AIRBORNE ORGANOPHOSPHATES IN THE AVIATION INDUSTRY

Sampling development and occupational exposure measurements

Dissertation for the degree of Philosophiae Doctor

by

Kasper Flatland Solbu

Department of Chemical and Biological Work Environment
National Institute of Occupational Health
Oslo, Norway

Department of Chemistry
Faculty of Mathematics and Natural Sciences
University of Oslo
Oslo, Norway

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til Kristin og Andrine

og vår første

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PREFACE

The autumn I submitted my M.Sc. manuscript ("Hovedfagsoppgave" in Norwegian), the Norwegian National Institute of Occupational Health (NIOH) announced a vacant position as research fellow with Prof. Dr. Pål Molander as project leader. Molander, who was co-supervisor during my M.Sc. studies, encouraged me to apply, and I eventually got the position. I was then thrown into the concerns of potential risk for exposure to organophosphates in aircraft cabin air. This is a case which had been addressed for several years, especially in the USA, UK and Australia, and which had appeared as a political issue and concern in Norway during April 2003 due to extensive publicity in the newspapers. There was thus a great challenge to enter this scientific field that included a high degree of attention from politicians and media. Therefore, I assumed full responsibility to ensure that the outcome of our research at NIOH would fulfill the expectations from The Norwegian Ministry of Labor, who ordered and financially supported the work, and from workers who were expecting to receive information on possible organophosphate occupational exposure levels. For successful accomplishment of this research, my education in analytical chemistry at the University of Oslo (UiO) was essential to manage the analytical work and handling of samples for chemical analyses. Moreover, necessary knowledge of air sampling methodologies was obtained at NIOH from skilled colleagues, in addition to valuable self-experience obtained during these years. The collection of air samples has been a time-consuming and challenging work, which has required all my endurance to fulfill the necessary sampling.

The work presented herein has been carried out at the National Institute of Occupational Health (NIOH), Norway, under supervision of Prof. Dr. Pål Molander. I am especially thankful to Molander for sharing his expertise in writing scientific papers. I am also grateful to the co-supervision of Elsa Lundanes (UiO) and Steinar Øvrebø (NIOH), in addition to all co-authors for their valuable contributions during this work.

I would also like to thank my colleagues at NIOH for sharing their knowledge and skills and for contributing to the good working environment I have experienced.

During the field work I have been in touch with a great number of people, who are too many to be mentioned here. I must therefore in general thank the participating aviation companies and their employees for their fine collaboration and genuine interest in this study.

I am of course grateful to my always supporting family and my close friends for all good times over the years. Finally and most important, I must express my greatest appreciation to the two most special girls in my life, my daughter Andrine and my wife Kristin, for their love and unique enrichment of my life. I cannot imagine my life without you – and I am really looking forward to the soon expansion of our little family!

Kasper F. Solbu
Asker, April 2011

LIST OF PAPERS

This thesis is based on the following papers, which will be referred to in the text by their respective roman numerals (corresponding author in bold font).

Paper I Determination of airborne trialkyl and triaryl organophosphates originating from hydraulic fluids by gas chromatography–mass spectrometry: Development of methodology for combined aerosol and vapor sampling.
K. Solbu, S. Thorud, M. Hersson, S. Øvrebø, D.G. Ellingsen, E. Lundanes, and P. Molander.
J. Chromatogr. , A, **2007**, *1161*, 275-283.

Paper II Compact semi-automatic incident sampler for personal monitoring of volatile organic compounds in occupational air.
K. Solbu, M. Hersson, S. Thorud, E. Lundanes, T. Nilsen, O. Synnes, D.G. Ellingsen, and P. Molander.
J. Environ. Monit. , **2010**, *12*, 1195-1202.

Paper III Exposure to airborne organophosphates originating from hydraulic and turbine oils among aviation technicians and loaders.
K. Solbu, H.L. Daae, S. Thorud, D.G. Ellingsen, E. Lundanes, and P. Molander.
J. Environ. Monit. , **2010**, *12*, 2259-2268.

Paper IV Organophosphates in aircraft cabin and cockpit air: Method development and measurements of contaminants.
K. Solbu, H.L. Daae, R. Olsen, S. Thorud, D.G. Ellingsen, T. Lindgren, B. Bakke, E. Lundanes, and P. Molander.
J. Environ. Monit. , **2011**, DOI: 10.1039/c0em00763c.

ABSTRACT

During the last decade, there has been an increased concern of impact to human health from exposure to lubricants and organophosphates (OPs) for workers in the aviation industry. In spite of this concern, neither methods for assessing such exposure nor relevant exposure data for air concentrations of OPs could be found in the scientific literature. This revealed a need for development of such methods and work task related exposure measurements of OPs in the aviation industry in general. The four papers presented in this thesis describe development of sampling methodology and their use in the aviation industry for assessment of OPs in occupational air.

Paper I describes the method development needed for air sampling of OPs originating from lubricants such as hydraulic and turbine oils. Combinations of adsorbents, filters and extraction/desorption solvents were evaluated with respect to air sampling and analysis by gas chromatography–mass spectrometry (GC-MS) of six OPs[*] in presence of lubricants. The combination of Chromosorb 106 and 37 mm filter cassette with glass fiber filter and dichloromethane (DCM) as extraction/desorption solvent and tri-n-amyl phosphate (TnAP) as volumetric internal standard, was demonstrated to be well suited for sampling of airborne OPs originating from hydraulic and turbine oils.

While conventional pumped air sampling with a sampling train is documented in **Paper I**, **Paper II** describes development and evaluation of a semi-automatic sampler tailored for collecting volatile organic compounds, including certain OPs. This "incident sampler" is based on a pre-activated sampling unit that is stored at the work place of interest and a final simple activation performed by the worker that is subjected to the exposure. Intoxication of workers due to incidental chemical exposure has shown to be of high relevance. For instance, pilot incapacitation is the ultimate safety threat and consequently underlines the importance of revealing possible unknown contaminants in their working atmosphere. For that reason, the availability of an incident sampler in environments with risk of sudden chemical exposure is presented as an important tool to reveal possible contaminants from incidental air contamination. Ten such samplers were therefore

[*] Triisobutyl phosphate (TiBP), tri-n-butyl phosphate (TnBP), triphenyl phosphate (TPP), tri-*o*-cresyl phosphate (ToCP), tri-*m*-cresyl phosphate (TmCP), and tri-*p*-cresyl phosphate (TpCP)

installed in aircrafts within a 12 month period (**Paper IV**). However, neither of these aircrafts experienced such contamination incidents during this period, and the samplers were thus never activated during such incidents.

Paper III presents air measurements during loader and technician work operations. 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. Additionally, 75 combined VOC/OP/oil and 40 combined OP/oil samples were collected from aircraft cargo rooms and from jet engine tail pipes during loading work operations, respectively, while 16 samples were collected during provoked situations related to technician work. 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 highest TnBP exposure was during pressure drop in the wheel wells in one of the airplane models (maximum 9 mg/m^3), and the butyl phosphates were also found to be present at background concentrations of 1-30 $\mu g/m^3$. The potential for higher exposure levels during worst case situations was also investigated, for instance by exposure provocations and direct measurements close to the exposure sources such as jet engine tail pipes where maximum oil aerosol and TCP levels were 240 and 30 mg/m^3, respectively.

Measurements of contaminants in cabin air are presented in **Paper IV**. A set of tailored sampling methods were applied, including development of new long-term sample methods based on deposition to a wipe surface area and an activated charcoal cloth installed on walls inside the airplane. In total, 167 pumped within-day OP/VOC samples and 108 long-term samples were collected in cabin and cockpit air from 40 unique aircrafts during 47 commercial flights. Total-VOC was measured using sampling with thermal desorption tubes, and was determined in all 71 such samples (min-max 0.20-2.7 mg/m^3). For pumped within-day air sampling, TnBP levels were highest in model A airplanes and were detected in all airplane flights (n=76, min-max 0.02-4.1 $\mu g/m^3$), while TCP was detected only on samples collected from four flights in model C airplanes (min-max <LOQ-0.29 $\mu g/m^3$). TCP was, however, present in 11 out of 12 long-term wipe samples in model C airplanes and in all six HEPA filters from model A airplanes (1.1-42 ng/g per flight hour). TCP concentrations 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 (5.1±1.1 μg/m^3) as compared to after engine replacement (p=0.02) during ground test.

The four papers presented in this thesis thus encompass new air sampling methodologies and their application for characterization of OP contamination levels in the aviation industry, in addition to determination of oil aerosol and tVOC. This has resulted in collection of nearly 900 samples during general work tasks for technician and loaders, and in cockpit and cabin air during commercial flights, which is a substantial contribution to the knowledge of occupational exposure to OPs in this industry.

