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PAPER

Organophosphates in aircraft cabin and cockpit air—method development and measurements of contaminants

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Methods for measurements and the potential for occupational exposure to organophosphates (OPs) originating from turbine and hydraulic oils among flying personnel in the aviation industry are described. Different sampling methods were applied, including active within-day methods for OPs and VOCs, newly developed passive long-term sample methods (deposition of OPs to wipe surface areas and to activated charcoal cloths), and measurements of OPs in high-efficiency particulate air (HEPA) recirculation filters ($n = 6$). In total, 95 and 72 within-day OP and VOC samples, respectively, have been collected during 47 flights in six different models of turbine jet engine, propeller and helicopter aircrafts ($n = 40$). In general, the OP air levels from the within-day samples were low. The most relevant OP in this regard originating from turbine and engine oils, tricresyl phosphate (TCP), was detected in only 4% of the samples (min–max <LOQ–0.29 μg m^{-3}). TCP was however detected in 39% of the wipe samples ($n = 56$) and in all HEPA-filters. Other OPs, as dibutylphenyl phosphate (DBPP) and tri-*n*-butyl phosphate (TnBP) originating from hydraulic oils were more prominent in the samples, illustrated by determination of TnBP in all of the within-day samples collected from airplanes ($n = 76$, min–max 0.02–4.1 μg m^{-3}). All samples were collected under normal flight conditions. However, the TCP concentration during ground testing in an airplane that had experienced leakage of turbine oil with subsequent contamination of the cabin and cockpit air, was an order of magnitude higher as compared to after engine replacement ($p = 0.02$).

1 Introduction

The presence of a range of contaminants in aircraft cabin and cockpit air has been highlighted in several studies.[1–4] The cabin air supply in most jet aircrafts is obtained by extraction of heated and compressed bleed air from the jet engine cores, prior to mixing with filtered recycled cabin air.[5] Thus, the potential for contamination of cabin air with chemicals originating from turbine oils used as lubricant in the engines has been addressed.[6] Furthermore, the aircraft hydraulic reservoir vent is connected to the cabin air ventilation system, with potential for hydraulic oil

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Environmental impact

The manuscript describes methods for measurements and the potential for occupational exposure to organophosphates (OPs) originating from turbine and hydraulic oils among flying personnel in the aviation industry. Exposure to hydraulic and turbine oils has for several years been of concern due to so-called "smoke-in-cabin" incidents during commercial flights where the air supplied to the cockpit and cabin has been contaminated by the turbine oil containing OPs that may harm human health. Despite the addressed concerns and potential risk for exposure to OPs in aircraft cabin air, no peer-reviewed studies presenting measurements of such OPs in cabin air during commercial flights exist to the best of our knowledge. The expressed health concerns related to OP exposures in combination with the lack of related air sampling and tailored sampling methodologies have revealed a need for such. This first study therefore focuses on potential occupational OP exposure during commercial flights, including eventual incidents.

aerosols to enter the cabin air.[7] Turbine oils are used as lubricants and anti-wear agents for turbines and engines and are mostly composed of mineral or synthetic base oils containing additives, such as organophosphates (OP), to enhance their lubrication, anti-corrosion, flame retardant and pressure-transferring properties.[8] Hydraulic oils also consist of or contain OPs, such as butyl phosphates.[8]

Several reports on smoke-in-cabin incidents due to engine oil leaks are described in a recent review.[7] Health symptoms ranging from irritation to acute intoxication among passengers and flight crew members in relation to smoke-in-cabin incidents have been reported.[9] Moreover, OPs originating from turbine oils have been suggested as major contaminants of concern during such incidents.[10,11]

In general, exposure to organophosphorus compounds can cause sub-acute, delayed and chronic neurological, neurobehavioral, and psychiatric syndromes,[12–15] and neurotoxicity following long-term, low-level exposure has also been reported.[16] The neurotoxic effects of the OP tricresyl phosphate (TCP) isomer tri-*o*-cresyl phosphate (ToCP) have been well documented,[17–19] and toxic effects of the OPs triphenyl phosphate (TPP)[20–23] and tri-*n*-butyl phosphate (TnBP)[23–26] are also known. TCP, TnBP, and TPP are, among other OPs, widely used in turbine or hydraulic oils in use in the aviation industry. Furthermore, the possible formation of unknown organophosphorus products during oil leaks with deposition on hot surfaces has been addressed.[27,28] Laboratory studies have shown the formation of the neurotoxin trimethylolpropane phosphate (TMPP) from TCP and trimethylolpropane ester at elevated temperatures.[6]

In spite of the addressed concerns and potential risk for exposure to OPs in aircraft cabin air, exposure studies of OPs originating from turbine and hydraulic oils in the scientific literature are very limited.[8] This may be because required sampling methodology only recently has been published.[29] The infrequent and sudden nature of smoke-in-cabin incidents makes exposure measurements challenging, although specially designed incident samplers recently have been described.[30,31] However, there is also a need for investigation of possible OP contamination in cabin air in general.

The aim of this study was to determine the contamination levels of OPs originating from hydraulic and turbine oils in aircraft cabins during ordinary flights, including eventual incidents. A sub-aim was to develop, evaluate, and apply new methodology to be included as potential samplers, to obtain both short-term and long-term methods based on traditional air monitoring approaches as well as on surrogate methods giving indirect measures of OP air contamination.

2 Experimental

2.1 Materials and reagents

The use of organophosphates, solvents, adsorbents, pumps, filter cassettes and filters has been described previously.[8] Millex®HV filter units were purchased from Millipore Corp. (Billerica, MA, USA), 3M™ aluminium foil tape from 3M Corp. (St Paul, MN, USA), Klinion® 5 × 5 cm sterile non-woven compresses from Medeco BV (Oud-Bejerland, The Netherlands), and Leukosilk® tape from BSN medical GmbH (Hamburg, Germany). Zorflex® FM50K knitted activated charcoal cloths (ACC) and high-efficiency particulate air (HEPA) filters (Pall Aeropower Corp., Port Washington, NY, USA) were kindly donated by Chemviron Carbon (Houghton-le-Spring, UK) and one of the airline companies, respectively. The cold trap system including additional glassware was purchased from KGW-Isotherm (Karlsruhe, Germany).

All oil samples were obtained from the airline companies and the oil types and compositions of organophosphates used in the aircraft models included in this study are shown in Table 1. According to the material safety data sheets (MSDSs) the 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. All turbine oils contained ≤5% TCP.

