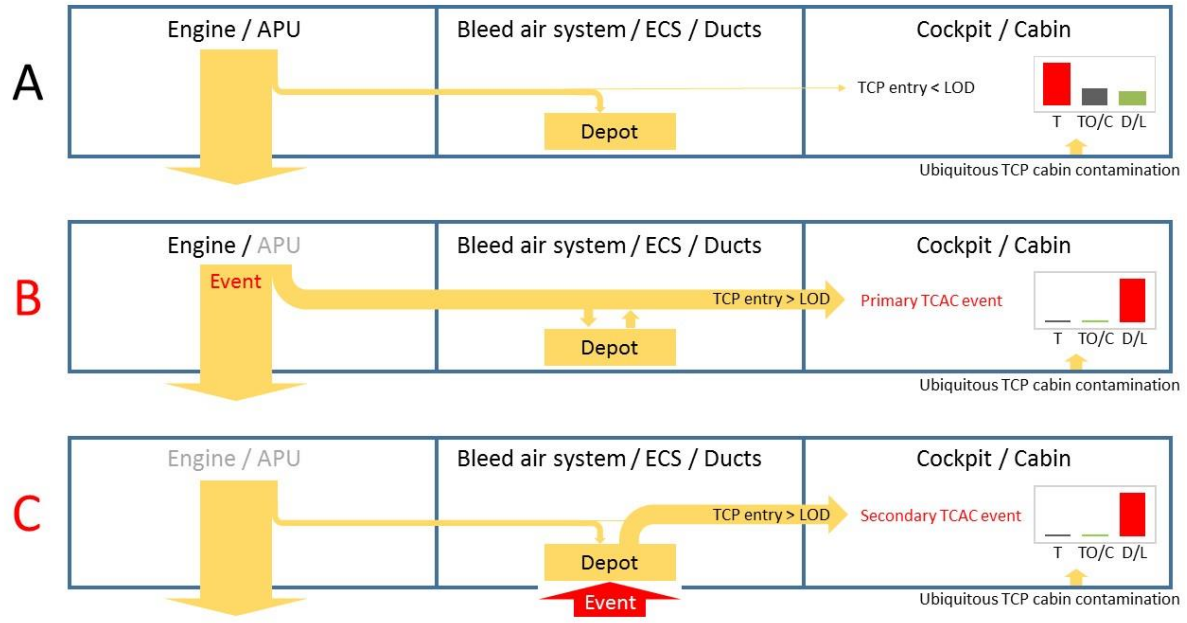


Figure 64 Possible primary and secondary sources of TCP contamination in affected aircraft compartments causing TCAC-events. A) Event free situation with creeping oil component deposits in the bleed air/ECS/ducts compartment (Depot). Only amounts below the limit of detection (LOD) of TCP containing engine oil is assumed to enter the aircraft cabin. Most of possible engine oil leakage at the primary source (engine/APU) leave the aircraft through the exhaust jet (thick arrow pointing downwards), making the interior within the cockpit cabin compartment the solely sources of the widely detectable TCP contamination in aircraft. Thus the pictogram indicates flight phase depending "thinning effect" (T = **t**axi-out; TO/C = **t**ake **o**ff/**c**limb; D/L = **d**escent/**l**anding)). B) Sealing failure in engines may cause primary TCAC-events with high contamination loads which cannot be deposited due to capacity limitations. Note, the APU is not likely to cause primary TCAC-events in-flight since the use is most of the time on-ground. The pictogram shows exemplary the observed high TCP release during descent and landing phase. C) Event triggered oil component release at the descent/landing phase from contaminant deposits = secondary TCAC-event. Primary contamination sources (engine/APU) are not directly involved. Triggering events can be any physico-chemical influences on the deposit in the associated compartments (red arrow). Note cabin air measurements cannot distinguish between primary and secondary TCAC-events (see pictograms).

