

Determination of Tricresyl Phosphate Air Contamination in Aircraft

G. DENOLA^{1,2}, P. J. HANHELA¹ and W. MAZUREK^{1*}

¹Maritime Platforms Division, Defence Science and Technology Organisation, Department of Defence, 506 Lorimer St., Fishermans Bend, Melbourne, Victoria, 3207, Australia

Received 12 January 2011; in final form 19 April 2011; published online 5 July 2011

Monitoring of tricresyl phosphate (TCP) contamination of cockpit air was undertaken in three types of military aircraft [fighter trainer (FT), fighter bomber (FB), and cargo transport (CT) aircraft]. The aircraft had a previous history of pilot complaints about cockpit air contamination suspected to originate from the engine bleed air supply through the entry of aircraft turbine engine oil (ATO) into the engine compressor. Air samples were collected in flight and on the ground during engine runs using sorbent tubes packed with Porapak Q and cellulose filters. A total of 78 air samples were analysed, from 46 different aircraft, and 48 samples were found to be below the limit of detection. Nine incidents of smoke/odour were identified during the study. The concentrations of toxic *o*-cresyl phosphate isomers were below the level of detection in all samples. The highest total TCP concentration was $51.3 \mu\text{g m}^{-3}$, while most were generally found to be $<5 \mu\text{g m}^{-3}$ compared with the 8-h time-weighted average exposure limit of $100 \mu\text{g m}^{-3}$ for tri-*o*-cresyl phosphate. The highest concentrations were found at high engine power. Although TCP contamination of cabin/cockpit air has been the subject of much concern in aviation, quantitative data are sparse.

Keywords: air contamination; aircraft; engine bleed air; toxicity; tricresyl phosphate

INTRODUCTION

Occurrence of bleed air contamination

Cockpit/cabin air contamination in both military and commercial aircraft may be due to a number of possible sources (NRC, 2002; Winder, 2006a,b; Murawski and Supplee, 2008). In Australia, during the 1990s, a series of widely publicized incidents occurred when passengers and crew claimed to have suffered acute and chronic health effects after exposure to smoke and fumes in the BAe 146 passenger aircraft (Easdown, 2010).

Aircraft cabin air contamination from the Environmental Control System (ECS) has been of foremost concern throughout the world (Hood, 2001;

Acohido, 2002; Winder, 2006b; Murawski and Supplee, 2008). The ECS uses engine bleed air to pressurize and ventilate the cockpit and cabin. Under certain circumstances, this may result in air contamination (in the form of smoke and odour) from the aircraft turbine engine oil (ATO), which contains many substances including an anti-wear agent [tricresyl phosphate (TCP)], phenyl- α -naphthylamine (PAN), and dioctyldiphenylamine (DODPA) as antioxidants in synthetic liquid polyester base (Australian Parliament Senate, 2000; Great Britain Parliament, 2000; Winder and Balouet, 2002; Hanhela *et al.*, 2005a,b).

In most jet aircraft, the ECS utilizes air from the compressor stage of the engine, where temperatures may exceed 350°C (NRC, 2002; Lebele-Alawa *et al.*, 2008) or even 500°C (van Netten and Leung, 2000). The air is cooled by passage through air/air and air/water heat-exchangers and then through a water coalescer consisting of a fabric bag impregnated with

*Author to whom correspondence should be addressed.

Tel: +61-39-62-68-427; fax: +61-39-62-68-282;

email: wally.mazurek@dsto.defence.gov.au

²Present address: Toxikos Consultants, PO Box 74, Caulfield East, Victoria 3145, Australia.

a synthetic wax. In addition to supplying the cockpit and cabin, the air is also used to cool the avionics.

The detection of TCP in aircraft

The potentially neurotoxic TCP (Fig. 1) anti-wear additive used in ATO has received much attention (Mackerer *et al.*, 1999; Australian Parliament Senate, 2000; Great Britain Parliament, 2000; van Netten and Leung, 2000; Winder and Balouet, 2002; Hocking, 2005; Winder, 2006a,b; Murawski and Supplee, 2008). Although there was much speculation about the effects on the passengers and crew, earlier studies could not identify the presence of TCP in the cabin air (Great Britain Parliament, 2000; Nagda *et al.*, 2001; CAA, 2004).

