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Article *in* Journal of Environmental Monitoring · December 2010

DOI: 10.1039/c0em00273a · Source: PubMed

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Exposure to airborne organophosphates originating from hydraulic and turbine oils among aviation technicians and loaders

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Received 8th June 2010, Accepted 2nd September 2010
DOI: 10.1039/c0em00273a

This study describes the potential for occupational exposure to organophosphates (OPs) originating from turbine and hydraulic oils, among ground personnel within the aviation industry. The OPs tri-*n*-butyl phosphate (TnBP), dibutyl phenyl phosphate (DBPP), triphenyl phosphate (TPP) and tricresyl phosphate (TCP) have been emphasized due to their use in such oils. Oil aerosol/vapor and total volatile organic compounds (tVOCs) in air were also determined. In total, 228 and 182 OPs and oil aerosol/vapor samples from technician and loader work tasks during work on 42 and 21 aircrafts, respectively, were collected in pairs. In general, the measured exposure levels were below the limit of quantification (LOQ) for 84%/98% (oil aerosol) and 82%/90% (TCP) of the samples collected during technician/loader work tasks. The air concentration ranges for all samples related to technician work were <LOQ-0.24 (oil aerosol) and <LOQ-9.4 (OPs) mg m^{-3}, with the highest OP exposure levels measured during wheel well maintenance. For loader work the corresponding air concentration ranges were <LOQ-2.4 (oil aerosol) and <LOQ-0.052 (OPs) mg m^{-3}, with the highest exposure levels measured during loading from jet engine aircrafts. Investigation of provoked exposure situations revealed substantially higher exposure levels of the contaminants when compared to regular conditions, illustrated by oil aerosol and TCP concentrations up to 240 and 31 mg m^{-3}, respectively. The tailored OP and the general oil aerosol sampling methods were compared, displaying the advantages of tailored OP sampling for such exposure assessments.

1 Introduction

Mineral and synthetic hydraulic oils and lubricants such as turbine oils are used in the aviation industry as pressure- and heat-transferring, anti-wear, anti-corrosion and lubricating media. Most of these oils contain additives, such as organophosphates (OPs) as shown in Fig. 1, to enhance lubrication and anti-wear/anti-corrosion properties.[1,2] Many oils contain the OP tricresyl phosphate (TCP) isomers, as well as other triaryl or trialkyl phosphates, usually at concentrations below 1% (w/w).[2] Jet turbine oils, however, commonly contain higher concentrations of OPs with typical TCP concentration in the range 1–5%.[2,3]

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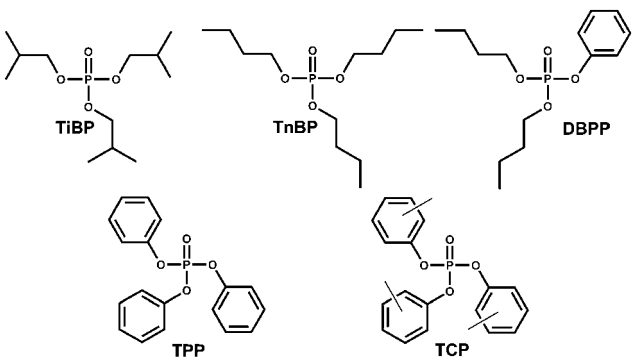

Fig. 1 Structures of triisobutyl phosphate (TiBP), tri-*n*-butyl phosphate (TnBP), dibutyl phenyl phosphate (DBPP) and tricresyl phosphate (TCP).

Environmental impact

The manuscript describes exposure of organophosphates originating from hydraulic and turbine oils among aviation technician and loaders. Exposure to hydraulic and turbine oils have for several years been of concern due to the content of organophosphates and their toxicological properties. Despite the large interest in this topic, no peer-reviewed studies presenting personal occupational exposure measurements of OPs originating from hydraulic and turbine oils or other lubricants exist to the best of our knowledge, probably because methods for tailored air measurements of OPs originating from turbine and hydraulic oils have not been available until recently. The expressed health concerns related to such exposures in combination with the lack of tailored exposure assessments reveal a need for work task related exposure measurements of OPs in the aviation industry in general. This first exposure assessment study focuses on potential OP exposure in relation to loader and technician work tasks.

Synthetic hydraulic oils used in the aviation industry often contain a large fraction of OPs, for instance butyl phosphates, due to the fire resistant properties of such compounds.[4]

Occupational exposure to synthetic and mineral base oils might pose a health risk itself,[5–7] but the oil additives, such as certain OPs, might be of higher toxicological concern. In general, exposure to organophosphorous compounds can cause subacute, delayed and chronic neurological, neurobehavioral and psychiatric syndromes.[8–11] Neurotoxicity following long-term, low-level exposure has also been reported.[12] The neurotoxic effects of the TCP isomer tri-*o*-cresyl phosphate (ToCP) have been well documented,[3,7,13–18] as well as the toxicity of triphenyl phosphate (TPP)[19–24] and tri-*n*-butyl phosphate (TnBP).[24–27] Furthermore, health issues in relation to the possible formation of unknown organophosphorous thermal decomposition products during oil leaks with deposition on hot surfaces such as turbines have been addressed in the literature.[28–35]

OPs in turbine oils have been suggested as major contaminants of concern in airplane cabin air during so called smoke-in-cabin incidents.[35–40] However, exposure to OPs from turbine and hydraulic fluids through vapors and aerosols may also occur during aviation ground personnel working operations.[41] Technician work may include exchange of oils, repair and maintenance of pressurized hydraulic systems and engines. Loaders are loading and unloading luggage close to aircrafts and hot engine tail pipes with a potential for exposure to emission of turbine oil aerosol and vapor, as well as to potential leak sources from hydraulic systems.