2.2 Chemical analyses

Determinations of OPs from all sampling methods were performed using gas chromatography electron ionization mass spectrometry (GC-EI-MS) with *m*/*z* target ions of 99 (TiBP, TnBP, TnAP), 175 (DBPP), 326 (TPP) and 368 (all TCP isomers), according to a previously described method.[8,29] This method utilizes a Varian VF-5ms capillary column for separation of OPs with 1 μL splitless injection and elution times up to 13 min (oven temperature 40–320 °C). The method's limit of detection for the OPs in solvent was 3 ng mL^{-1}. Total-VOC (tVOC) was determined using thermal desorption (TD) and GC-EI-MS as described previously,[8] and specific components were only determined in cases where they were distinctive in the chromatogram.

2.3 Development of new sampling methods

2.3.1 Wipe sampling. In laboratory experiments, six mounted units of 1 × 0.5 dm^2 areas of aluminium tape were cleaned and spiked with 100 μL of 30 μg mL^{-1} TiBP, TnBP, DBPP, TPP, and TCP (dissolved in DCM). The solvent was allowed to vaporize for at least 10 min and wipe compresses were moistened with approximately 1 mL DCM. The sample area was wiped according to a three step procedure by wiping the whole area with a medium pressure in the direction of the aluminium tape with the compress folded once (2.5 × 5 cm^2). The procedure was repeated after unfolding and refolding of the compress in the opposite direction. The wipe compress was transferred into a glass vial and sealed with a screw cap with a polytetrafluoroethylene membrane. The procedure was repeated with a second wipe compress. Each compress from the wipe sampling was extracted in 3 mL DCM solution with 3 μg mL^{-1} TnAP as internal volumetric standard and placed in an ultrasonic water bath for 15 min prior to determination of OPs. Recoveries of OPs present on the combined wipe samples relative to the amount applied on the surfaces were calculated.

2.3.2 Activated charcoal cloth sampling. Sampling recovery of OPs on activated charcoal cloths (ACC) was evaluated in the laboratory using six 5 × 5 cm^2 Zorflex® cloths spiked with 10 μL of 0.3 mg mL^{-1} TiBP, TnBP, DBPP, TPP, and TCP (dissolved in DCM). The DCM solvent was allowed to vaporize for at least 10 min, prior to extraction of OPs in 6 mL mixture of DMF

Table 1 Overview of the content of organophosphates in hydraulic and turbine oils for all aircrafts and by sampling spots

	Organophosphates		Sampling spots		
Aircraft models[a]	Hydraulic oil	Turbine oil	Cockpit	Cabin aft	Galley aft
Jet airplanes					
A	40–70% DBPP,[b] 20% TnBP[c]	<2.5% TCP[d]	X		X
B	40–70% DBPP, 20% TnBP	1–5% TCP	X	X	
Propeller airplanes					
C	60–80% TnBP, 1–5% TPP	1–5% TCP	X		X
D	0.1–0.9% TPP	1–5% TCP	X	X	[e]
E	60–80% TnBP, 1–5% TPP	1–5% TCP	X	X	X
Helicopters					
F	0.1–0.9% TPP	1–5% TCP	X	X	[e]
G	0.1–0.9% TPP	1–5% TCP	X	X	[e]

[a] The aircrafts have been grouped by models from different manufacturers. Some of the aircraft models contain resembling sub-models. Model E was not included in the field study measurements, but was encountered in relation to a contamination incident where samples were collected during subsequent ground testing. [b] Dibutylphenyl phosphate. [c] Tri-*n*-butyl phosphate. [d] Tricresyl phosphates. [e] Airplane model D and helicopters (models F and G) are not equipped with a galley.

(100 mL L^{-1}) in CS_2 and 3 μg mL^{-1} TnAP as internal volumetric standard in a 16 mL glass vial using an ultrasonic bath for 15 min.

The recovered amount of OPs was compared to the initial spiked amount. To evaluate the passive adsorption properties of the cloths, 18 pieces (25 cm^2 each) were mounted inside a 0.4 m^3 exposure chamber[29] for passive sampling. The day in advance, the nebulizer that contained an oil sample (olefin base oil with 10 mg g^{-1} of TiBP, TnBP, and TmCP each) had been operated for 30 min where the generated oil aerosol (~50 mg m^{-3}) had been pulled through the chamber. Air was pulled through the chamber for further 30 min after the spray was shut off. Oil film on the inner chamber surface then caused evaporation of TiBP and TnBP (but not TmCP) to the chamber atmosphere. Six cloths were each month removed from the chamber, transferred to a 16 mL glass vial, and prior to determination of OPs extracted in 6 mL of the CS_2–DMF mixture. The amounts of OPs adsorbed to the cloths were evaluated as a function of time (0–90 days). In addition, the OP concentration in the chamber was measured at days 0, 30, 60 and 90.

2.3.3 Characterization of spot samples from HEPA filters. HEPA filters used as recirculation filters in model A airplanes during the study are designed as a multiple folded filter to ensure a large surface area, inside a 45 × 51 × 12 cm^3 aluminium frame. To evaluate the potential of HEPA filter extraction as an indirect method for indications of OP contamination,[7] filter samples (10 g each) were cut from the centre of an unused HEPA filter.

Spike samples were prepared by adding 100 μL of a DCM solution containing 30 μg mL^{-1} of each TCP isomer (ToCP, TmCP, TpCP), while the blind samples were spiked with 100 μL pure DCM, using a 100 μL micro-volume syringe. Subsequent to solvent evaporation for 10 min, the samples were extracted with 220 mL acetonitrile (ACN) and ultrasonicated for 30 min. The extract was transferred through a funnel to a 250 mL Erlenmeyer flask. The remaining filter fraction in the funnel was washed with another 50 mL ACN and compressed with a glass tool to extract as much as possible of the absorbed solvent, prior to mixing with the first extract. The final extract was in three aliquots transferred to a 150 mL round-bottom flask, and each aliquot of approximately 100 mL solvent was evaporated using a vacuum system connected to a cold trap filled with liquid nitrogen to trap the evaporated solvent. The final residue was extracted twice with 5 mL ACN and transferred to a 16 mL glass vial. Further 2 mL ACN was added to the round-bottom flask to ensure complete residue transfer. The dissolved residue was then filtered through a 0.45 μm Millex®HV filter unit into a new glass vial, and the solvent was evaporated in a stream of N_2 gas directly in the glass vial under slight heating (40 °C). This final residue was dissolved in 3 mL DCM with internal volumetric standard (3 μg mL^{-1} TnAP). Recoveries of OPs from the filter sampling spots were evaluated by analyzing three unexposed (blinds) and three spiked sample spots.