It should be noted that each deposit could be a preferred sink for subsequent oil contamination (according to the chemical theorem "similia similibus solvuntur"). Reports of oil deposits in these aggregates and the deposition of black smears in the ducts are abundant. The chemical-

analytical investigation of ducts in real aircraft confirmed the presence of TCP and engine oil related contaminants [19]. Massive sealing failure on engines and APU and additionally triggered release from deposits ought to be a frequent cause for the occurrence of reported TCAC-events. These two possibilities of TCAC-events should always be considered separately and differentiated against the ubiquitous TCP occurrence (for example originating from the interior of the aircraft cabin) in aircraft cabins. The latter is probably the reason why low TCP levels are also detected in non-bleed air driven B787 aircraft. The possible oil contamination types are illustrated in more detail in Figure 64. Accordingly, a primary and secondary TCAC-event can be distinguished exclusively for bleed air operated aircraft. Primary and secondary refers, thereby, to the type of source responsible for the cabin air contamination.

Of particular interest are the secondary TCAC-events, as these are fed from deposits. Inspection the checking of the engines after a TCAC-event can therefore lead to no findings. It is even conceivable that the deposits are mainly fed by oil leaking from the APU. The APU can be used for example if maximum engine power is needed during taxi-out and/or take-off. During cruise the use of the APU is unlikely and limited to failure cases. A primary TCAC-event caused by the APU is, therefore, considered not very likely. Furthermore, it is less conceivable, that larger quantities (>100g) of oil or oil related contaminants are released during secondary TCAC-events. Secondary TCAC-events may therefore present less severe cases which can however still be associated with the conspicuous odour symptoms in an aircraft. The exact causes for the spontaneous release of pollutants from such deposits are still unclear and also controversial [19]. It is conceivable that mechanical or thermal stress or the introduction of solvents such as water or de-icing agents can trigger such an event. Due to the necessary formation of depositions new or overhauled aircraft should show no secondary TCAC-events. This assumption would be easy to verify by systematically recording and analyzing such events.

This complex release problem presented here also explains why TCP still remains a preferred indicator or label for bleed-air contamination, even if a low concentrated cross-contamination by cabin interior exists. The reasons for this are:

- TCP is analytically well detectable and has a defined proportion of engine oil
- Based on the measured TCP distribution, the spread of the more toxic ToCP and other conceivable ortho TCP can be directly derived.
- TCP is heat resistant and can withstand possible thermal stress in the relevant parts of the engine.
- High TCP concentrations are suitable for biomonitoring methods.
- Ubiquitous TCP levels are very low (cabin contaminant).

Often discussed alternative indicators for TCAC-events are oil pyrolysis products, alkanoic acids or n-alkanes. In addition to the complex distribution behaviour shown here, their cabin air concentrations are often very low, they have undefined reaction chemistries and possible cross-contamination levels higher than observed for TCP are common, making them not an ideal choice as indicators for TCAC-events.

Conclusion: TCAC-events have their cause in the bleed air system and can definitely not occur within the B787 fleet. The bleed air related TCAC-events can be divided into two categories:

- The primary TCAC-event can be assigned to a sealing failure or oil overfilling in the engine, which results in a measurable pollutant concentration in the cabin.
- A secondary TCAC-event, on the other hand, has its origin in deposited oil contaminants inside the bleed air system and the air conditioning system, which is caused by an assumed permanent low oil leakage of the engines and APU (primary sources).

These small oil leaks do not have direct access to the aircraft cabin which is in accordance with the available oil contaminant data. TCP remains an ideal indicator for both bleed air related TCAC-events due to its spread use and chemical properties.

8 Conclusions and recommendation for a large scale project plan

Overall, in the meaning of frequency, distribution, spectrum of substances and concentration ranges, this study displayed results comparable to well-known international studies on this issue. The literature search performed in the first part of this study has also not given any new insights into the cabin air quality issue. However, it showed that similar airborne contaminations are also observed in typically indoor environments like offices, schools, kinder gardens or dwellings.

Aldehydes and other VOCs were detected at levels that can be considered as not unusual for indoor air environments. Particularly with regard to the high density of occupants in aircraft, the effect of so-called bio-effluences VOCs shall be included in the discussion of emission sources in aircraft. Reaction products of VOCs with ozone, e.g. described by Nørgaard et al. 2014 [10], oil pyrolysis products [18], certain alkanoic acids or increased concentrations of n-alkanes were not detected. Those or similar products might have an impact on event-related odours in aircraft [11]. However, it should be noted that the odour perception may be orders of magnitude below the measurable contaminant concentrations.