Winder has recently reviewed air monitoring studies for aircraft cabin contamination.[42] Despite the large interest in this topic, no peer-reviewed studies presenting personal occupational exposure measurements of OPs originating from hydraulic and turbine oils or other lubricants exist to the best of our knowledge. Only two occupational hygiene reports from two car factories comprising in total eight stationary measurements sampled with a non-validated method have been reported.[43,44] The lack of such publications is probably because methods for tailored air measurements of OPs originating from turbine and hydraulic oils have not been available until recently.[45–47] Due to the health concern, there is thus a need for exposure measurements of OPs in the aviation industry in general, including loader and technician exposure assessments, due to their potential exposure to OPs through their work.

The aim of this study was to assess occupational exposure to OPs, oil aerosol/vapor and volatile organic compounds (VOCs) among aviation technicians and loaders with potential contact with turbine and hydraulic oils, including comparison of the tailored sampling method for determination of OPs with the general oil aerosol/vapor method.

2 Experimental

2.1 Selection of participants and work operation classification

Eight aviation industry enterprises operating in Norway, including airline and ground service companies, were invited to participate in the study. All companies agreed to participate. The aircraft models included in this study were limited by the aircraft fleets of the participating enterprises and comprised different jet and propeller aircrafts (Table 1).

Employees performing technician or loader work tasks with potential for exposure to OPs were selected in collaboration with health and safety executive (HSE) personnel and principal employee representatives, in accordance with the study protocol. One person out of the selected 37 technicians and 10 loaders refused to wear air sampling equipment, and was thus not included in the study. Air exposure samples from technician work operations were collected in the time period of two years, while the samples from loader work were collected during a period of two months.

Specific technician work operations with a potential of exposure to OPs were identified for exposure measurements. Similar work operations were grouped into the work task categories listed in Table 2. The oils and their OP content where classified according to their use in the specific work tasks. Furthermore, the air samples collected from loader work operations were categorized according to the engine type of the aircrafts to be loaded (jet or propeller engines).

Aviation technicians are working with maintenance and repair of aircrafts. Relevant work may include inspections, for instance boroscopy (visual inspection of narrow cavities inside the engine using an optical fiber instrument), handling of oils and different

Table 1 Number of collected personal (P) and stationary (S) organophosphate (OP), oil aerosol and thermal desorption (TD) samples among loaders and technicians according to aircraft model

	Technicians					Loaders					
		Oil		OP			Oil		OP		TD
Aircraft model	Aircrafts (unique)	P	S	P	S	Aircrafts (unique)	P	S	P	S	S
Jet aircrafts											
Boeing 737	31	25	28	25	28	11	44	14	44	14	14
Airbus A320	2	6	5	6	5	5	10	5	10	5	5
Lockheed Martin F-16	2	4	2	4	2	—	—	—	—	—	—
Propeller aircrafts											
Fokker 50	—	—	—	—	—	5	12	6	12	6	6
Bombardier Dash-8	4	8	10	8	10	—	—	—	—	—	—
Beechcraft King Air	1	2	1	2	1	—	—	—	—	—	—
Hercules C-130E/H	2	3	3	3	3	—	—	—	—	—	—
Others (aircraft parts)	—	7	10	7	10	—	—	—	—	—	—
Total	*42*	*55*	*59*	*55*	*59*	*21*	*66*	*25*	*66*	*25*	*25*

Table 2 Oil types and their OP content according to the material safety data sheet. The oils' use in different work tasks is also shown

	Hydraulic oils				Turbine oils			
	A	B	C	D	E	F	G	H
Work operation (n pair of samples)	TPP <1%	TPP <1%	TnBP 70–80%, TPP 1–5%	DBPP 40–70%, TnBP 20%	TCP <5%	TCP <2.5%	TCP 1–5%	TCP 1–5%
Technician work tasks								
Engine maintenance ($n = 28$)			×	×	×	×	×	
Oil filling ($n = 12$)				×		×		
Hydraulic reservoir maintenance ($n = 33$)	×	×	×	×				
Wheel well maintenance ($n = 41$)	×			×				
Loader work tasks								
Jet aircrafts ($n = 73$)				×		×		×
Propeller aircrafts ($n = 18$)	×						×	

types of maintenance. The technicians may be in direct contact with hydraulic and turbine oils during several work operations. A loader turn-around includes luggage unloading, luggage loading and pushing the aircraft out from the tarmac (push-back), making the aircraft ready for taxiing to airstrip.

2.2 Sampling

The numbers of collected personal and stationary samples are shown in Table 1. Personal samples ($n = 242$) were collected close to the workers breathing zone. Stationary samples ($n = 193$) were collected in cases where personal sampling was difficult for practical reasons, or as supplements to the personal samples. Furthermore, 68 stationary samples were collected in close vicinity to point sources such as hot jet engine tail pipes, as well as during provocations such as application of hydraulic oil on hot surfaces to simulate oil leaks, aiming to generate possible worst case air concentrations.

Both oil aerosol/vapor and OP samples were always collected in parallel with a combined filter cassette and adsorbent sampling train method as previously described.[45,48] Oil aerosol was collected on a glass fiber filter (Whatman GF/A, Maidstone, England, UK) with a backup filter of cellulose acetate with 0.8 mm pore size in 37 mm closed-faced styrene acrylonitrile aerosol cassettes (Millipore, Billerica, MA, USA). Oil vapor was collected on Anasorb CSC glass adsorbent tubes (SKC, Blendford Forum, UK) connected in series up-stream to the filter cassette to sample oil vapor and VOCs. Similarly, the OP sampler contained a glass fiber filter and a Chromosorb 106 glass adsorbent tube (SKC) to retain aerosols and vapors, respectively. In-house made air pumps were used for both oil and OP samplers at a flow of 1.4 and 1.5 L min^{-1}, respectively. In total, 228 and 207 parallel samples were collected from technician and loader work tasks, respectively (Table 1).