2.4 Field study

2.4.1 Selection of airline companies and aircrafts. Four airline companies in Norway were invited to participate in the study, and all of them accepted the invitation. The companies were selected based on their variety in aircraft fleets in order to include a broad selection of aircrafts which were considered to be representative for the commercial aircraft fleets in Norway. The study comprised 40 unique aircrafts distributed on jet airplanes, propeller airplanes, and helicopters (Table 2).

2.4.2 Sampling strategy. Only stationary sampling was performed, because the cabin crew and pilots for practical and safety reasons were restricted from wearing personal samplers during commercial flights. Sampling spots were also restricted because sampling equipment should not be observed by passengers. Thus, the sampling spots (Table 1) were located beneath the ceiling in the centre of the galley aft (on the wall towards cabin) and in the cockpit on the wall behind the pilot seat. Cabin aft sample spots were located in the ceiling in the rear of the cabin.

The individual aircrafts were selected in collaboration with operation managers, health safety executive (HSE) personnel, and principal employee representatives. The aircrafts of interest were identified the day before each air sampling. To reduce the complexity of the field logistics, only aircrafts staying at the airport overnight and those that were scheduled with returns to

Table 2 Summary over number of unique aircrafts of each aircraft model, *n*, and of specific samples collected in these aircrafts, *k*, included in the field study

Aircraft models	Filter/ads. OPs[a] *n* (*k*)	TD tube tVOC[b] *n* (*k*)	ACC[c] OPs *n*(*k*)	Wipe OPs *n* (*k*)
Jet airplanes				
A	15 (30)	15 (30)	14 (30)	14 (30)
B	9 (22)	—	—	—
Propeller airplanes				
C	6 (12)	6 (12)	6 (12)	6 (12)
D	6 (12)	6 (12)	6 (12)	6 (12)
Helicopters				
F	1 (7)	1 (7)	—	—
G	3 (12)	3 (12)	—	—
Total	40 (95)	31 (72)	26 (54)	26 (54)

[a] Sampling of organophosphates. [b] Total volatile organic compounds (sampling with TD tubes). [c] Activated charcoal cloth.

the same origin at the end of the next day were included. Measurements were carried out on flights from one Swedish and eight Norwegian airports during a period of two years.

2.4.3 Sample collection. The set of samplers included both established sampling methods and newly developed methods, and comprised of active air-pulled combined filter/adsorbent methods, VOC thermal desorption adsorbent tube samplers, tailor-made incident samplers, wipe sampling from cabin wall surfaces, trapping on activated charcoal cloths mounted on cabin wall surfaces, and finally extraction of aircraft air supply HEPA recirculation filters. Table 2 shows the extent of the different sampling methods distributed on the various aircraft models.

Active sampling on combined filter/adsorbent train. OPs were collected on a glass fiber filter in a 37 mm closed-faced aerosol cassette in serial up-stream to a Chromosorb 106 glass adsorbent tube to retain aerosols and vapors, respectively, using an in-house made pump at a flow rate of 1.5 L min^{-1}. This was in accordance with a previously published method.[29] The sampling equipment was installed at night when the aircrafts were not in operation. The sample pumps were started the following day after removal of caps and nuts from the sampler heads, at latest 30–60 min before the first flight of the day, or between two flights later that day, depending on the planned sampling duration (4–10 hours). In general, two samples were collected in each aircraft at each event, from a total of 40 unique aircrafts. The general limit of quantification (LOQ) for OP in air was 75 ng m^{-3} based on a four hour sampling time and assuming total recovery on the filter only.

Active VOC sampling. VOCs were collected on stainless steel thermal desorption (TD) adsorbent tubes packed with Tenax TA 60/80 mesh adsorbent material at a flow rate of 50 mL min^{-1}, according to a previously published procedure.[8] The sampling duration was 2–10 hours. In general, two samples were collected in each aircraft at each event, from a total of 26 unique aircrafts.

Incident sampling. Ten previously described incident samplers[30] were distributed in the cockpits of ten preselected aircrafts within a period of 12 months for sampling during potential sudden and unexpected incidents.

Wipe sampling. In general, two aluminium tape wipe areas (3–6 dm^2, dependent on space available) were established on the cockpit and galley walls in each airplane, in a total of 26 unique airplanes. The area was after installation wiped twice with compresses, and analysis of the second wipe was always performed to ensure that the wipe area initially did not contain OPs.

The wipe sampling areas were allowed to be exposed for a period of 1–3 months. Two field blind wipe compress samples were collected subsequent to the first cleaning procedure and in advance of the second wipe treatment of the exposed area. These field blind compress samples were only moistened with DCM and folded prior to transfer to the glass vials. The glass vials with compress samples were stored in a freezer within 48 hours and kept frozen until analysis. The contamination levels were calculated based on the absolute mass of each OP recovered by extraction from the wipes, divided by the surface area and days of exposure (ng dm^{-2} per day). LOQ for the wipe sampling was 0.008 μg dm^{-2} based on a wipe sampling area of 10 × 35 cm^2.

Activated charcoal cloth sampling. Activated charcoal cloths (ACC) (12 × 12 cm^2) were mounted to the cabin wall using a 2 cm wide Leukosilk® tape that covered 1 cm along the circumference of the cloth, leaving a 10 × 10 cm^2 cloth area as active surface. Each cloth was mounted close to the aluminium foil tape wipe area, in order to allow comparisons between the two approaches. Furthermore, the cloth was installed 10 min after the installation of the aluminium foil wipe area, in order to prevent contamination of solvent vapor from the initial wipe area cleaning procedure.

The charcoal cloths were allowed to be exposed for a period of one to three months, and were collected at the same period of time as the wipe samples. However, the charcoal cloths were dismounted prior to wipe samples, in order to avoid solvent contamination. The cloth was cut out of the tape frame using a scalpel and immediately transferred to a glass vial. To obtain a field blind sample, a new cloth was subsequently taped to the same spot and immediately demounted and transferred to a second glass vial. Further sample treatment was carried out in accordance with the previously described procedure.

In general, two sampling areas were established in each aircraft, in a total of 26 unique aircrafts. The contamination levels were calculated based on the absolute mass of each OP recovered by extraction from the wipes divided by the surface area and days of exposure (ng dm^{-2} per day). LOQ for the ACC sampling was 0.11 μg dm^{-2} based on complete recovery from a cloth area of 10 × 10 cm^2.