ABBREVIATIONS

ACC	Activated charcoal cloth
AChE	Acetylcholinesterase
ACN	Acetonitrile
COPIND	Chronic organophosphate-induced neuropsychiatric disorder
DBPP	Dibutylphenyl phosphate
EP	Extreme pressure
FT-IR	Fourier transform–infrared spectrophotometry
GC-MS / -FID	Gas chromatography–mass spectrometry / –flame ionization detector
HEPA	High efficiency particulate air
IMS	Intermediate syndrome
LOQ	Limit of quantification
NTE	Neuropathy target esterase
OP / OPs	Organophosphate / Organophosphates
OPICN	Organophosphate-induced chronic neurotoxicity
OPIDN	Organophosphate-induced delayed neuropathy
OPIDP	Organophosphate-induced delayed polyneuropathy
PTFE	Polytetrafluoroethylene
RSD	Relative standard deviation
SIM	Selected ion monitoring
TCP	Tricresyl phosphate (mixture of isomers)
TD	Thermal desorption
TiBP	Triisobutyl phosphate
TmCP	Tri-*m*-cresyl phosphate (*m*-TCP)
TMPE	Trimethylolpropane ester
TMPP	Trimethylolpropane phosphate
TnAP	Tri-n-amyl phosphate (tri-n-pentyl phosphate)
TnBP	Tri-n-butyl phosphate
ToCP	Tri-*o*-cresyl phosphate (*o*-TCP)
TpCP	Tri-*p*-cresyl phosphate (*p*-TCP)
TPP	Triphenyl phosphate
VOC / tVOC	Volatile organic compounds / total-VOC
w/w	Weight in weight (used with mass fraction percentage)

1 INTRODUCTION

1.1 Hydraulic and turbine oils

Hydraulic oils and turbine oils (Figure 1-1) constitute a large group of fluids used in the industry as pressure- and heat-transferring, anti-wear, anti-corrosion and lubricating media.[1,2] Thus, such fluids are categorized by their intended use and not by their chemical composition, and are composed of base oils and possible additives. The synthetic base oils within aviation appear mainly to be synthetic hydrocarbons (such as poly-α-olefins), polyalkylene glycols and phosphate esters,[1] while the mineral base oils are made up from refined petroleum oils and are thus complex mixtures of aliphatic and aromatic hydrocarbons.[1,2] Synthetic hydraulic oils used in the aviation industry often contain a large fraction of phosphate esters due to the fire resistant properties of such compounds.[1-3] Premium mineral oils are by themselves excellent hydraulic fluids, and would continue to serve effectively in long periods even if the additives were consumed or removed in service.[2]

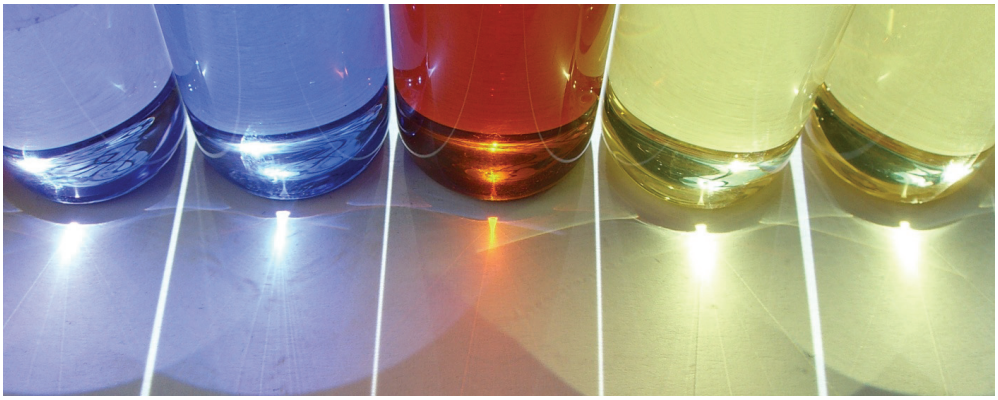


Figure 1-1: Hydraulic and turbine oils, which are containing phosphate esters, stored in glass vials.

1.2 Organophosphates (phosphate esters)

"Organophosphates" and "phosphate esters" are general terms for esters of phosphoric acid. However, organophosphate-like substances have traditionally also been assigned to this term, which thus encompasses organic substances that contain a phosphoryl (P=O) or a

thiophosphoryl (P=S) bond.[4,5] They are essentially esters, amides or thiolic derivatives of phosphoric, phosphonic or phosphinic acids (Figure 1-2), with different arrangements of attached oxygen, carbon, nitrogen or sulfur atoms, and have been classified into 14 types.[5] The majority of these compounds are used as pesticides, but are also widely used as nerve agents, flame retardants and parasiticides.[4,5] For instance, tabun (ethyl dimethylamido-cyanophosphate) and sarin (isopropyl methylfluorophosphate) are well known compounds (Figure 1-3), which originally were developed in search for more efficient pesticides, but has also been used in chemical warfare due to their highly neurotoxic properties.[6,7]

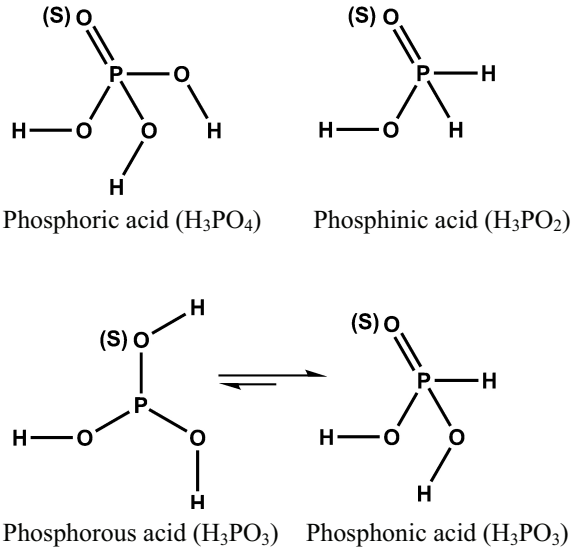


Figure 1-2: Structures of phosphoric, phosphinic, and the tautomers phosphorous and phosphonic acids.[8] Thiolic derivates are shown in the figure with "(S)", where S replaces O.

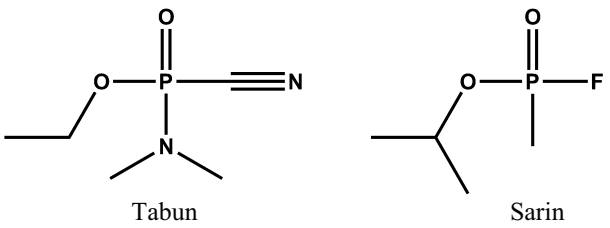


Figure 1-3: Structures of tabun (ethyl dimethylamidocyanophosphate) and sarin (isopropyl methylfluorophosphate)

The organophosphates (OPs) that are referred to as the esters of phosphoric acids are known for their widespread industrial use, such as flame-inhibitors, plasticizers, additives in insecticides/pesticides, and as extreme pressure (EP) additives in hydraulic oils and lubricants.[1,2] The EP additives are used in turbine oils to enhance lubrication and anti-wear/anti-corrosion properties.[9,10] Many of these oils contain the OP tricresyl phosphate (TCP) isomers, as well as other triaryl or trialkyl OPs (Figure 1-4), usually at concentrations below 1% (w/w).[10] Jet turbine oils, however, commonly contain higher concentrations of OPs with typical TCP concentration in the range 1-5%.[10,11] Among the typical OPs used in hydraulic and turbine oils in the aviation industry, are the butyl phosphates triisobutyl phosphate (TiBP), tri-n-butyl phosphate (TnBP), and dibutylphenyl phosphate (DBPP) (Figure 1-4). These are widely used in high-performance hydraulic oils for jet aircrafts (**Papers III & IV**).

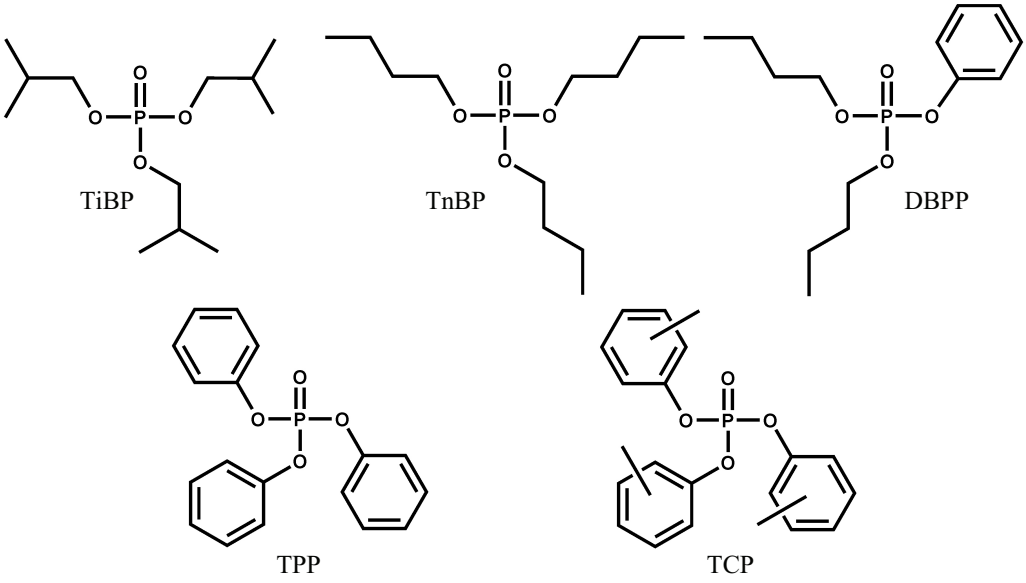


Figure 1-4: Structures of triisobutyl phosphate (TiBP), tri-n-butyl phosphate (TnBP), dibutylphenyl phosphate (DBPP) and tricresyl phosphate (TCP, general structure of isomers)

1.3 Toxicology of organophosphates

Occupational exposure to synthetic and mineral base oils might pose a health risk itself,[12-14] but the oil additives, such as certain OPs, might be of higher toxicological concern. In general, certain OPs are capable of producing acute, intermediate and delayed poisoning. Acute poisoning emerges within a few minutes to a few hours after exposure, typically by ingestion, and is caused by irreversible inhibition of the acetylcholinesterase (AChE) enzyme, which results in accumulation of acetylcholine in the synapse of the nerve, followed by increased and persistent nerve activity.[15-17] In addition to the acute cholinergic poisoning, some OPs are also capable of producing several subacute, delayed and chronic neurological, neurobehavioral and psychiatric syndromes. These include the intermediate syndrome (IMS), the OP-induced delayed neuropathy/polyneuropathy (OPIDN/OPIDP), and a number of chronic neurological and psychiatric manifestations lumped under the term "chronic organophosphate-induced neuropsychiatric disorder" (COPIND).[18,19]

Recovery from the acute cholinergic poisoning is in some cases interrupted by IMS, which typically occurs within 24 to 96 hours after the acute poisoning. IMS is then affecting conscious patients without cholinergic signs, and involve the muscles of respiration, proximal limb muscles, neck flexors, and muscles innervated by motor cranial nerves.[5,20] The delayed syndrome (OPIDN/OPIDP) typically occurs 2–3 weeks after acute exposure and causes numbness and weakness of the lower extremities, followed by progressive ascending weakness of limb muscles.[21,22] The disease entity is believed to be due to the inhibition of the neuronal protein neuropathy target esterase (NTE).[23-26] Studies have also shown a positive link between OP exposure and development of COPIND, also following long-term and low-level exposure,[27,28] which has been referred to as OP-induced chronic neurotoxicity (OPICN).[21]