Loaders were equipped with one oil aerosol/vapor sampler and one OP sampler. The samples were collected for each turn-around with duration of 20–40 min. Two or four loaders carried air sampling equipment during each turn-around. In addition, stationary air sampling in the aircraft cargo rooms ($n = 25$) was performed. These samplers were supplemented with thermal desorption (TD) tubes to collect VOCs, using stainless steel tubes packed with Tenax TA 60/80 mesh adsorbent material operated at a flow rate of 50 mL min^{-1} (SKC PocketPump).

Technicians were also equipped with one oil aerosol/vapor sampler and one OP sampler. 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, such as pouring oil into air craft oil reservoirs or oil dispensers. Thus, 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).

2.3 Analytical procedures

The oil aerosol/vapor and OP samples were analyzed according to previously described methods, based on liquid desorption and Fourier transform infrared spectrophotometry (FT-IR) and gas chromatography mass spectrometry (GC-MS) determinations, respectively.[45,48] Determination of the OP di-*n*-butyl phenyl phosphate (DBPP) was also included in the OP method, using the MS target and qualifier ions of m/z 175 and 286, respectively. The oil vapor samples collected up-stream to the oil aerosol filter were desorbed in 1.5 mL CS_2 and qualitatively analyzed with FT-IR. By presence of hydrocarbons, quantification was performed with GC equipped with flame ionization detection (FID) (Perkin Elmer Autosystem XL, Waltham, MA, USA), using a 25 m × 0.25 mm CP-Sil 8 CB capillary column with 0.25 μm film thickness (Varian, Palo Alto, CA, USA) and 99.9999% helium (Yara Industrial, Oslo, Norway) as carrier gas at a flow rate of 1 mL min^{-1}. The GC-oven temperature program was set at an initial temperature of 40 °C with a linear temperature increase of 6 °C min^{-1} up to 250 °C which was held for 24 min. C_8–C_{18} *n*-alkanes were used as external calibration compounds. The sample components were classified as oil vapor components only if their chromatographic profiles matched the profiles from the individual oil of interest. Otherwise, the components were classified as VOCs.

The TD samples were analyzed with Perkin Elmer ATD 400 automatic thermal desorption injector system and a Hewlett-Packard (Avondale, PA, USA) 5890 Series II GC connected to a HP MSD 5971 electron ionization (EI) quadrupole MS, using a VF-5 ms capillary column (30 m × 0.32 mm with 1 μm film thickness, CP8957, Varian) and helium as carrier gas at a flow rate of 1 mL min^{-1}. All other parameters have been described previously.[47] Quantification was performed as toluene equivalents from an external standard.

Calibration solutions of *n*-alkanes (C_8–C_{18}) in the range 0.3–60 μg mL^{-1} were made by serial volumetric dilution of a stock solution (300 mg of each alkane in 10 mL CS_2) using 1 mL volumetric pipette, 10–100 μL Hamilton glass microvolume syringes (Reno, NV, USA) and 10 mL volumetric flasks. The calibration solutions were stored in glass vials sealed by PTFE screw cap at 5 °C up to 3 months.

The TD calibration solution of toluene (15 μg mL^{-1}) was made by volumetric dilution of a stock solution (15 mg toluene in 10 mL methanol). Seven μL of this diluted standard (105 ng) was injected into a nitrogen stream in a GC-injector at room temperature and was transferred in gas phase onto Tenax TA adsorbent tubes by flushing for 10 min with nitrogen.

2.4 Reagents

TiBP, TnBP, TPP, *N*,*N*-dimethyl formamide (DMF), dichloromethane (DCM) ACS reagent and methanol (purge-and-trap) were purchased from Sigma-Aldrich (St Louis, MO, USA). Tri-*n*-pentyl phosphate (tri-*n*-amyl phosphate, TnAP) was purchased from TCI (Tokyo, Japan). ToCP, TmCP and TpCP were obtained from Acros (Geel, Belgium). DBPP was kindly donated by Solutia Inc. (St Louis, MO, USA). CS_2 glass distilled grade was purchased from Rathburn (Walkerburn, UK). 1,1,2-Trifluoro trichloroethane (Freon 113) was obtained from VWR (West Chester, PA, USA). All reference substances were of 96% purity or greater.

2.5 Statistics

The majority of the measured personal OP samples in this study were in the lower concentration range, with a large fraction of the exposure measurements for some of the OPs below the method limit of quantifications (LOQs). The minimum value is then expressed by the term <LOQ and not by an exact value since the LOQ value varies depending on the sampling time. In order to sort out representative work tasks where a sufficient number of the collected samples contained the relevant OPs (OPs present in the oil in use for the specific work task) for further statistical treatment and table inclusion, a practical lower limit of OP quantitation in ≥75% of the specific samples was chosen as the limit for inclusion in the tables. The remaining measurements might, however, also be of interest as individual or minor groups of individual samples, and are hence discussed individually if considered of specific interest.

Descriptive statistical measurements, such as maximum, minimum, median and 90th percentile concentrations were calculated. Median and 90th percentile in the tables were calculated using a fixed value of 50% of the LOQ for the samples below LOQ. The non-parametric two-independent sample test (Mann–Whitney U-test) was applied to assess the level of statistical significance between two groups. The software package SPSS, version 17.0 (SPSS Inc., Chicago, IL, USA) was used for statistical calculations.