Characterization of spot samples from HEPA filters. New HEPA-filters were installed into six unique airplanes (model A) by a qualified technician to ensure clean treatment of the filters. Clean nitrile gloves were used to prevent contamination to the filters during handling, and the filter hatch was equipped with warning signs to ensure that no technicians should interfere during the installation period of 1–3 months (corresponding to 200–600 flight hours). The exposed HEPA filters were uninstalled by the same technician and put into the plastic bag and

cardboard box that the replacing recirculation filters were delivered in. The filters were then collected from the aircraft hangar within two working days and later stored in a storage room up to three months prior to analysis. An unused HEPA filter that had been installed into and immediately removed from an airplane, served as comparison.

One spot sample (10 g) was cut from the centre of each of the six HEPA filters and from the field blind filter, and were processed according to the previously described procedure. The contamination levels were calculated based on the absolute mass of each OP recovered from the spot sample divided by the mass of the HEPA filter spot sample and flight hours (ng g^{-1} per h).

2.5 Statistical analyses

When the minimum or median OP values were below the LOQ, this is for practical reasons expressed by the term "<LOQ" because the LOQ of each individual OP depends on the sampling time.

For the included groups of samples, standard measures of central tendency and distributions were calculated (median, minimum, maximum, and 90th percentile). The non-parametric two-independent sample test (Mann–Whitney *U*-test) was applied to assess the level of statistical significance between two groups (confidence interval of 95%). Dixon's *Q*-test was applied to identify outliers. Origin® (OriginLab Corp., Northampton, MA, USA) was used for calculation of Pearson's correlation coefficient (*R*) and studentized standardized residuals from linear regression plots. SPSS version 17.0 for Windows (SPSS Inc., Chicago, IL, USA) was used for all statistical analyses.

3 Results and discussion

3.1 Development and evaluation of passive long-term sampling methodology

Air sampling of oil mist and VOCs has been well described,[8,32–34] while methods for air sampling of OPs originating from hydraulic and turbine oils have not been published in the peer-reviewed scientific literature until recently.[29,31] Methodology for long-term sampling of OPs and spot sampling from HEPA filters was, however, not available, necessitating method development and evaluation prior to field use.

3.1.1 Wipe sampling. Different wipe sampling methods have previously shown potential for measurement of dermal exposures and deposited contaminants on surfaces.[35–38] Non-authorized wipe spot sampling of OPs from aircraft walls has also previously been tested to a limited extent, where TCP was detected.[39] However, the surfaces on the interior walls in aircrafts are often made of different types of polymeric materials with the potential of being dissolved in wipe compress organic solvents. Moreover, the surfaces' adsorbent properties and wipe recovery are unknown and may also vary between different aircrafts. Therefore, we used aluminium tape which resists organic solvents, to achieve a uniform surface material for all sampling spot areas. DCM has previously shown excellent solubility properties for the OPs of interest and compatibility with the GC-MS method in use, and is used for extraction of OPs from glass fiber filters.[29] DCM was thus initially evaluated as wipe compress solvent and extraction solvent to extract OPs. Non-woven compresses have previously been reported as superior to other wipe materials,[40] and were thus explored in the present study as well.

The recovered amounts of OPs from the wipe surface were compared to the initial spiked amount, yielding recoveries of 94–103% (RSD 3–6%) for all alkyl (TiBP, TnBP, DBPP) and aryl (TPP, TCP) phosphates included in this study, supporting that wipe sampling with DCM as solvent is suitable for indirect measurements of OPs originating from lubricants. Analysis of blank sample compresses confirmed no interfering background.

3.1.2 Activated charcoal cloth sampling. Wipe sampling is in general only fully suitable for non-volatile components, and there was thus a need to include methodology for trapping of the more volatile OPs and potential thermal decomposition product. ACCs[41] have previously been explored for several applications, such as air and water filtration[42,43] and passive dermal sampling.[44–46] Morover, ACCs are manufactured from a textile precursor,[41] taking advantage of textile characteristics with respect to the shape, size and large surface, in addition to the activated carbon adsorbing properties. ACC sampling was therefore evaluated for passive long-term sampling of OPs from cabin air. Different types of ACCs were initially evaluated for their strength, physical robustness and chromatographic background noise from blank cloth extracts. The knitted Zorflex® FM50K cloth was proven to possess a high degree of robustness, as opposed to woven cloths which easily unraveled during handling. Furthermore, this cloth is convenient to handle during extraction procedures, with minimal interfering chromatographic background noise. The FM50K also has a large activated carbon surface, illustrated by a total surface of 1300–2000 m^2 for 10 × 10 cm^2 cloth,[47] and was thus selected for the extended evaluations as described.

Adsorption of the aryl phosphates to the ACC was strong, and none of the initially evaluated solvents or solvent mixtures (CS_2, CS_2–DMF, toluene, DCM, methyl-*tert*-butyl ether, methanol) provided complete extraction of these components from the cloths under investigation. The recoveries of the aryl phosphates on the FM50K cloth ($n = 6$) were 25 ± 2% (TPP), 61 ± 2% (ToCP), 43 ± 2% (TmCP) and 32 ± 2% (TpCP) when using the optimum solvent combination (100 mL L^{-1} DMF in CS_2). The use of higher portions of DMF, which might improve the extractions, was restricted by increasing peak fronting effects in the chromatogram. Nevertheless, the good precision of the method allowed for use of correction factors based on the individual recoveries. The alkyl phosphates, however, were nearly fully recovered from this cloth illustrated by recoveries in the range 94–98% ($n = 6$, RSD 1.5–2.2%) when using the same solvent mixture, which is in accordance with our previous experiences on extraction of OPs from charcoal adsorbents.[29]

The Zorflex® FM50K cloths were subjected to a long-term exposure experiment in an exposure chamber with a TiBP and TnBP layer on the inner surface of chamber, resulting in continuous release of these semi-volatile OPs to the chamber atmosphere. The air concentrations of TiBP and TnBP in the chamber were measured monthly. Air concentrations of TiBP and TnBP at day 0 were 9.2 and 5.8 μg m^{-3}, respectively, with a linear declining tendency of approximately 0.041 ($n = 3$,

$R = 0.993$) and 0.035 μg m^{-3} ($n = 3$, $R = 0.995$) per day throughout the test period of three months. At the same occasions ($n = 3$) six cloths were removed from the chamber, and the adsorbed masses of TiBP and TnBP on the cloths were measured. The average TiBP and TnBP levels on the cloths each month revealed a linear uptake of 7.7 ($n = 3$, $R = 0.997$) and 4.1 μg dm^{-2} ($n = 3$, $R = 0.998$) per day, respectively (linear regression, forced intercept in origo, RSD 9–19%). Thus, the OP uptake was apparently not affected by the concentration drop during the sample time period, illustrating the rather limited potential of such methods for quantitative measurements only. The monthly collection of the air samples may also have contributed to the concentration drop in the exposure chamber.