In relation to OPs used in hydraulic and turbine oils, the OP neurotoxic effects of the TCP isomer tri-*o*-cresyl phosphate (ToCP) have been well documented.[11,14,29-32] Similar effects of *meta*- or *para*-isomers of TCP[†] have not been shown,[33,34] but the literature available on this subject for TmCP and TpCP is limited and other possible toxic effects cannot be excluded. In addition, differences in toxicity of the ten structural isomers of TCP have been

[†] The *meta*- and *para*-isomers of TCP are tri-*m*-cresyl phosphate (TmCP) and tri-*p*-cresyl phosphate (TpCP).

shown (Figure 1-5), where the mono-*ortho* TCP isomers[‡] were identified as the most toxic with reference to OPIDN.[29,35-37]

Triphenyl phosphate (TPP) is a potent inhibitor of human blood monocyte carboxylesterase enzyme activity and may also lead to allergic contact dermatitis and hemolytic effects.[38-42] Tri-n-butyl phosphate (TnBP) has shown cytotoxic properties and may also cause tumors, although such tumors have been suggested to be induced by nongenotoxic mechanisms.[43-45] In addition, an additive joint acute toxicity of TBP and TPP has been shown, investigated by lethal concentrations with daphnia magnia as test organism.[46]

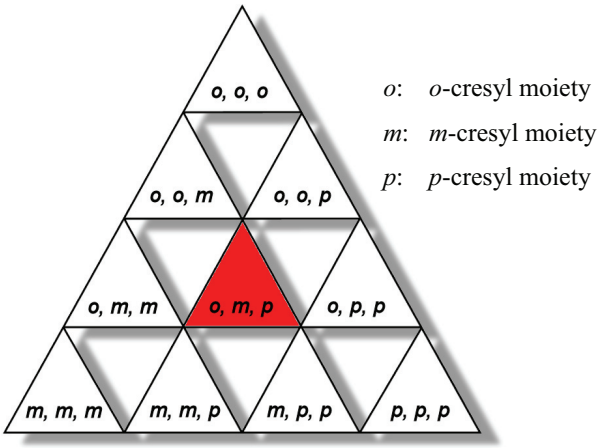


Figure 1-5: Triangle of structural TCP-isomers with possible combinations of *o*-, *m*- and *p*-cresyl moieties, shown with tri-*m*-, tri-*o*-, and tri-*p*-TCP in each corner of the triangle. The *omp*-TCP with three different cresyl moieties (indicated in red color) is considered to be the most toxic TCP isomer with reference to OPIDN.[35]

The possible formation of unknown toxic organophosphorus thermal decomposition products during oil leaks with deposition on hot surfaces such as turbines has been addressed.[47-51] For instance, laboratory studies have well described the formation of the neurotoxin trimethylolpropane phosphate (TMPP) from TCP and trimethylolpropane ester (TMPE) at elevated temperatures,[52-57] and potential formation of similar decomposition products can therefore not be ignored. TMPP is recognized as a potent convulsant that

[‡] "Mono-*ortho* TCP isomers" includes isomers of TCP with one *o*-cresyl moiety only. The two other cresyl moieties are thus combinations of *p*- and *m*- cresyl. This corresponds to the three isomers at the third row (from the top) in Figure 1-5.

causes epileptiform seizures potentially followed by death,[53,58,59] and treatment with doses below seizure threshold resulting in long-term behavioral sensitization has also been demonstrated.[60] Figure 1-6 shows the structures of the reagents and product for the formation of TMPP (vapor pressure 0.24 torr[61]).

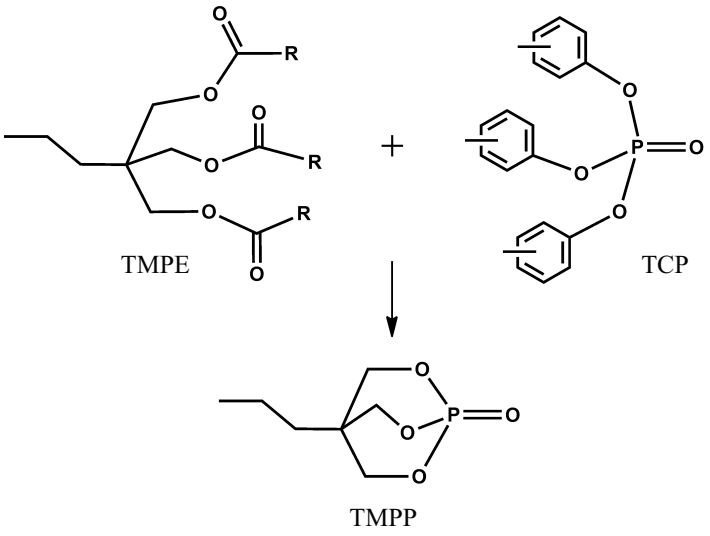


Figure 1-6: Formation of the neurotoxin trimethylolpropane phosphate (TMPP) from trimethylolpropane ester (TMPE) and TCP.[62,63]

1.4 Health effects of organophosphates

With exception of one study,[64] there are no analytical studies that specifically investigate the causal relation between OP exposure and neurotoxic effects on humans. However, several patient reports from the early 20th century that describe the impact on human health from such OP exposure can be found. For instance, consumption of illegal TCP-contaminated beverages imported from Jamaica to USA in the early 1930th induced epidemics of paralysis, especially in the lower limbs,[29,65] in addition to outbreaks of poisoning from ingestion of contaminated cooking oils, medication and flour in Europe, Asia and Africa.[66] Moreover, a mechanist from Scandinavia was exposed to hydraulic oils for several years and also suffered from paralysis.[67] In all these cases the poisoning in focus was paralysis of the peripheral nervous system, possibly with reduced nerve conduction velocity.[67]

1.5 Organophosphate exposure

Hydraulic and turbine oils are often used in systems with high pressure and temperature, which increase the potential for generation of oil mist, spray and vapor as opposed to oils used under normal conditions. Exposure to OPs from turbine and hydraulic oils through vapors and aerosols may occur during aviation ground personnel working operations.[68] 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. Cabin crew may also be exposed to turbine oils due to the fact that cabin air is bled off from the engine core, and OPs have been suggested as major contaminants of concern in airplane cabin air during so called smoke-in-cabin incidents.[69-74] Air monitoring studies for aircraft cabin contamination has also been reviewed,[75] and describes several reports on contamination of cabin air.

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.[76,77] The lack of such studies and methods is probably because methods for tailored air measurements of OPs originating from turbine and hydraulic oils have not been available prior to this study. Due to the health concern, exposure measurements of OPs in the aviation industry in general are needed, as well as loader and technician exposure assessments due to the potential exposure to OPs through their work.

1.6 Aims of thesis

The aims of this thesis were to develop methods for measurements of OPs in air originating from hydraulic and turbine oils, and characterize OP air levels in aircraft air and work-related OP exposure in the aviation industry. To realize these objectives we have:

1) Developed methodology for measuring OP in air originating from hydraulic and turbine oils (**Paper I**), and methodology for long-term air sampling and analysis of HEPA-filters (**Paper IV**).

2) Developed a personal incident sampler with simple operation for sampling of volatile organic compounds and semi-volatile OPs during incidents, which also were installed in aircraft cockpits ready for use during commercial flights (**Papers II & IV**).

3) Performed exposure measurements with air sampling of OPs, oil aerosols and VOCs during aviation loader and technician work operations (**Paper III**).

4) Performed air sampling of OP and VOC contaminants in cabin air during commercial civil flights (**Paper IV**).

2 RESULTS AND DISCUSSION

2.1 Development of analytical methodology and sampling

2.1.1 Analytical methods

A wide range of OPs exists, but only a limited number of these compounds are present in lubricants for use in Norway. These OPs have been documented to include tributyl phosphates, triphenyl phosphates and tricresyl phosphates,[10] but analytical methods for determination of these OPs originating from hydraulic and turbine oils were prior to this study not available. Therefore, development of such methodology was necessary and a mixture of commercially available OPs was used for the analytical method development. These OPs have a considerably difference in volatility, which is illustrated by vapor pressures of 0.02 torr (TiBP), 0.004 (TnBP), 3×10^{-4} (DBPP), 10^{-6} (TPP/ToCP), and 10^{-7} (TmCP/TpCP) at 25 ˚C, and boiling points from 261 ˚C (TiBP) to ca. 400 (TCP) at 760 torr.[61] A volatile organic compound is defined as any organic compound having a vapor pressure of 0.01 kPa (0.0013 torr) or more at 293.15 K, or having a corresponding volatility under the particular conditions of use.[78] Thus, the tributyl phosphates TiBP and TnBP classify as volatile within this definition. This large distribution in volatility required a steep temperature program for the gas chromatography–mass spectrometry (GC-MS) analysis. Thus, a temperature range of 40 to 320 ºC was programmed within the first 10 min after GC sample injection, resulting in a separation time of 13 min as shown in Figure 2-1 (**Paper I**).

In addition to OP sampling, parallel sampling of oil aerosol/vapor or VOCs were collected for comparison of the tailored sampling method for determination of OPs with the general oil aerosol/vapor method, or for supplementary air samples in general, respectively. Procedures for determination of oil mist[79-81] and VOCs[82-84] have previously been well described in the literature and standard methods were therefore applied: Total-VOC (tVOC) from active air sampling and samples from incident samplers were measured using thermal desorption (TD) and GC-MS (**Papers II, III & IV**); oil aerosol and oil vapor samples were determined by liquid desorption and Fourier transform–infrared

spectrophotometry (FT-IR) and gas chromatography–flame ionization detector (GC-FID), respectively (**Papers I & III)**.