3 Results and discussion

3.1 Organophosphate content in oils

Several hydraulic and turbine oils containing OPs are used within the aviation industry (Table 2). Hydraulic oil A is according to the material safety data sheet (MSDS) composed of mineral oil containing <1% TPP, while the other hydraulic and turbine oils are synthetic oils containing <1 to 5% TPP, 1–5% TCP or 20–80% butyl phosphates, or a combination of these OPs. The OP content in the oils given in the MSDS were confirmed by OP analysis of some of the oil batches under study, displaying only minor qualitative or quantitative differences between the data stated in the MSDS and the analyses. However, there were some small quantitative differences in content between different batches of the same oils. A report from the Norwegian Petroleum Institute states that especially the content of TCP *ortho*-isomers in lubricants has been reduced in the last 30–40 years.[2] In the present study the TCP isomer profile of a new oil batch was compared to the profile of a freshly opened batch of the same oil type that had been stored for approximately 10 years (Fig. 2). The TCP content of the new oil batch with a recent production date was 32 mg g^{-1} (STD = 3 mg g^{-1}, n = 3) where TmCP constituted 22% of the total amount of *meta*/*para*-TCP isomers. The TCP content in the older oil was 21.8 mg g^{-1} (STD = 1.1 mg g^{-1}, n = 3) where TmCP constituted 33% of the *meta*/*para*-TCP isomers, illustrating both the varying content of TCP in the oils in general as well as differences within the isomer distribution. Due to the lack of analytical standards it was not possible to confirm the presence of *o*-isomers of TCP in the oil samples, although the first eluting components in the lower traces of Fig. 2 might be *o*-isomers, in accordance with resembling chromatographic profiles from De Nola *et al.*[49] However, the content of these components in the oils were low (<0.1 and <0.05 mg g^{-1} for old and new oil, respectively).

3.2 Sampling efficiency

The filter in the OP sampling train collects aerosols from the sampled air. Vapors and compounds evaporated from the filter are trapped on the adsorbent. We have previously demonstrated the sampler's sampling efficiency of different OPs, including the distribution of OPs on the filter and adsorbent, based on laboratory spiking experiments.[45] Analyses of the OP samples in the present study showed that the OPs in general were recovered from the filter only, with the exception of 17 out of 414 samples where TnBP also was detected on the adsorbent with masses of 0.2 to 39% of the total TnBP mass (3–880 μg). Thus, the convention of adsorbent up-stream to the filter cassette is necessary to ensure a full recovery of the semi-volatile butyl phosphates. In addition, the hypothesis of generation of possible more volatile OP thermal desorption products of unknown nature necessitates the addition of an adsorbent to the filter sampler, although no such compounds have been identified in this study.

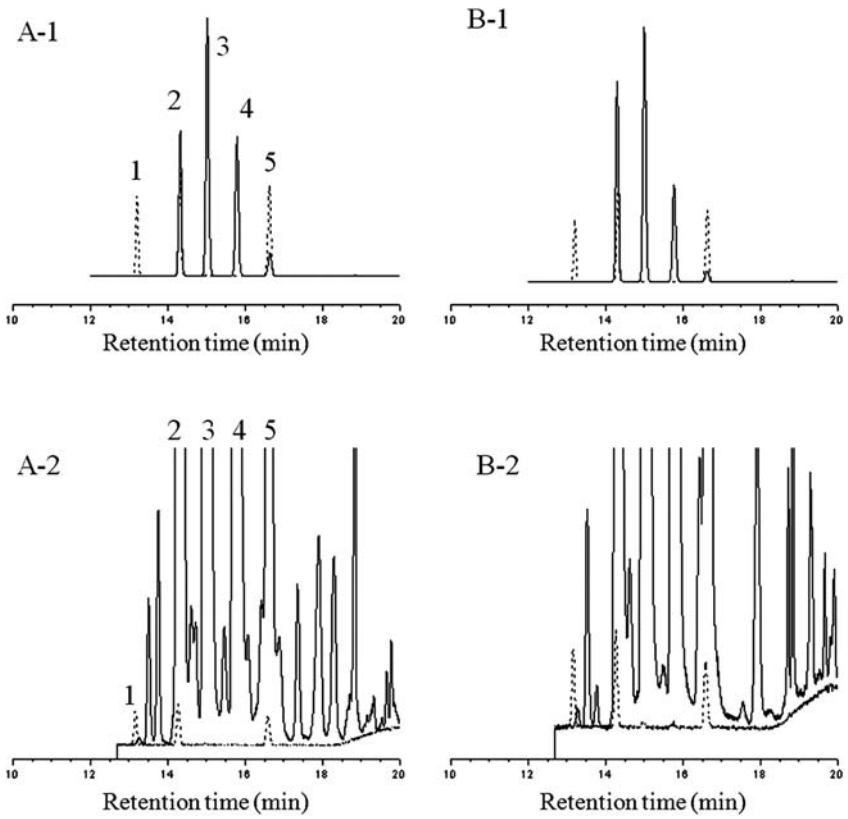

Fig. 2 Chromatographic profiles of the different analyzed oil batches (old, A-1/A-2; new, B-1/B-2) compared to two different standard concentration levels, using GC-MS (SIM mode, *m/z* 368 target ion). Top chromatograms (A/B-1) are compared to a 9 ng (to detector) calibration solution (stapled line), while bottom chromatograms (A/B-2) are compared to a 9 pg (to detector) calibration solution (stapled line). The major peaks shown are: (1) *o*-TCP, (2) *m*-TCP, (3) *mmp*-TCP, (4) *mpp*-TCP and (5) *p*-TCP.

3.3 Exposure measurements

3.3.1 Technicians. Aviation technicians handle turbine and hydraulic oils frequently during various work tasks, in addition to working close to heated and pressurized systems which have a potential to generate oil aerosols or vapors. The technician work tasks were divided into four different major categories, which all consisted of several resembling minor work operations (Table 2). Table 3 shows the air concentrations of OP and tVOC components in cases where ≥75% of the samples related to the specific work tasks were above the methods' LOQ (hydraulic reservoir maintenance work are not included in the table due to presence of OPs in only 8–46% of the samples).