On A321 flights, occasional increases of propylene glycol levels in cabin air were noticed, which could be explained by the application of de-icing fluid during the winter period. A few VOC, also at low levels, may be observed due to the occurrence of special events or individual actions. During in-flight services or individual body care several volatile food ingredients or cosmetic products are released into the cabin air, which are regarded as time-related emission events. The use of mothballs (naphthalene) or leaks in the air-conditioning system (PFC) was also observed.

Only the frequent occurrence of an unknown fraction of isoalkanes especially during the take-off/climb phases has caused attention, even if no critical concentrations were observed. The assessment of the acceptable pollutant concentrations in aircraft is difficult from regulatory point of view because the aircraft is a workplace for the crew and a public place for the passengers. However, under consideration of occupational exposure limits (OELs, typically considered as time-weighted average for 8-h exposure) and/or indoor air guideline values the cabin air monitored in this study were of good quality. Indoor air guidelines provide a higher level of protection, because in contrast to the OELs, they are typically defined assuming an exposure of 24 hours, and taking into account sensitive individuals (children, old people or sick people). Taking indoor air guidelines into consideration the cabin air is no object of any

concerns. It is worth to be mentioned, that no single detected contamination reached critical or unusual concentrations for indoor environments.
This is in agreement with the statements from Wolkoff et al. [7]. This research group approached the question from a risk assessment perspective. They compiled a large data set from literature to perform a risk assessment for the adverse effects that are reported in association with cabin air and compared it with office air. Air concentrations of non-reactive volatile organic compounds (VOCs) and ozone-initiated terpene reaction products in cabin air and in office air which are reported in different air monitoring studies were gathered and combined. For the contaminants, OELs or other threshold levels were compiled; for ToCP they introduced a tolerable daily intake value (TDI). Wolkoff et al. used for their health risk assessment a "worst-case scenario" assuming a simultaneous constant exposure to identified maximum ToCP concentrations in aircraft and offices over the time course of 8 hours. Hazard quotients or indexes were defined as the summed ratio(s) (%) of compound concentration(s) divided by the identified threshold values. The worst case is given because critical exposure levels typically would occur only during infrequent incidents and only for a short time. All in all, the authors conclude that for both cabin and office air the measured concentrations are not likely to be associated with reported symptoms.

To state the obvious, there is no contaminant-free indoor environment. The aircraft cabin is no exception. However, due to the exceptional high air exchange rates in aircraft, the cabin air has been proven to be less polluted compared to normal indoor environments (e.g., offices, dwellings, etc.). Volatile contaminations in the cabin are thus depleted quickly. Since, the bleed air itself is suspected to be the source of hazardous contaminants such as OPC a special attention was paid to the detection of TCP as a marker for engine oil contamination and the present physical ventilation situation in aircraft. Thanks to the extremely sensitive OPC analysis applied in this study, completely new insights were obtained. Furthermore, this is the first published study, which includes in-flight measurements on Boeing 787 aircraft.
The following important observations and conclusions among others can be drawn from the investigations:

Observation: The VOC burden in cabin air shows a highly comparable distribution and extent in comparison to other indoor environments. On average, cabin air is even less contaminated with pollutants. The only special characteristic is the slightly

increased occurrence of an isoalkane fraction with unknown origin during starting phases.

Conclusion: The values determined for VOC, CO_2, CO and ozone in the cabin can be considered as quite normal for indoor environments. Even if the isoalkane contamination does not reach critical concentrations, the cause should be investigated.

Observation: Most of the observed changes in cabin air contaminant concentrations during different flight phases are most likely related to variable air exchange rates. Their pattern can be described by the introduced "thinning effect".

Conclusion: Future cabin air measurements in aircraft comparing different flight phases should necessarily take the "thinning effect" into account to avoid misinterpretations.

Observations: TCP can be detected sporadically in small amounts in almost every aircraft type including the additional investigated non-bleed air operated B787. TCP-release is comparable with the release of other cabin contaminants and the observed changes in concentration over the different flight phases can be described by the newly postulated "thinning effect". The universal applicability of the "thinning effect" was also confirmed by data taken from other cabin air studies investigating flight phases.