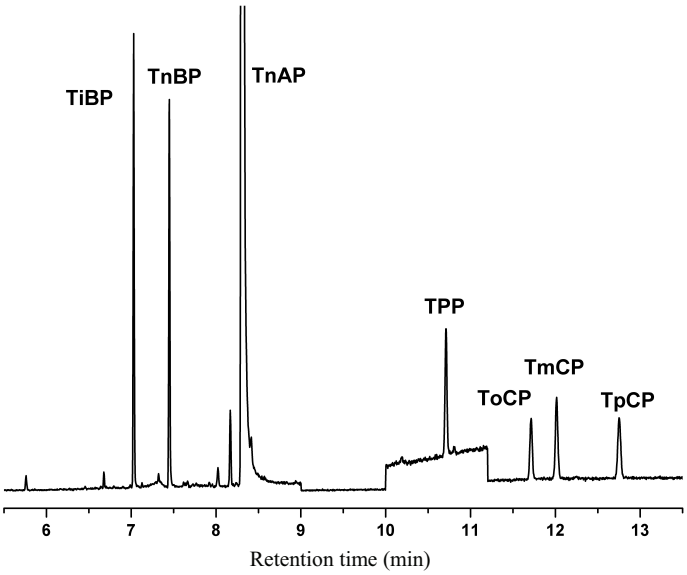


Figure 2-1: GC-MS (SIM) chromatogram from 1 µL splitless injection (280 °C injector temperature) of 30 pg of each of TiBP, TnBP, TPP, ToCP, TmCP, and TpCP, and 3 ng TnAP as volumetric internal standard (**Paper I**). The OPs were separated on a VF-5ms capillary column (30 m × 0.32 mm, d_f = 1.00 µm) with a He carrier gas flow rate at 1.5 mL/min. GC-oven temperature program: (1) 40 °C initial temperature (0.5 min hold time); (2) 50 °C/min up to 150 °C (2 min hold time); (3) 60 °C/min up to 280 °C; (4) 10 °C/min up to 320 °C (3 min hold time); (5) Further 20 min hold time (not shown) was applied to elute heavy components from certain synthetic oils.

2.1.2 Personal active air sampling

OP sampler with filter and adsorbent train (Paper I)

The large differences in the OPs' volatility required a sampling method, which utilizes a sampler containing a combined adsorbent tube and filter for efficient trapping of OPs present as both aerosols and vapors. The non-volatiles are trapped on the filter while volatiles and compounds evaporated from the filter are trapped on the adsorbent.

Different adsorbent materials were evaluated with respect to sampling efficiency and storage stability of the selected OPs, and several different desorption solvents or solvent

mixtures were evaluated for each adsorbent. Initially, the sampling recoveries on the adsorbents were investigated by spiking the adsorbent tubes with the OPs. Five adsorbents were chosen to represent a wide range of adsorbent types, including activated charcoal (Anasorb CSC and 747), organic porous polymers (Chromosorb 106 and XAD-2), and the highly polar silica gel (Figure 2-2), based upon our previous experience with these adsorbents for sampling of a wide variety of compounds.[85,86] From spiking experiments of all adsorbents, Chromosorb 106 were in combination with DCM found to provide near full recoveries after subjection to pumped air flow and after storage of up to three months. Chromosorb 106 was therefore chosen as the preferred adsorbent material, and efficient adsorbent sampling of TiBP and TnBP from vapor phase was finally demonstrated using a vapor atmosphere generator coupled to a parallel sampling exposure chamber.

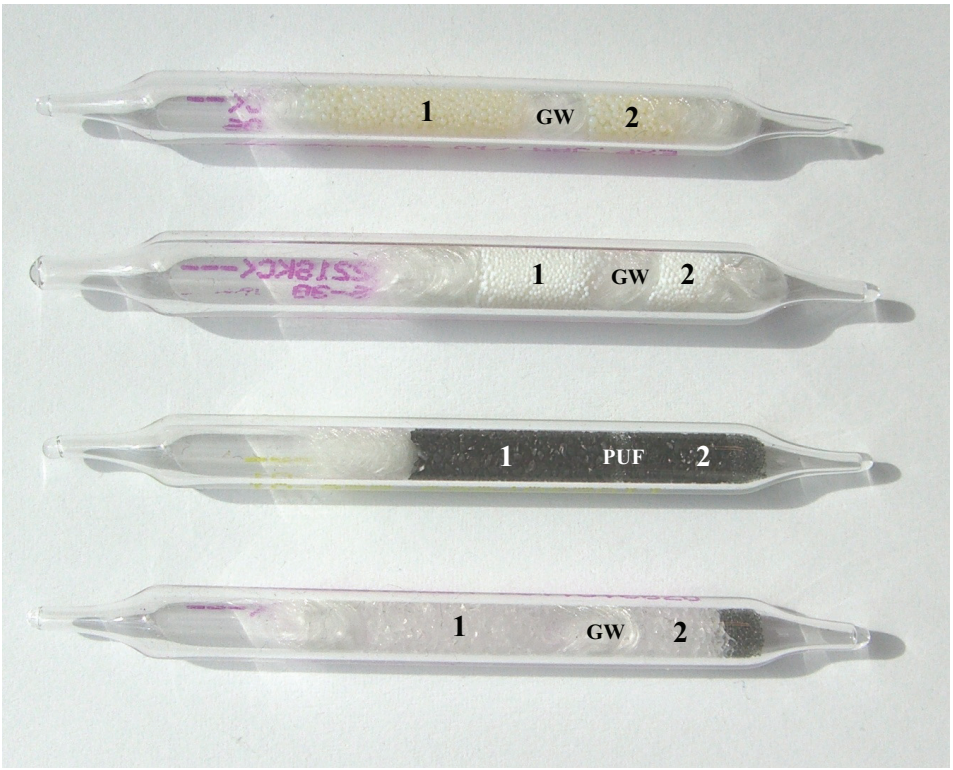


Figure 2-2: Glass tubes filled with different adsorbent materials. From top: Chromosorb 106, XAD-2, Anasorb CSC and silica gel. The smaller backup adsorbent layer (2) is separated from the main layer (1) with glass wool (GW) or polyurethane foam (PUF).

Initial experiments with CS_2 as extraction solvent of glass fiber filters revealed adsorption of OPs from the CS_2 solutions to the filter. Thus, further evaluation of polytetrafluoroethylene (PTFE) filters and glass fiber filters were performed with DCM as extraction solvent, and in combination with the most appropriate adsorbent tube, Chromosorb 106. Spiking experiments with subsequent subjection to pumped air flow showed that the aryl phosphates were fully recovered for both filters (100-104%), while recovery of TiBP and TnBP were 39-60% from glass fiber filter and 1-9% from PTFE filters. Loss of tributyl phosphates from filters illustrated the need for an adsorbent coupled downstream of the filter in order to fully collect tributyl phosphates even at ambient temperatures. The fraction of TiBP and TnBP that passed through the filters was recovered by the Chromosorb 106 adsorbent connected downstream yielding total recoveries for both the glass fiber and PTFE filters of 92-109%. However, the glass fiber filter was preferred due to its improved retention of volatile OPs as compared to the PTFE filter, in addition to the glass fiber filter's long-term documented capabilities with regard to oil aerosol sampling.

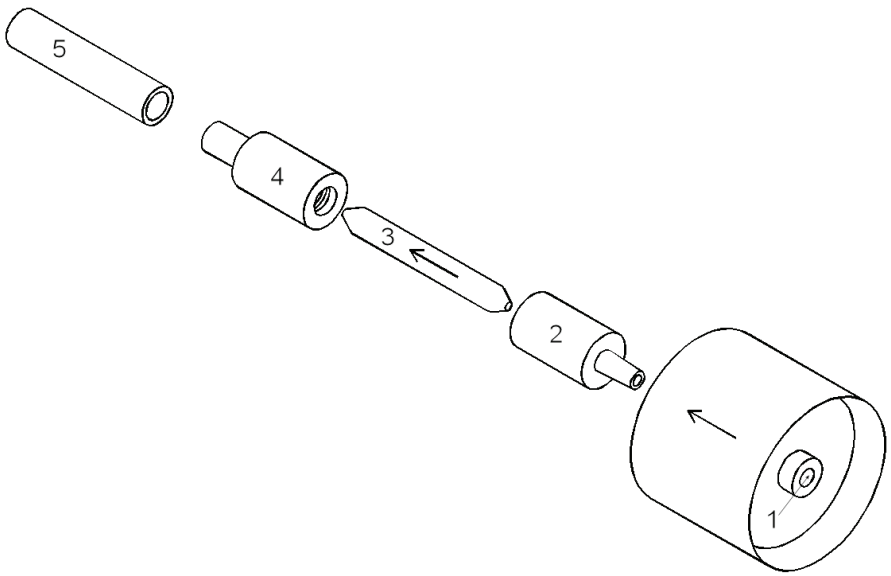


Figure 2-3: Sketch of the complete sampling train (12 cm total length), showing (1) inlet of the 37 mm filter cassette, (3) adsorbent tube (6 mm outer diameter), (2 and 4) inert interfaces, and (5) hose to the sampling pump. The arrows are showing the direction of sampling air flow.

A final recovery assessment of the combined filter and adsorbent sampling from an oil aerosol atmosphere demonstrated a total recovery of vapor and aerosol of 93-106% for TiBP, TnBP and TmCP in both a mineral and synthetic oil spray. Total recovery was defined as measured OP concentration in the oil aerosol relative to the OP concentration in the oil solution prior to nebulization. A sketch of the sampling train is shown in Figure 2-3.

Analyses of the OP samples (an example chromatogram is shown in Figure 2-4) collected during technician and loader work operations in the present study showed that the OPs in general were recovered from the filter only, with the exception that TnBP also was detected on the adsorbent in 17 out of 414 samples with masses of 0.2 to 39% of the total TnBP mass (3-880 µg) (**Paper III**). Thus, an adsorbent up-stream to the filter cassette was necessary to ensure full recovery of the volatile butyl phosphates. Moreover, the hypothesis of generation of possible volatile OP thermal decomposition products of unknown nature, necessitates the addition of an adsorbent to the filter sampler, although no such compounds have been identified in this study.