In 2005, Hanhela *et al.* reported the preliminary results of a survey of military aircraft for bleed air contamination from TCP, PAN, and DODPA as well as organophosphates from hydraulic fluids. The TCP concentration during a cockpit smoke event was also reported. Subsequently, two reports presented a few airborne TCP measurements for the BAe146 and the Boeing 757 (Muir *et al.*, 2008; van Netten, 2009).

Toxicity of TCP

The most toxic components of ATO are some of the 10 TCP isomers. Most organophosphates exert their acute toxic effects by the suppression of acetylcholinesterase, which can cause respiratory failure due to neuromuscular block. However, organophosphates such as TCP are also able to induce a delayed (1–2 weeks) neurodegenerative condition known as organophosphate-induced delayed neuropathy (OPIDN), which is known to affect both the central and peripheral nerves of birds and mammals (Nomeir and Abou-Donia, 1986; Mortensen and Ladefoged, 1992; Daughtrey *et al.*, 1996; Fowler *et al.*, 2001; Abou-Donia, 2003). The relationship between the chemical structure of many pure triaryl

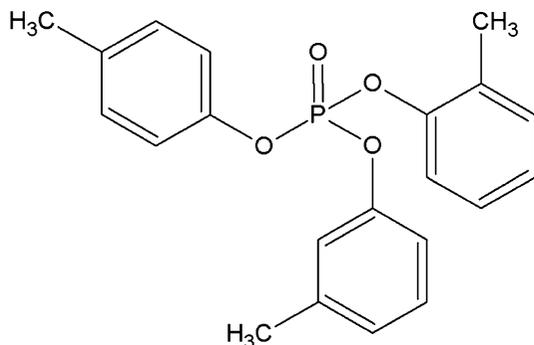


Fig. 1. TCP (*omp*-isomer).

phosphates and potency in causing OPIDN has been extensively studied and the relative neurotoxic activities of these compounds are well known. It has been recognized for at least 50 years that alkyl substituents at the ortho positions of the aromatic rings are responsible for the neurotoxic activity of TCP (Henschler, 1958, 1959). TCP synthesized from only *m*-cresol and *p*-cresol does not cause OPIDN (Mackerer *et al.*, 1999) but the possibility of chronic toxicity of this isomeric mix cannot be dismissed.

TCP (bp₁₀ ~265°C; Merck Index, 1976) is commonly manufactured from the reaction phosphorus oxychloride and a mixture of phenols, predominantly cresols, but other alkylated phenols are also present (Craig and Barth, 1990, 1999). Cresols occur in the form of three structural isomers, meta (*m*), para (*p*), and ortho (*o*) which are difficult to separate because of similar boiling points (202, 201.8, and 191–192°C, respectively) (Merck Index, 1976). These isomers react in various combinations to form 10 structural isomers of TCP (Winder and Balouet, 2002). The *oxx*-isomers (where *x* = *m/p*-cresyl) are regarded as the most toxic; 10 times more toxic than the tri-*o*-cresyl isomer and 2 times more toxic than the di-*o*-isomers. Hence, the toxicity of TCP is related to the *o*-cresyl isomer content with the *m*- and *p*-cresyl isomers having low toxicity (Henschler, 1958). Other *o*-alkyl substituted phosphates, such as those derived from ethyl phenols and xylols, are also neurotoxic (Craig and Barth, 1990, 1999). However, the toxicity of *o*-alkyl phosphates declines with the length of the alkyl group (Johannsen *et al.*, 1977) and the number of substituents. For example, xylol phosphate esters are far less toxic than TCP (Henschler, 1959). In addition, these compounds are present as trace impurities in TCP and are difficult to quantify occurring with a myriad of other phosphates in the liquid chromatogram (Kibby *et al.*, 2005).