Conclusion: The occurrence of TCP in the B787 and the associated observed "thinning effect" on its concentration course suggest an ubiquitous cabin air contamination in all aircraft types. Future cabin air measurements in aircraft should take general OPC contaminations into account and should implement analytical remedies to avoid misinterpretations.

Observation: A permanent external TCP/engine oil entry through bleed air has not been detected so far.

Conclusion: If any permanent TCP/engine oil entry caused by chronic sealing failure actually occurs, then it must have been below the applied detection limit of 2 ng/m^3. Any future measurement strategies focusing on permanent TCP/engine oil entry should be improved significantly to assure differentiation from likewise existent internal contamination (e.g., release from cabin interior, see above). However,

these extremely low amounts of contaminants should not affect the cabin air quality.

Observations: TCP was detected at three occasions in higher amounts than usual during certain flight phases in aircraft types with bleed air supply. The normally associated smell event was neither reported by the crew nor by the passengers.

Conclusion: These technical cabin air contaminations (TCAC) events have their origin in the bleed air technology. Primary (engine/APU) and secondary contaminant sources (oil deposits in bleed air system and air conditioning system) can be distinguished. Studies should be designed to identify these so far unknown secondary sources or sinks as well as the causes triggering secondary TCAC-events. The olfactory characteristics of TCAC-events are not yet understood and most of the reported smell events cannot have technical (oil-related) causes due to their known rareness of occurrence.

These findings have of course a great impact on the recommendations for a future large-scale project plan. Most importantly, one has to investigate the impact of the above postulated secondary TCAC-events. Note, this secondary exposure path can be also responsible for the more often reported smell events, when possibly non-toxic odourous compounds are released. A change in the moisture for example can have a great influence on the odour perception (wet dog effect or old sock smell). However, these odours are not harmful to health and should therefore be differentiated from oil-triggered TCAC-events, even if those TCAC-events are also not considered as harmful.

The investigation of oil-triggered TCAC-events is no longer possible with conventional methods. A continuation of the previous measurement series is also not considered as constructive, since encountering a real TCAC-event, which needs to be investigated in order to answer some of the questions, remains very unlikely. It is not recommendable to rely on luck alone due to the low number of engine oil triggered incidents [4, 5, 15, 16]. For the investigation of TCAC-events it may be necessary to use appropriate simulations. Simulation of bleed air contamination on ground in real aircraft cabin air environment may shed light on this gap of knowledge. Both possible TCAC-events, primary and secondary, need to be investigated in great detail, which would probably only be possible in a real aircraft.

The analytical set-up should be improved as well, since the origin of oil constituents need to be clearly identified. Further research is also needed to evaluate, whether bleed air is the prominent route of cabin air contamination by engine oil constituents or not. Due to the measured low level of contamination of cabin air with oil constituents, it is recommended not to search further for new low abundant markers or mostly artificial oil pyrolysis/hydrolysis products. The TCP isomers have already proven to be suitable markers for oil contamination especially if the exceptional ventilation conditions in the aeroplane are carefully considered (e.g., "thinning effect", exposure route, TCAC-event sources, etc.). The use of chemically labelled engine oil constituents (e.g., ^{13}C-TCP) can, furthermore, shed light on the total mass flow in possibly contaminated ducts of the ECS. In addition the ubiquitous presence of TCP in aircraft cabins should always be considered (e.g., textiles, floorings, circuit boards, plastics, outside air, etc.). Nevertheless, harmful contaminant concentrations have not been detected in any of the studies conducted so far. The above introduced simple calculations (Section 7) indicate even for TCAC-events no harmful consequences for the affected passengers and crews. In addition to this, the worst conceivable incident, a primary TCAC, is an extremely rare event. In the case of the certainly more frequent secondary TCAC-events, it is also necessary to check whether the smell impression does not exaggerate a possibly non-existent hazardousness of the contamination. Furthermore, there is not yet enough knowledge about the frequency of secondary TCAC-events. The non harmful odour events (e.g., cosmetics, food, exhaust gas) are probably more common and are then reported incorrectly as TCAC-event. Once again, the presence of an odour alone is not necessarily indicative of a toxic effect. Before an unnecessary complex medical procedure is established, an exact classification of the CAC-event should be made possible. In addition, it is regarded as important to investigate whether TCAC-events can be documented with medical parameters or not. The cabin air contamination concentrations measured so far, however, are very likely not detectable by currently applied bioanalytical methods. A risk assessment should always be based on the meaningful combination of occurrence frequency, exposure duration, contaminant concentration and health hazard. Taking into account the current data situation [7, 41, 42], which indicates a very low OPC incidence in aircraft, the still ongoing discussion about the so-called "aerotoxic syndrome" remains completely incomprehensible.