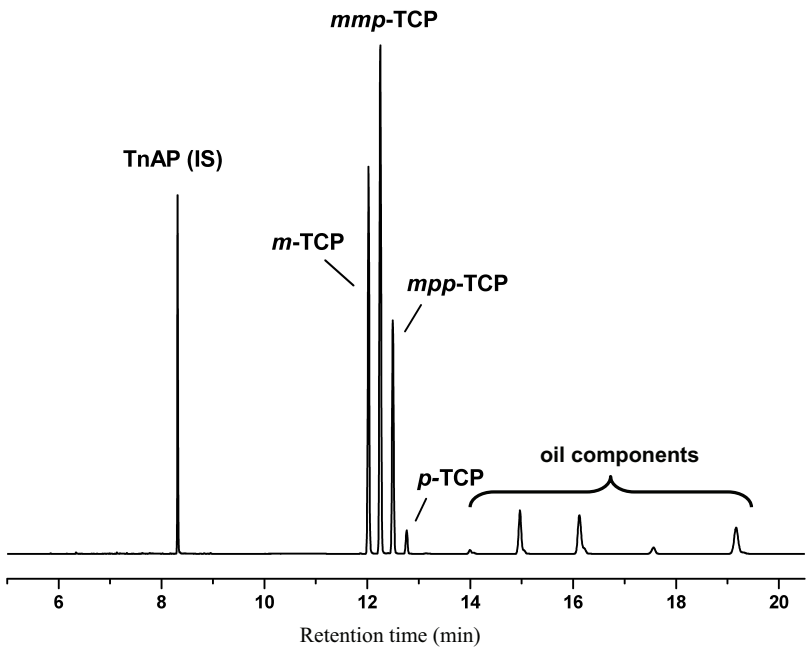


Figure 2-4: GC-MS (SIM) chromatogram of air sample exposed to aerosol from an engine oil (3 ng TnAP was added as volumetric internal standard (IS)) as described in **Paper I**. Conditions as in Figure 2-1.

Incident sampling

A simple and automatic sampler to be operated by workers who may be subjected to sudden and unexpected exposures was developed to enable simple air sampling over a short time and with a minimum of instructions for use (**Paper II**). The sampler encompasses a tube (glass or stainless steel) containing an adsorbent material in combination with a small membrane pump, and where the adsorbent is capped at both ends by gas tight solenoid valves (Figure 2-5). Activation is carried out by pulling a pin out of the sampler's housing, which triggers automatic air sampling with pre-programmed sampling time (30 min) and sampling flow rate (200 mL/min) with subsequent automatic shut-down. Volatile and semi-volatile organic compounds are collected on the adsorbent tube. The sampler is designed to prevent further exposure to the adsorbent material after use, allowing the complete sampler to be shipped to a laboratory for analysis. Reactivation of the sampler is not possible without opening the sampler, preventing contamination of the adsorbent by multiple usages or other user errors. The sampler can be modified to also include filter sampling of semi- or non-volatiles or combined adsorbent/filter sampling of mixed atmospheres.

The developed incident sampler's performance was evaluated for flow stability, storage stability, robustness, and sampling efficiency in VOC and OP atmospheres (**Paper II**). Thus, the incident sampler was shown to have sampling capabilities of VOCs similar to well characterized standard occupational hygiene sampling equipment, illustrating the potential use of the incident sampler for quantitative measurements. In an additionally laboratory experiment, an oil solution containing TiBP was applied to a hot surface to simulate a heated oil leak. With respect to TiBP, analyses of adsorbent tubes exposed to the generated head space atmosphere showed no significant differences between Tenax TA thermal desorption tube and Chromosorb 106 glass tube, in spite of different analysis techniques (**Paper II**). This supports the documentation on the sampler's robustness. Chromatographic profiles obtained from the two methods are shown in Figure 2-6.

For sampling during sudden and unexpected incidents with potential of exposure to semi-volatile OPs and possible volatile decomposition products, ten incident samplers (Figure 2-7) were distributed in ten different aircrafts. These were, however, never taken into use during sudden and unexpected contamination of the cockpit air, because such incidents did not occur during the study period (**Paper IV**).

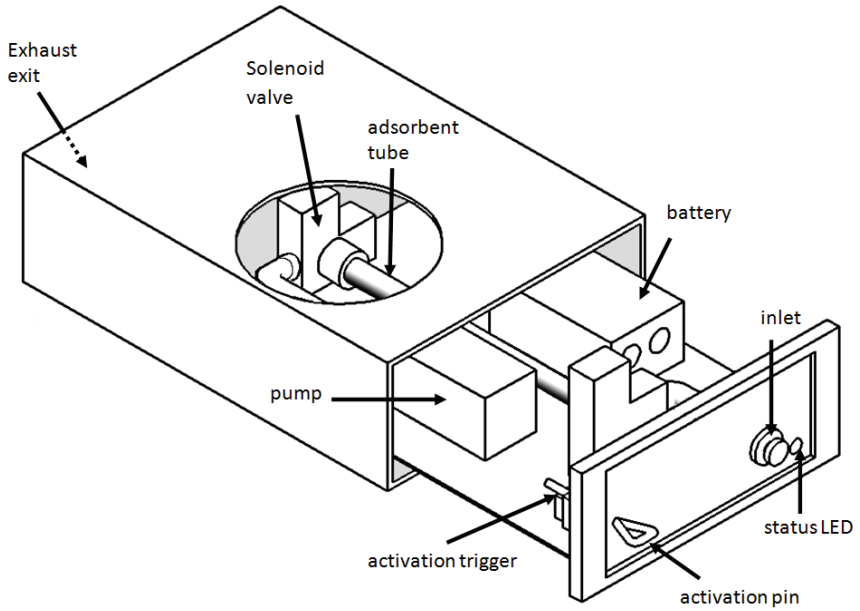


Figure 2-5: "Open view" 3D sketch of the incident sampler (**Paper II**)

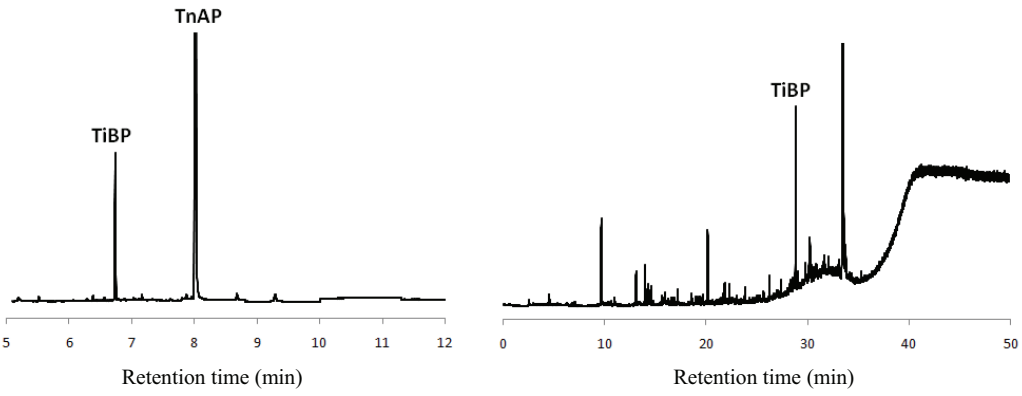


Figure 2-6 : Analyses of two different adsorbent tubes exposed to the same head space atmosphere above oil solution applied to a hot surface. **Left**: GC-EI-MS SIM (m/z 99) chromatographic profile of TiBP trapped on Chromosorb 106. Conditions as in Figure 2-1. **Right**: GC-EI-MS scan chromatographic profile of trapped VOCs and TiBP on Tenax TA thermal desorption (TD) tube**.** The components were eluted on a VF-5ms capillary column (30 m × 0.32 mm, d_f = 1.00 µm) with a He carrier gas flow rate at 1.0 mL/min. GC-oven temperature program: (1) 40 °C initial temperature (7 min hold time); (2) 8 °C/min up to 300 °C (12 min hold time). (**Paper II**)

Figure 2-7: Picture of the incident sampler (**Paper II**)

2.1.3 Indirect semi-quantitative methods

Wipe sampling wall areas and activated charcoal cloths were applied to measure possible deposition of OPs from cabin air for a longer period of time than obtained from the within-day air sampling.

Wipe sampling (Paper IV)

Different wipe sampling methods have been described and shown to be helpful to measure dermal exposure and deposited compounds on surfaces.[87-90] Wipe sampling with the use of compresses was therefore considered useful to evaluate deposition of contaminants on the interior walls originating from the air ventilation system. 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 organic solvents absorbed in the wipe compresses. Moreover, the surfaces' adsorbent properties and wipe recovery are unknown and may also

vary between different aircrafts. Therefore, we used aluminum tape, which resists organic solvents, to achieve a uniform surface material for all sampling spot areas at the laboratory and in aircrafts. DCM has previously shown excellent solubility properties for the OPs of interest and compatibility with the GC-MS method in use, and was used for extraction of OPs from glass fiber filters (**Paper I**). 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,[91] and were thus explored in the present study as well. Compresses exist in different sizes, but 5×5 cm was chosen as the most convenient size for the practical use.

During laboratory experiments, the recovered amount of OPs from the wipe surface was compared to the initial spiked amount, yielding recoveries of 94-103% (RSD 3-6%) for all alkyl and aryl phosphates in this study, supporting the assumption that wipe sampling with DCM as solvent is suitable for indirect measurements of OPs originating from lubricants. For spot sampling in aircrafts, a wipe area of 3-6 dm^2 (dependent on space available) was constructed using the aluminum foil tape (Figure 2-8). The aluminum wipe area was cleaned using a specific wipe procedure and the used compresses were stored for comparison. The same wipe procedure was performed after 1-3 months to allow determination of the compounds that potentially had deposited on the surface.