3.1.3 HEPA-filter analysis. HEPA filters are used in aircrafts for filtration of the recirculated air and to remove airborne particulates, including bacteria and viruses. Typically 50% of the incoming air is mixed with the recirculated air that passes the HEPA filter, giving a mixture of bleed air and filtered recirculated bleed air as air supply to the cabin.[5] The HEPA filter may retain non-volatiles, and determination of TCP from HEPA filters may therefore represent an indirect measure of OP presence in cabin air.[7] The relative long-term use of the HEPA filters make available an indirect measure of contamination over time, and a relation to flight hours allows for semi-quantitative approaches.

The large surface of the HEPA filter restricted extraction of the whole filter. Thus, a spot of approximately 10 g in the centre of the filter was cut out to serve as sample. DCM was initially evaluated as extraction solvent, based on our previous positive experiences with this solvent for extraction of OPs from glass fiber filters.[29] However, DCM was unsuitable as extraction solvent from the HEPA filters due to that polymeric material in the filter was dissolved and subsequently clogged the filters used during sample preparation. Methanol did not completely wet the filter and was also discarded as extraction solvent. The use of ACN, however, did not result in such problems, and provided nearly full recovery of the TCP isomers in the range 96–109% ($n = 3$, RSD 1.8–2.4%) based on spiking experiments. A comprehensive multiple step sample preparation procedure was necessary in order to obtain high recoveries. The final step was evaporation of the ACN solution to dryness prior to redissolving in a smaller volume of GC method compatible DCM, providing enhanced method sensitivity by a concentration factor of 100.

3.2 Field study

None of the aircrafts included in the study were reported to experience unusual contamination incidents during the study period. Thus, the measured levels reported in this study are considered representative for normal flight conditions.

The OP content in the oils in use in the investigated aircrafts given by the MSDSs was generally confirmed by OP determination of some of the oil batches under study. However, some small quantitative differences in content between different batches of the same oils have previously been reported.[8] Furthermore, low concentrations of certain OP components can potentially be present in the oils while still not be listed in the MSDSs.[48,49]

A major logistic challenge is the limited potential for planning and completion of activities according to the protocol. Sudden alterations in flight schedules were frequent, and the demand for flexibility for the airline companies had to be taken into account in the study design. Thus, long-term detailed planning of sampling was not an option. Flight routes for specific aircrafts were frequently altered after initiation of short-term sampling equipment, resulting in rejection of samples collected from aircrafts that were routed to another airport than first scheduled. Furthermore, different intervals between major maintenances of the aircrafts also contributed to the rejection of long-term passive samples in cases where these samplers were installed in aircrafts that were subjected to maintenance during the sampling period.

3.2.1 Within-day sampling of OPs and VOCs from cabin air. In general, the OP levels in the within-day samples collected in cabin and cockpit air during commercial flights were low. TCP, which was present in all turbine/engine oils in use in the aircrafts included in this study, was determined in four out of 95 samples (4.2%), all of them from model C airplanes (median <LOQ, min–max <LOQ–0.29 μg m^{-3}). No *ortho*-isomers of TCP were identified. TPP, which is used only in the hydraulic oils of the propeller airplanes and helicopters included in the study, was detected in one out of 43 (2.3%) of these samples (0.11 μg m^{-3}, model C).

TnBP, which was in the hydraulic oils of all aircrafts in this study, except in model D airplanes and the helicopters (models F and G), was detected in all samples collected during airplane flights ($n = 76$, median 0.44 μg m^{-3}, min–max 0.024–4.1), and in 58% of the helicopter flights ($n = 19$, median 0.091 μg m^{-3}, min–max <LOQ–1.5), as shown in Table 3. The TnBP levels in samples from model A airplanes (median 1.1 μg m^{-3}, min–max 0.41–4.1) were significantly higher ($p < 0.001$) than those from model B (median 0.16 μg m^{-3}, min–max 0.02–1.0) and C (median 0.54 μg m^{-3}, min–max 0.23–0.96) airplanes. This might be explained by differences in the hydraulic system between the airplane models.

The TnBP levels in the aircrafts using hydraulic oils containing TnBP were significantly higher than in model D airplanes and the helicopters ($p < 0.001$), which possibly are subjected to TnBP mainly released to air from hydraulic oils in use in other aircrafts at the airport. However, the TnBP levels shown were different in one of the aircraft models depending on the sampling location, and were significantly higher ($p = 0.025$) in the cockpit than in the galley, respectively, of model C airplanes ($n = 6/6$, median 0.71/0.41 μg m^{-3}). This is probably due to differences in vicinity to the emission source(s) and/or effects possibly related to ventilation and differences in air exchange between cockpit and cabin/galley.

DBPP was a hydraulic oil ingredient only in model A and B airplanes and was detected in 47 out of 52 samples from these airplanes. However, DBPP was also detected in all samples from model C airplanes. The DBPP concentration levels in the model B airplanes (median 0.046 μg m^{-3}, min–max <LOQ–0.31) were significantly lower ($p < 0.001$) than in model C (median 0.13 μg m^{-3}, min–max 0.076–0.23) and model A airplanes (median 0.20 μg m^{-3}, min–max 0.07–0.77). The increased DBPP levels in model C aircrafts may therefore be due to continuous air sampling during subsequent flights, which also included the time

Table 3 Summary of within-day cabin air TnBP levels (μg m^{-3}) in the specific aircraft models included in the field study

	Jet airplanes		Propeller airplanes		Helicopters	
Aircraft models	A	B	C	D	F	G
k^a	15	9	6	6	1	3
n^b	30	22	12	12	7	12
%>LOQ	100%	100%	100%	100%	57%	58%
Median	1.1	0.16	0.54	0.07	0.06	0.05
Minimum	0.41	0.02	0.23	<0.03	<0.06	<0.04
Maximum	4.1	1.0	0.96	0.23	1.5	0.20
90th percentile	2.1	0.38	0.83	0.20	0.69	0.08

^{a} Number of unique aircrafts. ^{b} Number of measurements.

on ground and subjection to the surrounding air at the airport. On the contrary, for the long-distance flights with model B airplanes, the sampling included only the time between takeoff and touchdown. Moreover, the DBPP levels in model A airplanes were significantly higher than in model C airplanes ($p = 0.032$) which is as expected due to the use of DBPP in hydraulic oils in model A airplanes only. DBPP present in model C airplanes may therefore be due to contamination from model A and B airplanes and the surrounding air. DBPP was only detected in one (0.25 μg m^{-3}) out of 19 samples from helicopters and in none of the samples from model D airplanes in accordance with the use of non-DBPP hydraulic oil. Moreover, these aircrafts were operating at locations separated from model A and B airplanes, avoiding a general background concentration level of DBPP (and TnBP).