Nevertheless, the occurrence of oil-triggered CAC-events (TCAC-event) is sometimes accompanied by reports of dramatic consequences for the affected subjects. Not all previously reported cases of severe neurological deficits are yet comprehensible and other causes such as hyperventilation are under discussion. The neurologic impairment is sometimes attributed to

chronic and/or acute oil-triggered contaminant exposure [10, 35]. Experts consider this impact due to the observed low contaminant levels as implausible and suggest other causes instead [8, 46]. A realistic TCAC-event simulation and a human exposure study conducted in parallel would give exclusive access to

a) observable neurological changes in behaviour and perception and
b) bioanalysis data in regards to TCP and their derivatives in urine and blood.

Such a complex simulation has the potential to elucidate the often stated neurological impact and may be of immense value with regard to the feasibility of biomonitoring. A realistic TCAC-event simulation and if feasible a human exposure study can provide the contamination data which is urgently needed for a solid risk assessment. The results and the risk assessment should then be presented in a plausible, comprehensive and understandable way to the general public and the employees of the airlines (risk communication). Finally, it is necessary to identify ways in which the potential risk of bleed air contamination can be reduced or controlled. Even if the toxicological risk can already be classified as very low, risk mitigation by technical means is always desirable. However, risk mitigation should stay in a reasonable ratio to the benefit. In summary, the following recommendations for a future large scale project plan can be made:

- Thematic focus on occupational safety and human health in aircraft cabins with respect to **chronic** and **acute bleed air contamination** exposure caused by primary and secondary TCAC-events.

- Implementation of a real TCAC-event simulation accompanied by
  - the analytical investigation of exposure paths
  - the search for a distinction between primary and secondary TCAC-event
  - consideration of other hitherto unknown toxic oil components
  - the use of isotope labelled oil constituents

- Determination of chronic oil exposure during normal flight operation by
  - the implementation of a suitable long-term sampling strategy
  - the use of isotope labelled oil constituents (if feasible)
  - taking into account the ventilation conditions (air exchange rates)
  - further investigations on the newly discovered isoalkane fraction (chapter 7.2)

- Investigation on the impact of severe primary TCAC-events on human health and well-being by
    - human exposure studies incl. biomonitoring of blood and urine
    - neurotoxic testing and metabolome studies (control and exposure group) might give insight on other factors as source of discomfort during exposure in an aircraft

  Important note: All conducted measurement campaigns and their subsequent thorough analysis and interpretation clearly indicate that even a severe primary TCAC-event does not pose any danger to the health of aircraft occupants. Before starting any human exposure studies technical simulations are required to ensure that the conditions chosen for exposure studies are indeed safe for the test subjects and in parallel represent realistic conditions as far as possible. A detailed documentation of the chosen exposure scenario is a prerequisite for the required submission of the study plan to the ethic committee.

  A human exposure study is the long-needed tool to provide an unequivocal and sound data set to end the misguided discussion on cabin air quality once and for all. The idea of "neuro toxic TCAC-events" can create fear which occasionally can lead to people feeling or developing respective corresponding symptoms at the occurrence of smell-events. This, misdiagnosis as well as data misinterpretation fuel the on-going debate for which no agreement between the participating parties (pro and contra) is anticipated in the foreseeable future.

  The suggested human exposure study provides the opportunity of alleviating this fear and of assessing all bioanalytical methods and medical tests used so far for their suitability in detecting TCAC-event related health problems. Human exposure can be seen as an important contribution to the objectification of the currently misguided discussion on cabin air quality.