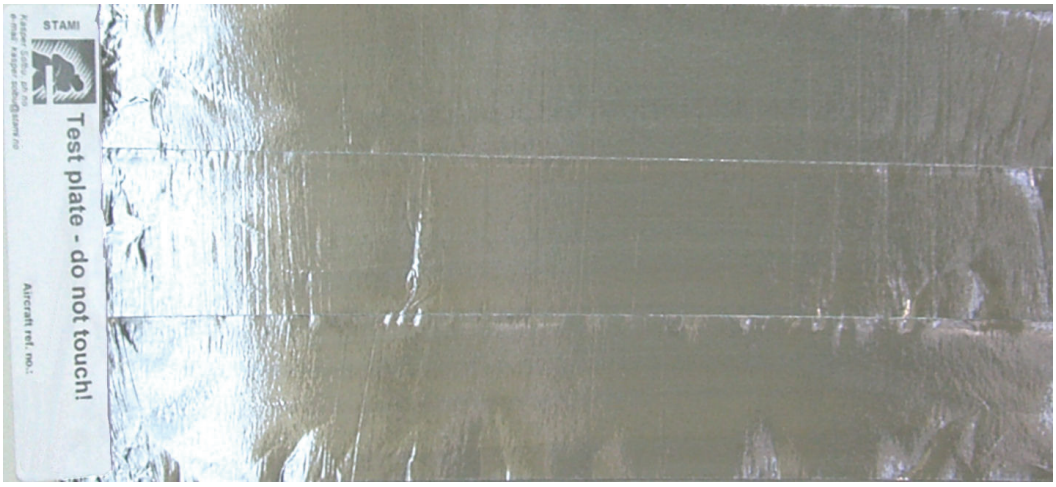


Figure 2-8: Wipe area (15×30 cm^2) of aluminum tape installed in an aircraft

Sampling with activated charcoal cloth (ACC) (Paper IV)

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 volatile thermal decomposition products. ACCs have previously been explored for several applications, such as air and water filtration[92,93] and passive dermal sampling.[94-96] Morover, ACCs are manufactured from a textile precursor,[97] 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, and the knitted Zorflex® FM50K cloth was considered to be suitable for further evaluation.

Adsorption of the aryl phosphates to the ACC was strong, and none of the initially evaluated solvents or solvent mixtures 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 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. 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. These findings were in accordance with our previous experiences on extraction of OPs from charcoal adsorbents (**Paper I**).

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 the chamber, resulting in continuous release of these volatile OPs to the chamber atmosphere. During method development, 18 cloths (5×5 cm) were mounted inside a 0.4 m^3 exposure chamber (described in **Paper I**) for passive sampling, and each month six cloths were removed and the adsorbed masses of TiBP and TnBP were measured. The average TiBP and TnBP levels on the cloths each month revealed a linear uptake of 7.7 µg/dm^2 per day (R=0.997) and 4.1 (R=0.998), respectively (forced intercept in origo, RSD 9-19%). Thus, the OP uptake was apparently not affected by a concentration drop during the sample time period, illustrating the rather limited potential of such methods for quantitative measurements only.

The contamination levels in aircrafts 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/days). The limit of quantification (LOQ) for the ACC sampling was 0.11 µg/dm^2 based on complete recovery from a cloth area of 10×10 cm^2, which was used for sampling in aircrafts.

For long-term sampling in aircrafts, ACCs (12×12 cm^2) were attached to the wall using a 2 cm wide tape that covered 1 cm along the circumference of the cloth, revealing a 10×10 cm^2 cloth area (Figure 2-9). In general, two sampling areas were established in each aircraft (cockpit and cabin/galley), in a total of 26 unique aircrafts. After an installation time period of 1-3 months, the cloth was cut out of the tape frame and transferred to a clean glass container. 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.

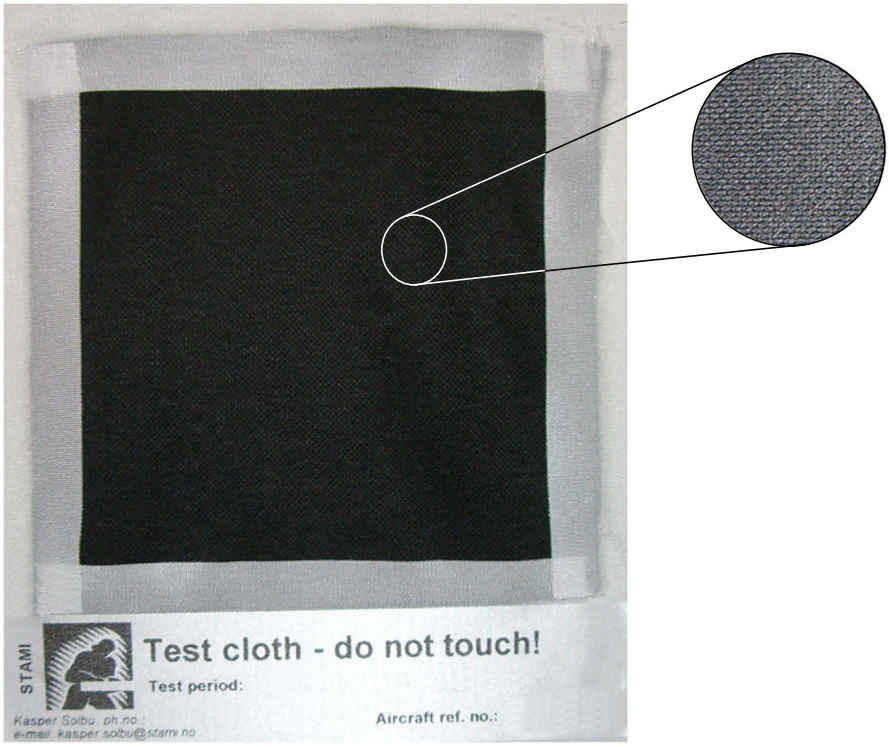


Figure 2-9: Activated charcoal cloth with a magnified spot, which shows the surface structure of the knitted textile

Spot samples from high efficiency particulate air (HEPA) filters.

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.[98] 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.[75] 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 HEPA-filters used as recirculation filters (model A airplanes) during the study were constructed as a multiple folded filter, and thus with a large surface area, inside a 45×51×12 cm aluminum frame. Evaluation of solvents for extraction showed that acetonitrile (ACN) was best suited. Recoveries of OPs from the HEPA-filters were evaluated using three unexposed samples (blinds) and three spiked samples from an unused HEPA filter prepared by adding 100 µL of a DCM solution containing 30 µg/mL of ToCP, TmCP, and TpCP each. A comprehensive multiple step sample preparation procedure was necessary in order to obtain high recoveries, where the three TCP isomers were nearly fully recovered from the spiked HEPA-filters (96-109%, RSD 1.8-2.4%). 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.

2.2 Exposure measurements

2.2.1 Technicians (Paper III)

Work categories

Aviation technicians handle turbine and hydraulic oils frequently during various work tasks, in addition to working close to heated and pressurized systems that 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 shown in Table 2-1 that also includes the oil types in use.

Table 2-1: Oil types and their OP content according to the material safety data sheet. The oils' use in different work tasks is also shown (**Paper III**).

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

During engine maintenance the technicians are working close to the engine. Important engine maintenance work tasks include boroscopy (Figure 2-10), 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 (Figure 2-10) of jet fuel and turbine oils (oils E-H), which may result in exposure to the volatile compounds or from generation of oil spray. 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 (Figure 2-11), or filling of oil dispensers indoors. These tasks possess exposure potential from releases of vapors from the oil reservoirs.

Hydraulic reservoir maintenance includes inspection and maintenance connected to the hydraulic reservoirs (oils A-C) except in the wheel well, for instance testing or maintenance of hydraulic parts (Figure 2-12). Wheel well maintenance work tasks include hydraulic pressure drop (where the hydraulic system is vented by the opening of a valve on the sidewall in the wheel well, Figure 2-13), filter exchanges and inspections in wheel wells (oils A and D).

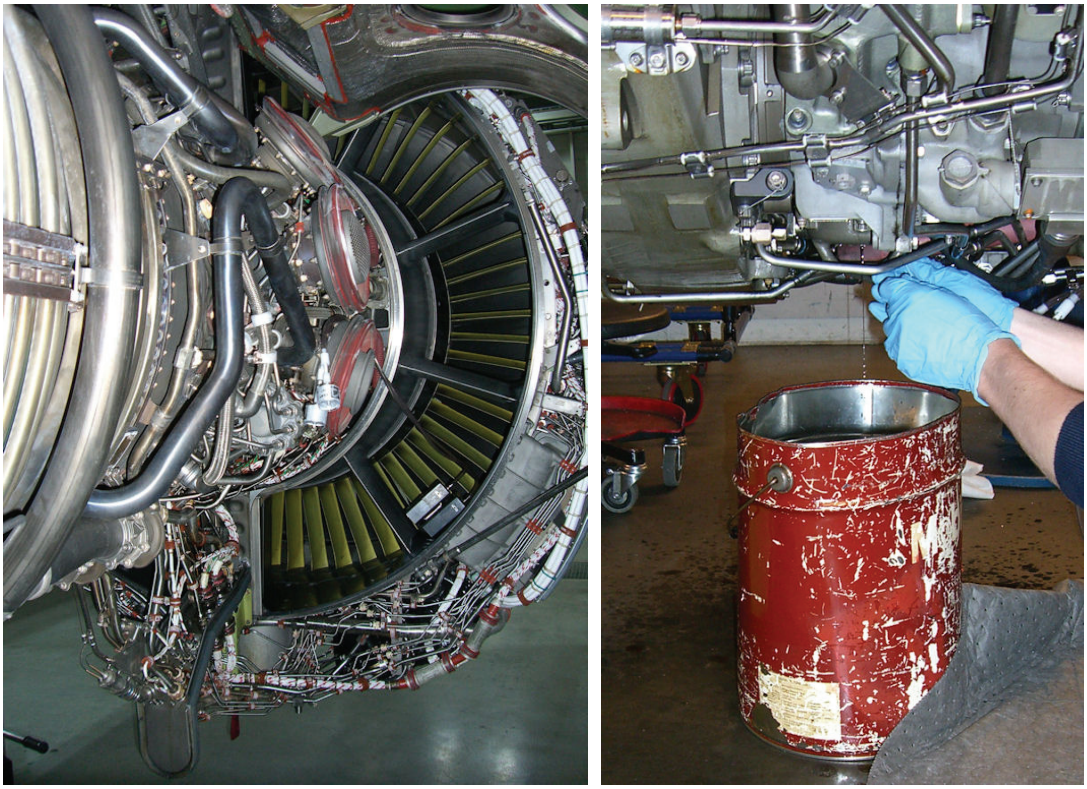


Figure 2-10: Engine maintenance. To the left - airplane engine opened for engine inspection (boroscopy); to the right - draining of jet fuel and oil from aircraft engine.