TCP, TPP and oil aerosol were detected only occasionally in the technician work samples. TCP was for instance quantified in

Table 3 The tVOC and the OP exposure levels among technicians only where ≥75%[b] of the samples related to the specific work tasks was above the methods' LOQ

	Personal				Stationary				
	Median	Min	Max	90th perc.	Median	Min	Max	90th perc.	P^a
Engine maintenance	$n = 15$				$n = 13$				
tVOC/mg m^{-3}	3.4	0.050	34	20	0.28	0.047	8.1	6.4	0.30
TnBP/μg m^{-3}	15	5.7	45	38	12	4.2	37	19	0.32
DBPP/μg m^{-3}	3.2	<LOQ	18	15	7.1	<LOQ	13	12	0.32
Oil filling	$n = 6$				$n = 6$				
tVOC/mg m^{-3}	0.54	<LOQ	3.4	2.8	0.43	0.087	1.5	1.3	0.42
TnBP/μg m^{-3}	35	22	56	46	24	9.1	51	46	0.42
DBPP/μg m^{-3}	22	11	35	34	7.8	2.3	27	19	0.025
Wheel well maintenance	$n = 19$				$n = 22$				
TnBP/μg m^{-3}	160	43	9400	1900	180	33	7300	1200	0.96
DBPP/μg m^{-3}	46	0.69	1700	190	23	0.52	430	250	0.21

[a] Mann–Whitney U, non-parametric two-independent sample test (calculated between stationary and personal samples). [b] DBPP and tVOC were 87% (engine maintenance) and 83% (oil filling) in personal samples, respectively, while DBPP was 93% in stationary samples. All other entries were 100%.

only 21 (median 0.36 μg m^{-3}, min–max 0.13–120) out of 114 samples. *ortho*-Isomers of TCP were not determined above LOQ in any of the samples. Of the 114 personal and stationary technicians work task samples, TnBP, DBPP and the other organophosphates were identified in 82% (median 38 μg m^{-3}, min–max <LOQ-9400), 80% (median 7.6 μg m^{-3}, min–max <LOQ-1700) and ≤26% of the samples, respectively. In addition, tVOC, oil aerosol and oil vapor were determined in 68% (median 0.36 mg m^{-3}, min–max <LOQ-34), 16% (median 0.085 mg m^{-3}, min–max <LOQ-45) and 9% (median 0.090 mg m^{-3}, min–max <LOQ-150) of the samples.

The technician work tasks were to a great extent performed in hangars where other work operations were performed simultaneously, possibly resulting in working atmospheres containing several components. Still, the different work tasks were for the most associated with different exposure potential for the different OPs, determined by the oils in use for the specific tasks. Table 4 shows the concentrations of OP in air according to the different oil types used during the specific work tasks. TPP and TCP were determined in only 36 and 24% of the collected samples, respectively. Their maximum measured concentrations were well below those of the butyl phosphates (TnBP and DBPP) which were identified in all samples where they were expected to be present. The different exposure levels between the butyl phosphates and TCP/TPP might be explained by the lower concentration of TCP/TPP in the oils as compared to the butyl phosphates. Also, less vapor formation due to the lower volatility of TCP/TPP as compared to the more volatile butyl phosphates may be an explanation. Visual evaluation of the various work tasks by a trained occupational hygienist did not disclose any large differences between working procedures and cleanliness that can explain these differences.

Considering all technician work samples ($n = 114$), no statistically significant differences were found between the measured concentrations from the personal and stationary samples displayed in Table 3, with the exception of DBPP during oil filling ($p = 0.025$). This significant difference for DBPP and not for TnBP ($p = 0.96$) is difficult to explain, since both compounds originated from the same oil (oil D). However, the general picture is that personal and stationary samples are equivalent, which supports the use of stationary samples as a valid substitute for personal sampling in cases where personal sampling is inconvenient. Thus, stationary and personal samples are statistically treated as equals in the further discussions.

3.3.1.1 Engine maintenance work tasks. During engine maintenance the technicians are working close to the engine. Important engine maintenance work tasks include boroscopy, outside inspections, disassembly and replacement of engine parts, service or repair. These tasks were performed on cooled engine and turbine parts, and vapors due to heating of oils were therefore not expected. However, engine disassembly also included draining of jet fuel and turbine oils (oil E–H) which may result in exposure to the volatile compounds or from generation of oil spray.

Low air concentrations of butyl phosphates (median 9.8 μg m^{-3}, min–max <LOQ-45) were measured during engine maintenance (Table 3), although specific work operations did not include use of oils containing butyl phosphates (oils C and D). Likewise, air concentrations of TnBP (median 15 μg m^{-3}, min–max 9.4–25) and DBPP (median 11 μg m^{-3}, min–max 7.1–18) were determined in all samples collected during engine boroscopy ($n = 10$) performed in hangar, although oils containing butyl phosphates were not in use close to this procedure. This might indicate a general indoor concentration of butyl phosphates. Paralleled collected oil aerosol measurements also supported that the oil aerosol and the butyl phosphates originated from other sources than the local engines. TCP was only quantified in six samples collected during engine disassembly work operations (median 0.82 μg m^{-3}, min–max 0.18–120), and oil aerosol was determined for two of these samples (0.24 and 1.4 mg m^{-3}). TCP was not detected in the 22 other engine maintenance samples, although oil aerosol was detected in nine of these samples (median <LOQ, min–max <LOQ-0.13 mg m^{-3}), most probably due to contributions from other oils than those containing TCP. Total-VOC was determined in all samples ($n = 28$, median 2.7 mg m^{-3}, range 0.05–34) where the highest concentration was measured during engine maintenance work tasks, and could from observations of the work during engine disassembly be explained by extensive spill of jet fuel. Oil aerosol was determined in 39% of the samples ($n = 28$, median <LOQ, range <LOQ-1.4 mg m^{-3}), and the maximum concentration was measured from stationary sampling during engine disassembly.