- Consideration or search for additional pollutant sources causing OPC contamination in aircraft by
    - investigations of aircraft furnishings, equipment and operating procedures
    - including measurements of ambient air (airport)

- Qualified risk assessment of bleed-air contaminations by
    - including valid exposure data for chronic and acute exposure (so far incomplete)

  - including the data of all previous studies and taking into account current authority decisions (ECHA)

- Elaboration of risk mitigation strategies for reduction of possible bleed air contamination (e.g., improved maintenance, implementation of oil contaminant detection techniques)

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take-off values the concentrations in µg/m^3 are additionally given (median values in white numbers) for comparability reasons. Note that the outcome is totally consistent although different methodologies were used for VOC, OPC and aldehyde detection. The compound selection focuses, with exception of TCP (normally detected in concentrations far below 0.01 µg/m^3), on contaminants representative for the aircraft cabins. However, almost all detected cabin VOC follow this concentration course. An opposing trend was found for discontinuous release only. The white number given in the bar for all VOC represent the sum of all VOC (µg/m^3) measured during the taxi-out flight phase. These values are also given for all other presented contaminants. In case of toluene (commonly known indoor contaminant), perfluorinated compounds (PFC; air condition), naphthalene (mothballs), TBP (aircraft hydraulic oil) and short-chain aldehydes (interior, adhesive, etc.) an origin from engines are not considered to be very likely. Solely TCP is supposed to be related to undesired engine oil entry and serves, therefore, as a marker for bleed air contaminations. 83

Figure 53 Equilibrium conditions for measurable VOC concentrations illustrated by a box model for the non-ventilated state (A) and ventilated state (B). The arrow labelled S_i quantifies the source strength [mass/time] of various internal (i) volatile compounds while the arrows labelled Q indicate the mass flow [mass/time] related to the defined air exchange. Note, static equilibrium (C_s) is never achieved for real indoor situations, since air supply is vital for the occupants. However, for situations with very low air exchange unusual high VOC concentrations can be observed for given S_i. State B is therefore the rule, with exceptional high air exchange rates (>20 h^{-1}) being maintained in the aircraft. The high air exchange has important consequences on the measurable VOC concentrations (C_d) in the aircraft cabin (further explanations in the text). 85

Figure 54 Calculated carbon dioxide (CO_2) concentrations (Equation 1) in a fully occupied aircraft with consideration of typical flight parameters. The green curves give the concentration course of CO_2 for a hypothetical aircraft with 470 m^3 ventilated cabin volume (well mixed box) and an air exchange rate of 20 h^{-1}. The hypothetical aircraft is occupied by 345 passengers who start breathing at t_0. Each passenger releases 0.44 g CO_2 per minute and the ambient air contains 388 ppm CO_2. These conditions are very similar to an A340-6 aircraft. (A) In less than 10 min a dynamic equilibrium is established which is close to 1060 ppm, a commonly accepted value for appropriate air quality in indoor environments. Without passengers the CO_2 concentration would remain at 388 ppm (blue curves) according to the box model, since the outdoor air is, as the cabin air, "contaminated" with CO_2. This example shows that the simple box model can provide good predictions regarding the concentration profile of contaminants which are

the pictogram indicates flight phase depending “thinning effect” (T = **t**axi-out; TO/C = **t**ake **o**ff/**c**limb; D/L = **d**escent/**l**anding)). B) Sealing failure in engines may cause primary TCAC-events with high contamination loads which cannot be deposited due to capacity limitations. Note, the APU is not likely to cause primary TCAC-events in-flight since the use is most of the time on-ground. The pictogram shows exemplary the observed high TCP release during descent and landing phase. C) Event triggered oil component release at the descent/landing phase from contaminant deposits = secondary TCAC-event. Primary contamination sources (engine/APU) are not directly involved. Triggering events can be any physico-chemical influences on the deposit in the associated compartments (red arrow). Note cabin air measurements cannot distinguish between primary and secondary TCAC-events (see pictograms)..... 102

11 References

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12 Appendix A – Sample Volume Calculation

Please refer to the separate pdf document: “Appendix A - Sample Volume Calculation EASA 2014.C15 CAQ_ 2015.LVP.64 CAQ II”

13 Appendix B – Aldehydes

Please refer to the separate pdf document: “Appendix B - Aldehydes EASA 2014.C15 CAQ_ 2015.LVP.64 CAQ II”

14 Appendix C – Organophosphates

Please refer to the separate pdf document: “Appendix C - Organophosphates EASA 2014.C15 CAQ_ 2015.LVP.64 CAQ II”

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