Figure 2-11: Filling of turbine oil to aircraft engine

Figure 2-12: Top picture – testing of hydraulic device. Bottom picture – propeller adjustment and visible spray (shown with white arrows) of hydraulic oil from the reservoir

Figure 2-13: Pressure drop of hydraulic system prior to wheel well maintenance.

OP contamination levels (Technicians)

Table 2-2 shows the air concentrations of OPs and tVOC 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).

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 2-2, 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 were statistically treated as equals.

Table 2-2: Total-VOC and OP exposure levels among technicians related to the specific work tasks. Measured levels are shown only where ≥75% [#] of the samples was above the methods' LOQ (**Paper III**).

		Personal				Stationary				
		Median	Min.	Max.	90th perc.	Median	Min.	Max.	90th perc.	*P**
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	9 400	1 900	180	33	7 300	1 200	0.96
DBPP	(µg/m^3)	46	0.69	1 700	190	23	0.52	430	250	0.21

 # DBPP and tVOC were present in 87% (engine maintenance) and 83% (oil filling) of the personal samples, respectively, while DBPP was present in 93% of the stationary samples. All other entries were 100%.

*** Mann-Whitney U, non-parametric two-independent sample test (calculated between stationary and personal samples).**

TCP, TPP, and oil aerosol were detected only occasionally in the technician work samples. TCP was for instance quantified in only 21 (median 0.36 µg/m^3, min-max 0.13-120) out of 114 samples. The *ortho*-isomers of TCP were not detected in any of the samples. Of the 114 personal and stationary technicians work task samples, TnBP, DBPP and the other OPs 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, respectively. The butyl phosphates were also identified to appear as background concentrations (1-30 µg/m^3) in the hangars.

Wheel well maintenance 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 2-2). The highest exposure concentrations (1–5 min sampling time) were measured during manual opening of a vent port and subsequent pressure drop of the hydraulic system, and long-term sampling during the complete work in the wheel well (20–255 min sampling time) revealed that the initial oil spray was still present in the wheel well for a long time after the pressure drop.

The technician work tasks were largely conducted in hangars where other work operations were performed simultaneously, possibly resulting in working atmospheres containing several components. Still, the different work tasks were mostly associated with different exposure potential for the different OPs, determined by the oils in use for the specific tasks. Table 2-3 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 TPP/TCP might be explained by the lower concentration of TPP/TCP in the oils as compared to the butyl phosphates. Also, less vapor formation due to the lower volatility of TPP/TCP 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.

Table 2-3: OP concentrations in air during technician work task according to the different oil types used (hydraulic oils A-D and turbine oils E-H) (**Paper III**)

OP	Oil types	*n*	*n*>LOQ %	Median µg/m^3	Min. µg/m^3	Max. µg/m^3	90th perc. µg/m^3
TnBP	C, D	68	100%	89	9.1	9 400	710
DBPP	D	47	100%	28	2.3	1 700	210
TPP	A, B, C	86	36%	<LOQ	<LOQ	150	9.2
TCP	E, F, G, H	37	24%	<LOQ	<LOQ	280	12

Stationary spot sampling from simulated hydraulic leakages

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 under adverse circumstances than reflected by the low exposure levels disclosed during routine work tasks.

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).

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 was used. 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 min sampling time. TCP and oil aerosol concentrations at a height of 1.7 m in front of the test bench were 24 µg/m^3 and 0.40 mg/m^3, respectively. The highest TCP and oil aerosol air concentrations were determined 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 spot was closest to the oil emission source.

2.2.2 Loaders (Paper III)

Work categories

Loaders are loading and unloading aircraft luggage and are working close to aircrafts at the tarmac (Figures 2-14 and 2-15). 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, 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 aircraft construction. For instance, only the jet engines are equipped with a tail pipe, where oil aerosol may be generated (Figure 2-16).

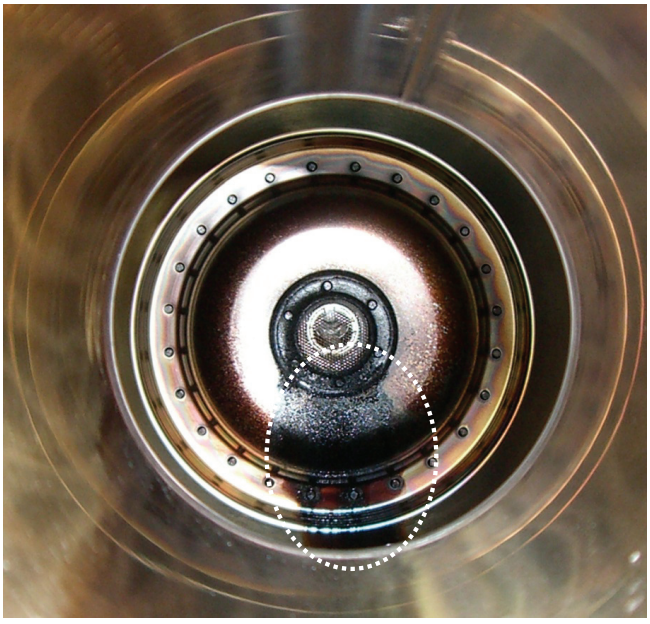
OP contamination levels (Loaders)

Table 2-4 displays 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 aircrafts (n=12, <0.7 µg/m^3). The maximum measured TCP exposure level was one order of magnitude

Figure 2-14: Loaders are pushing the aircraft out from the tarmac (push-back)

Figure 2-15: Loaders are unloading and loading luggage on an jet airplane. The tail pipe (outlet shown with white arrow) and engine are in the front to the right.

Figure 2-16: A view directly into the tail pipe with visible turbine oil leakage (white broken line). When the engine is in a hot state, the oil is vaporized followed by condensation and generation of oil mist. This is observed as a white cloud emitted from the tail pipe for at least 10 min after the aircraft has shut off the engines at the tarmac.



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 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.

Table 2-4: Exposure to VOCs, TnBP and DBPP during loader work tasks (**Paper III**)

		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				
tVOC (TD)	(mg/m^3)	0%	#	<LOQ	<LOQ	#	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%	#	<LOQ	0.8	#	47%	#	<LOQ	0.38	#
Propeller aircraft		*n*=12					*n*=6				
tVOC (TD)	(mg/m^3)	0%	#	<LOQ	<LOQ	#	100%	0.048	0.020	0.14	0.12
TnBP	(µg/m^3)	92%	0.64	<LOQ	1.3	1.3	50%	#	<LOQ	0.27	#
DBPP	(µg/m^3)	33%	#	<LOQ	0.28	#	n.d.	#	<LOQ	<LOQ	#
***p* (TnBP)**			0.006*								
***p* (tVOC)**								0.013*			

***Mann-Whitney U, non-parametric two-independent sample test (calculated between jet aircrafts and propeller aircrafts)**

 # Median and 90th percentile were not calculated for the compounds where less than 75% of the concentrations were below LOQ.

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 (Table 2-4), 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 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 statistically difference for TnBP exposure levels (p<0.001, median 1.0 and 37 μg/m^3, respectively), which was the only OP that was determined for more than 75% of all technician and loader samples. However, the loaders were working close to the hot engines and technicians in general 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 therefore 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 were not investigated in the present study.

Stationary spot sampling from turbine tail pipe outlets

Oil aerosol from the tail pipe exits could be observed up to 10 min after the engines were shut down, which was 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 aircrafts. 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 in 1-5 cm distance from hot tail pipe outlets within 10 min 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.

The *ortho*-isomers of TCP were not detected in any of the samples collected from loader and technician work tasks. 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 measurements during technician work tasks.

2.2.3 Cabin air (Paper IV)

OP contamination levels

Tailored methods for pumped within-day measurements of OPs and VOCs in occupational air, as well as newly developed and evaluated long-term methods, were successfully explored for determination of potential airborne exposure to OPs in aircraft cabin and cockpit air. The newly developed passive long-term sample methods included deposition of OPs to wipe surface areas and to activated charcoal cloths (ACCs). A pair of wipe and ACC areas was mounted on the wall of the cockpit and the cabin in each aircraft (n=26) and exposed for 1-3 months. Additionally, measurements of OPs from spot samples of HEPA recirculation filters (n=6) were performed. These HEPA filters had been used in model A airplanes for 21-86 days, which corresponded to 130-470 flight hours. An overview of the different aircraft models, turbine oils, and number of samples is shown in Table 2-5.

Within-day sampling. In total, 95 and 72 pumped within-day OP and VOC samples, respectively, were collected during 47 flights in six different types of turbine jet engine, propeller and helicopter aircrafts (n=40). In general, the measured air concentration levels of the OPs TiBP, TnBP, TPP, and TCP in this study are considered low (sub-μg/m^3), since many of the measurements showed values below the method LOQs for many of the OPs. The most relevant OPs in this regard originating from turbine and engine oils, tricresyl phosphates (TCP), were detected only in model C airplanes and in 4% of the samples (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).

Other OPs, as DBPP and 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, median 0.44 μg/m^3, min-max 0.02-4.1 μg/m^3). 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 nevertheless detected during all model D

Table 2-5: Overview of the content of organophosphates (OPs) in hydraulic and turbine oils for all aircraft models, in addition to number of unique aircrafts (*k*) of each aircraft model and of specific samples (*n*) collected in these aircrafts included in the field study (**Paper IV**).

	OP content in oils		Filter/ adsorbent	TD tube	ACC[5]	Wipe
			OPs	tVOC[4]	OPs	OPs
Aircraft models*	Hydraulic oil	Turbine oil	*k* (*n*)	*k (n)*	*k (n)*	*k (n)*
Jet airplanes						
A	40-70% DBPP[1], 20% TnBP[2]	<2.5% TCP[3]	15 (30)	15 (30)	14 (30)	14 (30)
B	40-70% DBPP, 20% TnBP	1-5% TCP	9 (22)	-	-	-
Propeller airplanes						
C	60-80% TnBP, 1-5% TPP	1-5% TCP	6 (12)	6 (12)	6 (12)	6 (12)
D	0.1-0.9% TPP	1-5% TCP	6 (12)	6 (12)	6 (12)	6 (12)
E	60-80% TnBP, 1-5% TPP	1-5% TCP				
Helicopters						
F	0.1-0.9% TPP	1-5% TCP	1 (7)	1 (7)	-	-
G	0.1-0.9% TPP	1-5% TCP	3 (12)	3 (12)	-	-
Total of aircrafts (*k*) and samples (*n*)			40 (95)	31 (72)	26 (54)	26 (54)

* 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 (eight OP filter/adsorbent, four TD and four oil aerosol filter/adsorbent) were collected during subsequent ground testing.