3.3.1.2 Oil filling work tasks. Oil filling work tasks include draining, filling or replacement of oils (oils D and F), for instance on aircrafts positioned at tarmac or in hangar, or filling of oil dispensers indoors. These tasks possess exposure potential from releases of vapors from the oil reservoirs. Table 3 shows that low air concentrations of TnBP and DBPP were measured during these work tasks ($n = 12$, median 23 μg m^{-3}, min–max 2.3–56). TPP (0.13 μg m^{-3}), TCP isomers (1.4 μg m^{-3}) and oil aerosol (1.1 mg m^{-3}) were quantified only in one parallel sampling during filling of oil F to an aircraft engine. Total-VOC was determined in 11 out of 12 samples during oil filling (median 0.41 mg m^{-3}, min–max <LOQ-3.4) and shows a general VOC background, while oil aerosol was not detected (<LOQ).

Table 4 OP concentrations in air according to the different oil types used (hydraulic oils A–D and turbine oils E–H)

OP	Oil types	*n*	*n* > LOQ (%)	Median/μg m^{-3}	Min/μg m^{-3}	Max/μg m^{-3}	90th perc./μg m^{-3}
Technicians							
TnBP	C, D	68	100	89	9.1	9400	710
DBPP	D	47	100	28	2.3	1700	210
TPP	A, B, C	86	36	<LOQ	<LOQ	150	9.2
TCP	E, F, G, H	37	24	<LOQ	<LOQ	280	12

3.3.1.3 Hydraulic reservoir maintenance work tasks. Hydraulic reservoir maintenance includes inspection and maintenance connected to the hydraulic reservoirs (oils A–C) except in the wheel well. TnBP, DBPP, TPP and TCP were determined in 20–56% of the samples. However, shorter work operation times resulted in shorter sampling times and therefore higher LOQs as compared to for instance Engine maintenance. TnBP was determined in 39% of the hydraulic reservoir maintenance work tasks ($n = 33$, median 0.13 μg m^{-3}, min–max <LOQ-170). The highest personal TnBP exposure levels (oil C) were observed in connection to test bench operations ($n = 6$, median 61 μg m^{-3}, min–max <LOQ-100) and during hydraulic leak searching and tube exchange in wheel wells and under the wings (40 and 170 μg m^{-3}). Still, a potential for higher exposure levels exists, if larger leakages than those observed during the present study occur. Oil aerosol and tVOC was determined in 6% (median <LOQ, min–max <LOQ-1.4) and 45% (median <LOQ, min–max <LOQ-4.2 mg m^{-3}) of the samples ($n = 33$), respectively. The only technician work where oil vapor was detected was during hydraulic reservoir maintenance when a mineral oil (oil A) was used ($n = 8$, median 13 mg m^{-3}, min–max 6.3–150), illustrating the mineral oils' potential for the formation of oil vapor.

3.3.1.4 Wheel well maintenance work tasks. Wheel well maintenance work tasks included pressure drops where the hydraulic system is vented by the opening of a valve on the sidewall in the wheel well, filter exchanges and inspections in wheel wells (oils A and D).

This work task group is associated with the highest measured exposure levels in the study, with maximum TnBP peak concentrations up to approximately 150 times greater than the maximum levels observed during the other work tasks under study (Table 3). The TnBP exposure occurred due to nebulization of oil deposits through the vent port orifice, resulting in contamination of the wheel well atmospheres prior to further work with the depressurized hydraulic systems. The highest exposure concentrations (1–5 min sampling time, max 9.4 mg m^{-3}) were measured during manual opening of a vent port and subsequent pressure drop of the hydraulic system. The TnBP median exposure level (personal and stationary samples) for this specific work operation was 190 μg m^{-3}, while the median for all other long term wheel well maintenance work operations was 115 μg m^{-3}. Thus, long term sampling during the complete work in the wheel well (sampling times 20–255 min) revealed that the initial oil spray was still present in the wheel well for a long time after the pressure drop. However, the TnBP air concentrations in the wheel wells also varied between aircrafts and different operating conditions. The majority of the TnBP exposure in the wheel well may, however, easily be prevented by special precautions, such as to perform venting of the hydraulic pressure at the tarmac prior to taxiing to the aircraft maintenance hangar. TPP, tVOC and oil aerosol were determined in 39% (median <LOQ, min–max <LOQ-150 μg m^{-3}), 56% (median 0.84 mg m^{-3}, min–max <LOQ-14) and 12% (median <LOQ, min–max <LOQ-0.13 mg m^{-3}) of the samples ($n = 41$), respectively.

3.3.2 Loaders. Loaders are loading and unloading luggage close to aircrafts at the tarmac. The aircrafts are usually in continuous use throughout the day, with the engines shut down for only 20–40 min between the flights. The aircraft engines are nearly always in a hot state at the tarmac, allowing vapors and aerosols to be formed from the heated and pressurized hydraulic and engine systems (oils C, D and F–H). Loaders may then be exposed to these oils and their OP additives through inhalation.