None of the oils used in this study was reported in the MSDSs to contain TiBP, although TiBP is known to be added as optionally minor amounts in hydraulic oils also containing TnBP.[48,49] TiBP was still detected in some of the samples, and was most prominent in model A airplanes by detection in 24 out of 30 samples (median 0.036 μg m^{-3}, min–max <LOQ–0.20). However, TiBP was also detected in 12 out of 19 helicopters (median 0.084 μg m^{-3}, min–max <LOQ–1.0) and in two model D airplanes (0.093, 0.11 μg m^{-3}), which were not significantly different from TiBP levels in model A airplanes ($p < 0.05$). This may indicate that TiBP, as well as some of the other OPs, is not originating from the oils only, but might also be present as contaminants due to their use as plasticizers and fire retardants in many materials with potential for emission to the cabin air.[50,51]

Levels of tVOC in cabin air have previously been reported to be in the range 0.01–4.4 mg m^{-3}, and the tVOC level is traditionally used as a general indicator for cabin air quality.[7] The tVOC levels in the present study were in the same range (0.20–2.7 mg m^{-3}, Table 4), supporting a statement that the samples were collected under normal flight conditions. Furthermore, it is important to interpret the OP measurements in relation to the tVOC levels.

The highest median tVOC concentration of 1.8 mg m^{-3} was measured during model G helicopter flights, and the concentration levels in model G helicopters were significantly higher than in model A, C, D, and F aircrafts ($p < 0.05$).

Toluene was the main component determined in all helicopter samples in the concentration range 0.01–0.58 mg m^{-3}, which corresponded to 1–33% of the tVOC concentrations, and stood out distinctly in most of the chromatographic profiles. Similar distinctive components were not identified in the airplane VOC samples, which showed a uniform distribution of numerous components in their resulting chromatographic profiles.

Incident sampling. During the study period, none of the ten preselected aircrafts where the incident samplers were installed experienced sudden and unexpected contamination incidents in cabin or cockpit air. Thus, the incident samplers were not activated during such incidents and no corresponding samples were available for chemical analysis.

3.2.2 Long-term sampling. Wipe ($n = 56$) and ACC ($n = 56$) passive samples were collected in pairs from cockpit and galley/cabin aft in model A, C, and D airplanes (Table 5). None of the aircrafts where passive long-term sampling was performed were reported to experience any contamination incidents during the study period.

Wipe sampling. Table 5 shows the measured OP concentrations from the wipe samples. Wipe sampling in general favors sampling of non-volatiles, such as the aryl phosphates TCP and TPP. TCP was in use in the turbine oils for all the investigated aircraft models. There were, however, some differences in TCP levels between the aircraft models under study. In model C airplanes, deposited TCP concentrations were determined in 92% of the collected samples with a median concentration of 2.3 ng dm^{-2} per day. Pumped within-day OP measurements from the same model C airplanes revealed TCP levels >LOQ in 33% of the samples, illustrating the potential of passive TCP wipe sampling for semi-quantitative long-term sampling. There was no significant difference between the measured TCP levels collected from cockpit (median 2.8 ng dm^{-2} per day, min–max 2.2–4.1) and galley (median 1.4 ng dm^{-2} per day, min–max 0.2–3.6) of model C airplanes. TCP was determined in 31 and 8% of the samples collected from model A and D airplanes, respectively. The highest TCP level (8.3 ng dm^{-2} per day) was, however, collected in a model D airplane. No *ortho*-isomers of TCP were found in any of the wipe samples.

TPP was only in use in hydraulic oils in two of the airplane models (C and D) and in the helicopters. TPP was determined in 75 and 92% of the model C and D airplanes, respectively, displaying medians of 0.61 and 0.90 ng dm^{-2} per day. TPP was also determined in 66% of the model A airplanes, although with a lower median of 0.37 ng dm^{-2} per day, probably reflecting general background levels of TPP from various sources.

Table 4 Summary of cabin air tVOC levels (mg m^{-3}) in the specific aircraft models included in the field study

	Jet airplanes	Propeller airplanes		Helicopters	
Aircraft models	A	C	D	F	G
k^b	15	6	6	1	3
n^c	29	12	11[a]	7	12
Median	0.72	0.56	0.91	0.61	1.8
Minimum	0.46	0.49	0.42	0.38	0.42
Maximum	1.3	1.0	1.3	0.88	2.7
90th percentile	1.1	0.83	1.2	0.86	2.6

[a] One outlier has been removed (3.9 mg m^{-3}), sampled from cockpit (Dixon's Q-test). [b] Number of unique aircrafts. [c] Number of measurements.

The more volatile alkyl phosphate TnBP is in use in hydraulic oils in model A and C airplanes, and was determined in 38 and 58% of these samples, respectively. DBPP used in hydraulic oils in model A airplanes was determined in 50% of these samples. Background levels of TnBP (0.30 and 0.32) but not DBPP were, however, determined in 2 out of 12 model D airplanes. OPs were not recovered from the blank samples.

Activated charcoal cloth sampling. The measured OP concentrations from the ACC samples sampled parallel to the wipe samples illustrate high recoveries also for the alkyl phosphates (Table 5). TnBP was determined in all ACC samples, also from the model D airplane samples where the hydraulic oils are not supposed to contain TnBP. The TnBP concentration levels in the D airplanes were well below the levels in model A and C airplanes. Significant differences in TnBP concentrations between samples collected in cockpit and cabin ($p < 0.05$) were found for model C (medians cockpit/galley 1200/770 ng dm^{-2} per day) and model A airplanes (medians 1200/740 ng dm^{-2} per day), but not in model D airplanes where the TnBP levels may be due to background levels only. Background levels of TiBP were also determined in all ACC samples. TiBP is in some cases added in minor amounts to the hydraulic oils,[48] at levels not specified in the MSDSs. TiBP is also known as a plasticizer[52] and an ubiquitous compound in the environment.[53]

DBPP, that is only in use in hydraulic oils used in model A airplanes, was determined in nearly all samples, however, at significantly lower levels in model D airplanes ($p < 0.001$). This may be because DBPP (and TnBP) appears as a general indoor contaminant in certain aircraft hangars originating from the hydraulic oils used in model A and C airplanes.[8] Additionally, the higher concentration levels of DBPP in model C airplanes as compared to model D airplanes may relate to the sharing of hangar for model A and C airplanes under study, while the model D airplanes use separate hangars.