The concentrations of TCP in a commonly used ATO have been reported to be ~2.5% with the *mmm*- and *mmp*-isomers constituting the major components of TCP (De Nola *et al.*, 2008). In ATO manufactured after 2001, the *oxx*-isomers were found to be in the range of 20–40 µg l⁻¹, while the *oox*- and *ooo*-isomers were below the limits of quantitation for the method. Earlier formulations of ATO contained TCP manufactured from cresols with higher *o*-cresol isomer content (Craig and Barth, 1990, 1999; De Nola *et al.*, 2008).

Australian Defence Force aircraft

To varying degrees, similar problems of cockpit smoke and fumes occur in Australian Defence Force (ADF) aircraft. A survey of ADF aircraft by the

Institute of Aviation Medicine (Royal Australian Air Force) over a 5-year period has catalogued incidences (Aviation Safety Occurrence Reports) of smoke and fumes in the cockpit/cabin (Singh, 2005). In 1987, Hercules C-130 aircraft were identified as being particularly problematic and incidents of odour were so severe that operations were restricted. A subsequent investigation, however, identified traces on the ECS water coalescer of such an aircraft but not in the flight deck air (Kelso *et al.*, 1988).

The aim of the study

The aim of this study was to develop a procedure for air monitoring of TCP in aircraft cockpit/cabin air and to survey TCP airborne concentrations in ADF aircraft in order to assess the potential risk to health of ground and flight crew from TCP exposure.

This report constitutes part of a study of organophosphate and amine air contamination in ADF aircraft (Hanhela *et al.*, 2005a,b; De Nola *et al.*, 2008).

EXPERIMENTAL

Materials and reagents

Tri-*o*-cresyl phosphate (96%), tri-*p*-cresyl phosphate (98%), and tri-*m*-cresyl phosphate (97%) were purchased from Acros Organics; TCP (a mixture of *o*-, *p*-, and *m*-isomers) was purchased from Fluka. Mobil Jet Oil II, batch E3C503, 21 April 03 (~2.5% TCP) was used as the ATO reference. Isohexane (Riedel-de-Haen Chromasolv) and dichloromethane (Unilab, redistilled) were used in the extraction of TCP from the filters and sorbents. PALL Life Sciences GN-4 Metricel (0.8 µm and 37 mm) hydrophilic mixed cellulose esters filters were used with a cellulose support pad and these were fitted into styrene acrylonitrile 37-mm Air Monitoring Cassettes. Porapak Q (50/80 mesh) was obtained from Altech Associates, Pty Ltd, Baulkham Hills, New South Wales, Australia.

Aircraft

The fighter trainer (FT), fighter bomber (FB), and cargo transport (CT) aircraft were introduced into service in 2001, 1973, and 1978/1999, respectively. In the case of the CT and FB aircraft, crews observed air contamination at high engine thrusts during take-off and ground engine runs at high power. Air monitoring in the cockpit of the FT aircraft was initiated after complaints of 'smoke' in the cockpit during the operation of the Auxiliary Power Unit (APU). The APU supplies power and cooling air while the aircraft is on the ground and the main engine is not

operating. In all cases, the aircraft used the same brand of ATO made to NATO code, O-156; USA and UK military specifications, MIL-PRF-23699f and Def. Stan. 91-101 Issue 3, consisting of a pentaerythritol/fatty acid polyester base, designed to operate under the high temperatures of a jet engine and the low pressures of high altitude flight. Commercial aircraft use similar or identical products (Winder and Balouet, 2002).

Sampling of ECS heat exchangers and coalescer bags for TCP

TCP contamination of ECS heat exchangers was determined by rinsing the isolated units with acetone (~500 ml) and concentrating the extract to ~20 ml on a rotary evaporator under reduced pressure. The coalescer bags were placed in a soxhlet extractor and extracted for ~6 h with acetone (500 ml). In both cases, the extracts were concentrated to ~20 ml and analysed by gas chromatography (GC) with a pulsed flame photometric detector (PFPD) (*vide infra*) with a 5-µl injection. The analysis was not quantitative. All other extracts and calibration standards were confined to iso-hexane medium.

Relevant air sampling methods

The monitoring approach adopted in this study has been based on other semi-volatile compounds such as sulphur mustard [1,1-thiobis(2-chloroethane); bp. 216°C] chemical warfare agent, using Porapak Q (Muir *et al.*, 2005). In this case, extraction with hexane yielded quantitative recovery. Similarly, hexane had been used for the extraction of TCP from Porapak Q sorbent after air sampling for TCP in aircraft cockpit air (Kelso *et al.*, 1988).