The exposure measurements for loaders were divided into two categories depending on whether the work task was performed on jet or propeller aircrafts, due to different oils in use and differences in construction of the aircraft. For instance, the propeller aircrafts engines are not equipped with tail pipe where oil aerosol might be generated. Table 5 shows that TnBP was determined in nearly every personal loader sample ($n = 66$) independent of the engine type. The exposure levels were generally low for TnBP (median 0.98 μg m^{-3}, min–max <LOQ-5.6, 98% > LOQ) and DBPP (median <LOQ, min–max <LOQ-0.84 μg m^{-3}, 38% >LOQ). TCP was determined in only five out of 54 personal samples (median <LOQ, min–max <LOQ-52 μg m^{-3}) when loading from jet aircrafts, but was never detected in samples from loader work operations on propeller aircraft ($n = 12$, <0.7 μg m^{-3}). The maximum measured TCP exposure level was one order of magnitude greater than for the maximum measured TnBP level, illustrating a greater potential for TCP exposure when present in the oils. This potential might increase if

Table 5 Exposure to VOCs, TnBP and DBPP during loader work tasks

	Personal samples					Stationary samples, cargo room				
	n > LOQ (%)	Median	Min	Max	90th perc.	n > LOQ (%)	Median	Min	Max	90th perc.
Jet aircraft	$n = 54$					$n = 19$				
VOC (ATD)/mg m^{-3}	0	[b]	<LOQ	<LOQ	[b]	100	0.19	0.035	2.1	1.1
TnBP/μg m^{-3}	100	1.1	0.38	5.6	2.4	100	1.2	0.40	13	3.8
DBPP/μg m^{-3}	39	[b]	<LOQ	0.8	[b]	47	[b]	<LOQ	0.38	[b]
Propeller aircraft	$n = 12$					$n = 6$				
VOC (ATD)/mg m^{-3}	0	[b]	<LOQ	<LOQ	[b]	100	0.048	0.020	0.14	0.12
TnBP/μg m^{-3}	92	0.64	<LOQ	1.3	1.3	50	[b]	<LOQ	0.27	[b]
DBPP/μg m^{-3}	33	[b]	<LOQ	0.28	[b]	n.d.	[b]	<LOQ	<LOQ	[b]
p(TnBP)		0.006[a]								
p(tVOC)							0.013[a]			

[a] Mann–Whitney U, non-parametric two-independent sample test (calculated between jet aircrafts and propeller aircrafts). [b] Median and 90th percentile were not calculated for the compounds where less than 75% of the concentrations were below LOQ.

leakages from the engine to the tail pipe magnifies and could also be dependent on the weather conditions. A potential for short term TCP peak exposures can thus not be excluded for loaders.

Oil vapor and tVOC concentrations that were measured in the oil aerosol sample train were below the LOQs for all loader work task samples. However, tVOC was determined with the TD method in all stationary cargo room samples (Tables 1 and 5), due to the enhanced sensitivity of this technique. Only two out of 66 personal oil aerosol samples showed air concentrations above the LOQ (1.3 mg m^{-3} and 2.4 mg m^{-3}).

The working atmosphere contaminant levels varied depending on the engine type on the aircraft to be loaded. For instance, the TnBP levels were significantly higher for the jet aircrafts as compared to the propeller aircrafts (personal sampling, $p = 0.005$, median 1.1 and 0.64 μg m^{-3}, respectively). Also the tVOC concentrations were higher in the cargo rooms of the jet aircrafts (stationary sampling, $p = 0.011$, median 0.19 and 0.048 mg m^{-3}, respectively). Thus, emissions of vapors appear to be greater from the jets than from the propeller aircrafts.

In general, the OP exposure was lower for loaders than for technicians, as for instance shown by statistical difference for TnBP exposure levels ($p < 0.001$, median 1 and 37 μg m^{-3}, respectively), which was the only OP that was determined for more than 75% of all technician and loader samples. Although the loaders were working close to the hot engines and technicians were working on aircrafts with engines turned off for at least four hours prior to the work tasks, the lower exposure levels for the loaders might be explained by the fact that the technicians were working closer to the point sources of exposure and that most of their work was carried out indoors in aircraft hangars. The exposure conditions for loaders may be dependent on weather conditions such as wind force, temperature and precipitation, but these parameters are not investigated in the present study.

3.4 Worst case exposures and simulated leakages

The overall exposure levels to OPs and oil aerosol/vapor among technicians and loaders were low. However, the exposure measurements did not cover any unforeseen events such as large leaks and spills. According to the workers such events occur occasionally. Thus, it was decided to simulate leakages that resulted in OP air concentrations that could occur in worst case exposure situations.

3.4.1 Stationary spot sampling from turbine tail pipe outlets. Oil aerosol from the tail pipe exit could be observed up to ten minutes after the engines were shut down, which may be due to evaporation and subsequent condensation of the oil in the tail pipes. This is a potential source of exposure for personnel working in the vicinity of the aircraft. Measurements close to the tail pipe outlets were therefore performed to assess concentrations at that point source. Stationary parallel sampling ($n = 20$) of oil aerosol and OPs were collected at 1–5 cm distance from hot tail pipe outlet within 10 minutes after the aircrafts had turned off the engine at the tarmac arrival prior to the turn-around procedure. The average sampling time was approximately three minutes. TCP was determined in all samples at rather high concentrations (median 1.5 mg m^{-3}, 90th percentile 10, min–max 0.030–31), while oil aerosol was determined in 15 of the samples at levels above the LOQ (median 26 mg m^{-3}, 90th percentile 150, min–max <LOQ-240). TnBP and DBPP were determined in five and seven samples with maximum concentrations of 16 and 9 μg m^{-3}, respectively. No major leaks resulting in excessive oil introduction into the tail pipes were observed during the measurements. Such leaks are occasionally reported, and might result in substantially increased air concentrations of oil aerosol and OPs close to the tail pipe.

ortho-Isomers of TCP were not detected in any of the samples. The cresyl and butyl phosphates were not detected from measurements in the propeller aircraft exhaust pipes. Furthermore, seven samples were collected from cold tail pipes in aircraft hangar at night after more than four hours of turbine shut-down. Only one of these samples contained TCP (32 μg m^{-3}). However, TnBP (median 16, min–max 8.5–27 μg m^{-3}) and DBPP (median 2.1, min–max 1.2–7.3 μg m^{-3}) were determined in all seven samples, probably reflecting the background levels of these compounds in the aircraft hangar air, in accordance with previous experiences.