TCP was determined in only two (7.8 and 270 ng dm^{-2} per day) out of 56 cloth samples collected in model A airplanes (6%). The wipe samples collected in parallel from these airplanes contained TCP in concentrations above the quantitation limit only in the former sample (0.37 ng dm^{-2} per day). Thus, the highest concentration was measured in the cloth sample, 270 ng dm^{-2} per day, which is substantially higher than in all other collected ACC and wipe samples (max 8.2 ng dm^{-2} per day), supporting a conclusion of contamination of the cloth from an unknown TCP-containing source. This illustrates the vulnerability of ACC sampling from spots that are not completely out of reach from potential direct contact by cabin crew members or technicians during the sampling period.

While TPP was determined in 75% of the ACC samples from model D airplanes, TPP was determined only in the samples collected from the cockpit in the model C airplanes, and not in the galley samples. However, TPP was also determined in 47% of the samples from model A airplanes, although no oils with TPP are supposed to be in use in these airplanes. OPs were not recovered from the blank samples.

Comparison of wipe and cloth sampling. The ACC areas (1 dm^2) were in general smaller than the wipe areas (3–6 dm^2) and were in addition extracted in a four times greater solvent volume, resulting in higher LOQs for the cloth sampling with a factor of 10–20 for the individual OPs.

In order to compare the sampling characteristics of the wipe and ACC sampling methods, parallelly collected wipe and ACC samples containing OPs originating from oils in use in the specific aircrafts were identified. DBPP and TPP were measured simultaneously on parallel wipe and cloth samples from 16 and 9 model A and D airplanes, respectively. Fig. 1 shows that sampling of non-volatile TPP correlates well between wipe and cloth sampling, with a correlation coefficient of $R = 0.97$ (one outlier removed in accordance with a Dixon's Q-test applied on the studentized standardized residuals). However, poor correlation was obtained for the samples containing the semi-volatile DBPP. Furthermore, the DBPP levels on the ACC samples were significantly higher than on wipe samples ($p < 0.05$). Thus, the ACC adsorption properties increase the sampling efficiency of both the semi-volatile and volatile OPs, as opposed to wipe sampling that is based on deposition only and favors sampling of non-volatiles. This is especially evident for TnBP where the measured concentration levels on the ACC samples were 2–880 times higher than the wipe samples collected in parallel for the cases where TnBP was detected on both samples ($n = 21$, median 89, 90th percentile 280 ng dm^{-2} per day). This effect is even more pronounced for the more volatile background contaminant TiBP, which was present in only 4% of the wipe samples and in all ACC samples, despite the lower LOQ for the wipe sampling method.

Despite the universal capabilities of OP sampling and simple handling of samples for the ACC sampling method, wipe sampling is still to be preferred over ACC sampling for the non-volatile aryl phosphates, due to the lower LOQs and higher extraction recoveries for the wipe sampling method.

Table 5 Organophosphate concentrations on long-term (1–3 months) samples (wipe sampling and sampling on activated charcoal cloths), collected in cockpit and galley aft during commercial flights

	Model A airplanes ($k^a = 14$, $n^b = 32$)					Model C airplanes ($k = 6$, $n = 12$)					Model D airplanes ($k = 6$, $n = 12$)				
	TiBP[c]	TnBP[f]	DBPP[g]	TPP[h]	TCP[i]	TiBP	TnBP	DBPP	TPP	TCP	TiBP	TnBP	DBPP	TPP	TCP
Wipe samples															
%>LOQ	6%	38%	50%	66%	31%	0%	58%	67%	75%	92%	0%	17%	0%	92%	8%
Median[c]	*d*	*d*	*d*	0.37	*d*	*d*	0.20	0.25	0.61	2.3	*d*	*d*	*d*	0.90	*d*
Minimum[c]	<0.05	<0.05	<0.05	<0.05	<0.05	<0.10	<0.13	<0.13	<0.13	<0.18	<0.07	<0.07	<0.07	<0.3	<0.07
Maximum[c]	0.42	19	20	15	1.3	<0.24	2.0	1.7	2.6	4.1	<0.3	0.32	<0.3	2.3	8.3
90th percentile[c]	*d*	0.87	1.4	1.6	0.77	*d*	1.0	0.79	2.5	3.8	*d*	0.29	*d*	1.9	*d*
Charcoal cloth															
%>LOQ	100%	100%	100%	47%	6%	100%	100%	100%	50%	0%	100%	100%	83%	75%	0%
Median[c]	96	970	210	*d*	*d*	41	860	190	*d*	*d*	76	110	8.3	2.0	*d*
Minimum[c]	5.9	330	59	<1.3	<1.3	26	490	120	<2	<2	40	56	1.7	<0.8	<0.9
Maximum[c]	390	16 000	970	7.6	270	68	1400	280	4.5	<4	120	500	140	4.7	<4
90th percentile[c]	260	3 100	410	6.2	*d*	63	1 300	250	4.1	*d*	110	480	76	4.3	*d*

[a] Number of unique aircrafts. [b] Number of measurements (wipe/cloth). [c] The unit is mass of compound per area per installation time (ng dm^{-2} per day). [d] Median/90th percentile concentration level was <LOQ. [e] Triisobutyl phosphate. [f] Tri-*n*-butyl phosphate. [g] Dibutylphenyl phosphate. [h] Triphenyl phosphate. [i] Tricresyl phosphates.

Fig. 1 Correlation of normalized TPP concentrations from wipe samples as a function of ACC samples in model D aircrafts (one outlier at $x = 0.49$, $y = 0.91$ not included), yielding a Pearson's correlation coefficient $R = 0.97$ ($R = 0.83$ with outlier included).