1) Dibutylphenyl phosphate, 2) Tri-n-butyl phosphate, 3) Tricresyl phosphates, 4) Total-VOC samples, 5) Activated charcoal cloth samples

Table 2-6: Summary of within-day TnBP levels (in $\mu g/m^3$) in cabin and cockpit air by aircraft during commercial flights (**Paper IV**)

	Jet airplanes		Propeller airplanes		Helicopters	
Aircraft models	A	B	C	D	F	G
k†	15	9	6	6	1	3
n‡	30	22	12	12	7	12
%>LOQ	100%	100%	100%	100%	57%	58%
Median	**1.1**	**0.16**	**0.54**	**0.074**	**0.061**	**0.051**
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**	**0.079**

†) Number of unique aircrafts
‡) Number of measurements

airplane flights and in 58% of the helicopter flights (n=19, median 0.091 µg/m^3, min-max <LOQ-1.5), as shown in Table 2-6. However, the TnBP levels in the airplanes using hydraulic oils containing TnBP were significantly higher than in the 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.

None of the oils used in this study was reported in the MSDSs to contain TiBP, although TiBP is known to be optionally added as minor amounts in hydraulic oils also containing TnBP.[3] 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.[99-102]

Wipe sampling. 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 where TCP was detected in 39% of the wipe samples (n=56) in concentrations from <LOQ to 8.3 ng/dm^2/day. For instance, deposited TCP concentrations in model C airplanes were determined in 92% of the collected samples (median 2.3 ng/dm^2/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-qualitative long-term sampling. TCP was determined in 31 and 8% of the samples collected from models A and D airplanes, respectively. The highest TCP level (8.3 ng/dm^2/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 airplanes (models C and D) and 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/day. TPP was also determined in

66% of the model A airplanes, although with a lower median (0.37 ng/dm^2/day), probably reflecting general background levels of TPP from various sources.

The volatile alkyl phosphate TnBP is in use in hydraulic oils in the 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.

Activated charcoal cloth (ACC) sampling. TCP was determined in only two (7.8 and 270 ng/dm^2/day) out of 56 ACC 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/day). Thus, the highest concentration was measured in the ACC sample, 270 ng/dm^2/day, which is substantially higher than in all other collected ACC and wipe samples (max 8.2 ng/dm^2/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.

The measured OP concentrations from the ACC samples collected parallel to the wipe samples illustrate high recoveries also for the alkyl phosphates. TnBP was determined in all ACC samples, also from the model D samples where the hydraulic oils are not supposed to contain TnBP. The TnBP concentration levels in the samples from model D airplanes were however significantly below the levels found in model A and C airplanes (p<0.05). Background levels of TiBP were also determined in all ACC samples.

DBPP, that is a component in hydraulic oils only 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 oil used in model A and C airplanes (**Paper III**). Additionally, the higher concentration levels of DBPP in model C as compared to model D airplanes may relate to the sharing of hangar for the model A and C airplanes under study, while model D airplanes use separate hangars.

Comparison of wipe and ACC sampling. The wipe and ACC methods were compared with regard to sampling of the semi-volatile DBPP and the non-volatile TPP, which were measured simultaneously on parallel wipe and cloth samples from 16 and 9 model A and D airplanes, respectively. The two methods correlated well with respect to TPP sampling (correlation coefficient factor R=0.97) but not for DBPP sampling. However, 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/day). This effect was 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 of the lower LOQ for the wipe sampling method.

Spot samples from HEPA-filters. TCP was detected in all six HEPA-filters (min-max 1.1-42 ng/g filter per flight hour) obtained from model A airplanes, supporting an assumption of the general presence of TCP in cabin and bleed air in aircrafts with turbine jet engines. Figure 2-17 shows the chromatographic profile from analysis of a HEPA-filter extract.

Engine leak and measurements of TCP

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. However, 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 during ground testing prior to the engine change. The arithmetic mean TCP concentration (no *ortho*-isomers) before replacement of the engine was 5.1±1.1 µg/m^3 (median 5.5, min-max 3.6-5.9) and was an order of magnitude higher than after engine

replacement. This significant difference (p=0.02) 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. This is to our knowledge the first TCP measurements reported in relation to an incident.

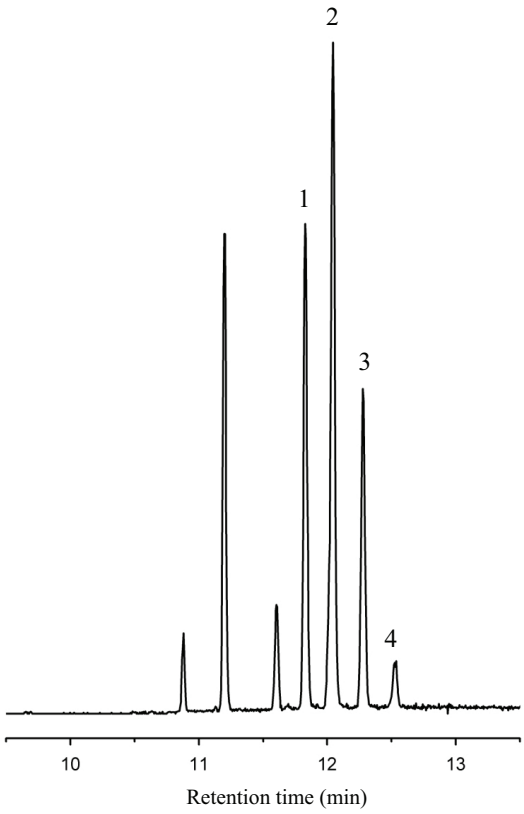


Figure 2-17: Chromatographic profile (extracted ion chromatogram, *m/z* 368) from analysis of a HEPA filter sample extract, using GC-MS in scan mode. The TCP peaks shown in the chromatogram are: (1) *m*-TCP, (2) *mmp*-TCP, (3) *mpp*-TCP and (4) *p*-TCP. The three peaks to the left are also due to compounds with *m/z* 368 in the mass fragment pattern, but are from the mass spectra and analysis in SIM mode confirmed not to origin from TCP-isomers (**Paper IV**). Other conditions are as described in Figure 2-1.

3 CONCLUSIONS

3.1 Achievements

The expressed health concerns related to OP exposures in combination with the lack of tailored exposure measurements revealed a need for work task related exposure measurements of OPs in the aviation industry in general. The present thesis has demonstrated development of new methodologies for air sampling of OPs and their applications in the aviation industry during technician and loader work operations and in cabin and cockpit air during commercial flights.

Paper I described the first scientifically published air sampling method for sampling of OPs originating from hydraulic and turbine oils. The method was applied to perform exposure measurements in the aviation industry during loader and technician work operations (**Paper III**) and in cabin/cockpit air (**Paper IV**). The method was also shown to be advantageous when compared to a traditional oil aerosol/vapor method for indirect OP measurements (**Paper III**). Moreover, use of the developed wipe sampling and activated charcoal cloth methods successfully demonstrated presence of TiBP, TnBP, TPP and TCP in aircraft cockpits and cabins during a long-term sampling, in addition to detection of TCP in HEPA filters (**Paper IV**).

The exposure assessment during loader and technician work operations (**Paper III**) is to our knowledge the first published scientific study ever reporting personal exposure measurements of OPs originating from hydraulic and turbine oils. Although these exposure measurements showed low working atmosphere concentrations of the OPs under study for most of the investigated work tasks (<0.1 mg/m^3 for 94% and 100% of the technician and loader samples, respectively),[§] some work operations were identified with potential for exposure to increased OP concentrations. Measurements during more critical circumstances, for instance during leaks or close to exposure sources, indicated a

[§] This concentration level (0.1 mg/m^3) corresponds to the threshold limit value–time-weighted average (TLV-TWA) in occupational air (8 hour day) for the most toxic OP in this study (ToCP), as established by American Conference of Governmental Industrial Hygienists.

substantially higher OP exposure potential under adverse circumstances than the low exposure levels disclosed during routine work tasks.

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, were successfully explored for determination of potential airborne exposure to OPs in aircraft cabin and cockpit air (**Paper IV**). In general, low levels of the OPs TiBP, TnBP, TPP and TCP (sub-μg/m^3) were shown, but TnBP was present in all air samples collected from airplanes. This is to our knowledge the first scientific study to report these OPs (TCP in particular) in cabin and cockpit air in aircrafts during civil commercial flights. Moreover, an incident sampler was developed for in-flight sampling during potential sudden and unexpected incidents (**Paper II**) and installed in ten aircraft cockpits (**Paper IV**). However, none of the preselected aircrafts were reported to experience such incidents in cockpit air during the installation period. There is thus still a lack of this kind of air samples and further emphasis should therefore be directed towards assessments of OP contamination in relation to incidents. This is illustrated by the measurements performed during ground testing of one airplane with a leakage of turbine oil into the cabin air, which revealed a potential for substantially higher TCP contamination in cabin air during such incidents (**Paper IV**).

3.2 Future perspectives

This study has presented new air sampling methodologies, which have been applied in the aviation industry resulting in collection of nearly 900 air measurement samples, including documentation of OPs' presence in a selection of aircraft models and during general work tasks for aviation technicians and loaders. The results from this study are therefore a substantial contribution to the knowledge of occupational exposure to OPs in the aviation industry. Possible similar future studies for other aircrafts or work tasks may therefore use the results reported herein as support. Most of all, measurements in cabin air during incidents with contamination from turbine oils are still needed. Future studies are therefore especially encouraged to endeavor performing such measurements to substantiate the concentration levels of airborne OPs, or other chemical compounds of relevance that may harm human health, that potentially may occur during such incidents.

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