3.4.2 Stationary spot sampling from simulated hydraulic leakages. In order to simulate oil leaks that may occur from the pressurized hydraulic system in aircrafts, a leaking oil pipe was prepared and connected to a hydraulic oil reservoir in a routinely used test chamber. Oil spray was generated for 5–15 s when hydraulic oil was fed to the oil pipe. The simulation ($n = 4$) of hydraulic oil leakage (oil C) in this test chamber generated high concentrations of oil spray (80–200 mg m^{-3}), TnBP (45–110 mg m^{-3}) and TPP (1.7–3.7 mg m^{-3}), based on 5 min stationary sampling in the chamber after the oil spray generation was shut off. Although the measured concentrations do not represent real exposure levels, they demonstrate the need for sufficient airways protection during such oil pipe testing and leakage searches.

A small amount (1 mL) of oil D was applied on the wheel brakes of two different aircrafts shortly after arrival at the tarmac to simulate oil spill or leakage from hot brakes (wheels) which occasionally is reported. The temperature at the brake surface was between 200 and 300 °C. A cloud of oil aerosol was generated after application, and butyl phosphate air concentrations ranging from 1.1 to 1.7 mg m^{-3} were measured ($n = 4$). In contrast, similar simulated leakage on cooled brake disks (60–70 °C) on two other aircrafts displayed butyl phosphate air concentrations from 5 to 69 μg m^{-3} ($n = 4$).

3.4.3 Stationary spot sampling from engine test bench. Engine parts with complete connection to realistic oil pressures and temperatures are routinely tested on a test bench as a part of the maintenance programs. At the mechanical work shop where such testing was performed on the aircrafts engines included in this study, a dedicated room with local ventilation spots were in use. During test bench operations of engine parts, oil aerosol (oil G) was formed from the test bench installation, and air measurements were performed with the ventilation system turned off. Two sets of stationary parallel OP and oil aerosol samplers were placed at different positions near the test bench using 100 minutes sampling time. TCP and oil aerosol concentrations at a height of 1.7 m in front of the test bench revealed air concentrations of 24 μg m^{-3} and 0.40 mg m^{-3}, respectively. The highest TCP and oil aerosol concentrations were determined at

approximately 0.2 m in front of a closed oil draining point below the engine part (280 μg m^{-3} and 6.6 mg m^{-3}, respectively), most likely since this sampling was near to the oil emission source.

3.5 Organophosphate and oil aerosol/vapor measurement correlation

Personal sampling of OPs originating from hydraulic or turbine oils has to our knowledge not previously been reported in the peer-reviewed scientific literature, although oil aerosol/vapor measurements have been carried out in cabin air.[42] Oil aerosol/vapor measurements can possibly be a substitute for OP sampling if the OP content in the oil is known, opening for calculations of the OP levels based on the measured oil aerosol/vapor levels. The experimental design in this study with parallel sampling of OPs and oil aerosol/vapor allows for investigation of the possible correlation of the measured concentration levels between the OPs and the oil aerosol/vapor samples.

Oil aerosol and the relevant OP were determined simultaneously in only 22 out of the 205 pairs of parallel samples. Out of these, seven sample pairs were collected when oil C (contains TnBP) was in use. The Pearson correlation between the measured TnBP concentrations *vs.* the expected TnBP concentration calculated from the oil aerosol measurements were high (R = 0.99). The ratio between measured and calculated concentrations was 1.03 (95% CI 0.68–1.4). However, the corresponding measured and calculated concentrations from samples collected when oils F–H (containing TCP) (n = 15) were in use did not correlate well (R = 0.70). However, the TCP samples were collected close to hot jet engine tail pipe, and oil aerosol composition variations might occur from the condensation process of less volatile OPs as compared to mechanically generated oil sprays. Thus, calculation of TCP concentrations based on such oil aerosol concentrations might suffer from poor accuracy and precision. The LOQs for the oil aerosol samples were between 200 and 5000 higher than the corresponding OP LOQs, depending on sampling time and oil type, allowing for quantification even of low abundance components with the OP method at concentration levels where oil aerosol is not detectable. Thus, the OP method's detection limit is favoring OP specific sampling instead of OP calculation based on oil aerosol sampling. Parallel sampling of OPs and oil aerosol/vapor should be preferred if the goal is to assess both OP and oil aerosol/vapor exposures.

4 Conclusions

A method developed for sampling of OPs has been successfully applied for occupational exposure measurements among technicians and loaders within the aviation industry. This is to our knowledge the first published scientific study ever reporting personal exposure measurements of OPs originating from hydraulic and turbine oils. The OP sampling method has been shown to be advantageous when compared to a traditional oil aerosol/vapor method for indirect OP measurements.

The exposure measurements showed low working atmosphere concentrations of the OPs under study for most of the investigated work tasks, generally below 0.1 mg m^{-3} (94% and 100% of the determinations for technician and loader samples, respectively). VOCs and the butyl phosphates TnBP and DBPP were identified in most of the samples, most probably due to their frequent use and greater volatility than TCP. The butyl phosphates were identified as background level in the hangars. Measurements during work operations in the wheel well showed short term butyl phosphate concentrations at the mg m^{-3} level.

The potential for higher exposure levels during more critical circumstances, for instance during leaks, also in combination with elevated temperature, was investigated by exposure provocations. Although the measured OP air concentrations from these experiments do not represent general concentration levels, these samples may indicate a substantially higher OP exposure potential under adverse circumstances than are reflected by the low exposure levels disclosed during routine work tasks.

Acknowledgements

The authors would like to thank the participating aviation companies and their employees for their collaboration and genuine interest in this study. The Norwegian Ministry of Labour is acknowledged for financial support.

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