3.2.3 Spot samples from HEPA-filters. Predefined spots from HEPA-filters ($n = 6$) from model A airplanes that had been used for 21–86 days (130–470 flight hours) were subjected to analysis to identify possible presence of TCP originating from cabin or bleed air. TCP was determined in all filter samples, supporting an assumption of the general presence of TCP in cabin and bleed air in aircrafts with turbine jet engines. The TCP level in one of the samples (42 ng g^{-1} h^{-1}) was, however, one order of magnitude higher than the levels on the other samples (median 2.6 ng g^{-1} h^{-1}, min–max 1.1–4.3), supporting a hypothesis of the presence of elevated TCP levels at one or several periods in this specific aircraft. Unfortunately, wipe sampling of TCP was not performed in the aircrafts during the installation time of the HEPA filters due to logistics, restricting the possibility for comparison to such measurements. The resulting chromatographic profile of the HEPA filter sample containing high levels of TCP (Fig. 2) displays the presence of the four *meta*/*para*-isomers of TCP. No traces of *ortho*-isomers were found, and TCP was not detected in the blind samples. Data on the long term stability of TCP on HEPA-filters in combination with continuous passing high air flows is not available. Thus, the possibility for losses of TCP from the HEPA-filter over time cannot be neglected.

3.3 Cabin air exposure measurements during engine ground testing after an engine leak episode

During the study period a model E airplane experienced a turbine oil leak with subsequent contamination of the cockpit/cabin air during a commercial flight. The airplane was immediately grounded pending replacement of the engine with leaking seals. Air sampling was performed during ground testing by operating the leaking airplane engine at full thrust both before (30 min) and after (60 min) the engine replacement, aiming to obtain air measurements as representative as possible for a smoke-in-cabin incident. A smell of burned oil was present in the cabin ground testing prior to the engine change. One combined set of OP, oil aerosol and TD samplers were placed in cockpit and galley,

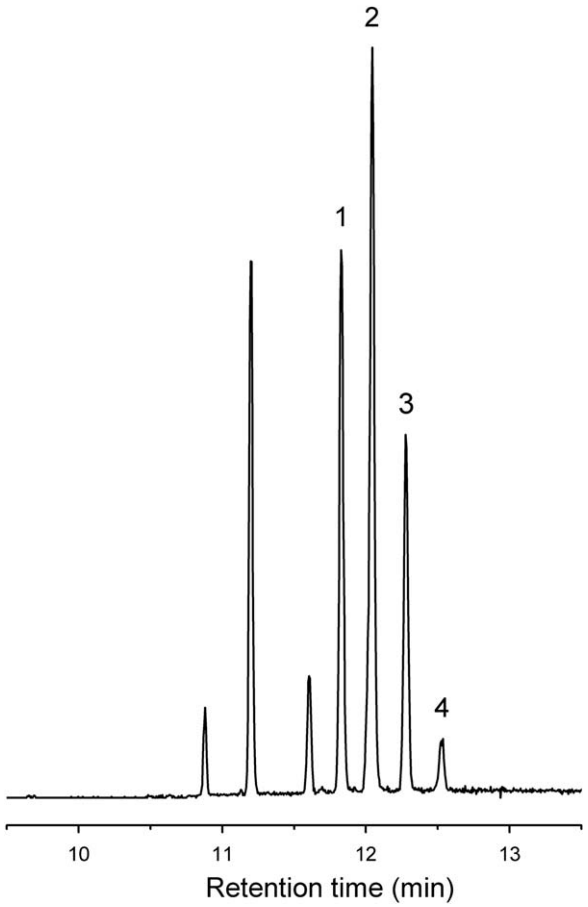

Fig. 2 Chromatographic profile (extracted ion chromatogram, *m/z* 368) from analysis of a model A airplane HEPA filter sample extract, using GC-MS in scan mode. The TCP peaks shown in the chromatogram are: (1) *m*-TCP, (2) *mmp*-TCP, (3) *mpp*-TCP and (4) *p*-TCP. The three peaks to the left were also due to compounds with *m/z* 368 in the mass fragment pattern, but from the mass spectra and analysis in SIM mode were confirmed not to origin from TCP isomers.

respectively, in addition to two extra spots of OP-samplers in the center of the cabin, giving a total of four individual OP samples and two TD/oil samples for each sampling period.

The arithmetic mean of TCP concentrations was an order of magnitude higher before (5.1 ± 1.1 μg m^{-3}, median 5.5, min–max 3.6–5.9) than after (0.47 ± 0.04 μg m^{-3}, median 0.47, min–max 0.41–0.51) replacement of the engine ($p = 0.02$). This difference supports a hypothesis of elevated TCP levels in cabin air during engine leaks resulting in smoke-in-cabin incidents. However, it is speculative to elaborate TCP cabin levels during smoke-in-cabin incidents at flights from these ground testing measurements. No TCP *ortho*-isomers were identified. This is to our knowledge the first TCP measurements reported in relation to an incident.

The oil type in use has in laboratory studies shown the potential for creation of the toxin TMPP at elevated temperatures under conditions resembling engine leaks.[54–57] However, this component was not identified in our measurements.

The tVOC levels were also only slightly increased ($p > 0.05$) after the engine replacement, always displaying concentrations ($n = 4$, 0.25–0.37 mg m^{-3}) well within the tVOC range under normal flight conditions. This observation clearly disclaims conventional TD tVOC measurements as a suitable substitute for tailored OP measurements.

The TnBP levels in the cabin air were not significantly ($p > 0.05$) influenced by the engine replacement, displaying levels in the range ($n = 8$, 2.1–12 μg m^{-3}), while the DBPP levels after the engine change actually significantly decreased ($p = 0.02$) from 0.39 ± 0.07 μg m^{-3} ($n = 4$, median 0.37, min–max 0.32–0.48) to 0.19 ± 0.03 μg m^{-3} ($n = 4$, median 0.19, min–max 0.16–0.22). All oil aerosol/vapor measurements were <LOQ (results not shown), which further adds to the applicability of tailored OP sampling methods.

4 Conclusions

Tailored methods for within-day measurements of OPs in occupational air, as well as newly developed and evaluated long-term methods based on passive deposition, have successfully been explored for determination of potential airborne exposure to OPs in aircraft cabin and cockpit air. Furthermore, the infrequent and sudden nature of potential incidents with resulting exposures of special concern, calls for availability for both short- and long-term sampling. The developed methods used in this study constitute a promising set of samplers for OP measurements in aircrafts in the future.

Although the measured OP levels in the aircraft air in general were low or below the method LOQs, there were some differences between the aircraft models and to some extent between different sampling locations in the aircrafts. The long-term sampling revealed the presence of most of OPs in the cabin air of the investigated aircrafts.

Measurements performed during ground testing of one airplane with a leakage of turbine oil into the cabin air revealed a potential for substantially higher TCP contamination in cabin air during such incidents, indicating that OP contamination is of relevance to smoke in cabin incidents. Further emphasis should be directed towards assessments of OP contamination in relation to such incidents, including potential thermal degradation products.

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