Glass fibre filters have also been used for sampling of oil aerosols. Recovery studies involved spiking with mineral oil. In these cases, extractions were carried out with cyclohexane (Simpson *et al.*, 2000, 2003), dichloromethane (Björklund *et al.*, 2004, Staaf and Östman, 2005), or carbon tetrachloride (NIOSH, 1996) after a predetermined amount of air had been passed through the filters to simulate air sampling.

Airborne organophosphate flame retardants and plasticizers have also been sampled using glass fibre filters and the samples were recovered by extraction with dichloromethane (Björklund *et al.*, 2004, Staaf and Östman, 2005). Air concentrations of organophosphate pesticides have also been determined by sampling using XAD-4 sorbent and samples were recovered by extraction with ethyl acetate (Harnly *et al.*, 2005).

More recently, a comprehensive study of monitoring techniques for airborne organophosphate-containing

lubricating oils was reported (Solbu *et al.*, 2007). Of the five sorbents examined, Chromosorb 106 (polystyrene, Castello and D'Amato, 1982) provided the best recovery when extracted with dichloromethane compared with other solvents (Solbu *et al.*, 2007). In addition, glass fibre (1.6 μm) filters were used for air sampling of the oil mist with sample recovery by extraction with dichloromethane (Solbu *et al.*, 2007). Mixed cellulose ester fibre filters and glass fibre filters are commonly used for collection of oil mist samples (Menichini, 1986; Simpson *et al.*, 2000, 2003) and are recommended by NIOSH (1996).

In a 2007 study for the UK Department of Transport, thermal desorption tubes, packed with Tenax and carbon molecular sieves and SPME (diffuse sampling) were used to monitor for volatile and semi-volatile compounds including TCP (Muir *et al.*, 2008). However, given the low volatility of TCP, thermal desorption is unlikely to be the ideal method of sample recovery for TCP.

Sampling procedures used in this study

In this study, aircraft air was sampled using filters and sorbent (Porapak Q) tubes. It can be reasonably expected that because of its low volatility, ATO and its components are present in air as an oil mist (liquid aerosols) and thus can be sampled on filters using NIOSH Method 5026 (NIOSH, 1996) for oil mists without significant loss of vapour (Simpson *et al.*, 2000, 2003; Solbu *et al.*, 2007). For situations where engine operating times were short (i.e. ground engine runs), 0.8- μm membrane filter cassettes were used at high flow rates for air sampling of TCP. For longer sampling periods, sorbent tubes were used at low flow rates. The sampling was managed by ground and flight crews who were instructed to ensure maximum sampling periods and encouraged to take samples during air contamination incidents.

Aircraft models were selected on the basis of the severity and frequency of bleed air contamination as reported by the Royal Australian Air Force, Institute of Aviation Medicine (Singh, 2005). However, the range of aircraft types was limited by availability and resources. Within each aircraft squadron, sampling was opportunistic.

The FB and FT aircraft are fitted with a two-seater cockpit, while the flight decks of CT aircraft are similar in size to the long-range commercial aircraft. Despite the space constraints, ground and flight crew were instructed to locate the air sampler as close as possible to the air vents. During ground engine runs, the cockpit/flight deck was closed unless otherwise stated.

Cockpit air samples from the FT aircraft were initially taken using sorbent tubes but later filters were used (for increased sample volume) while the aircraft was on the ground, with the APU running. Sorbent tube samples were used for air sampling of the CT aircraft in-flight and during ground engine runs. In the case of the FB aircraft, in-flight air samples were taken with sorbent tubes, while filters were used to sample cockpit air during ground engine runs. On each occasion, one sample was taken due to the small cockpits and busy schedules of the ground crew. Sample tubes and filters were capped during transport and no transport blanks were used.

Air sampling was carried out using Porapak Q (ethylvinyl benzene/divinyl benzene; Castello and D'Amato, 1982) sorbent tubes and Metrical filters. Sample recovery was by solvent extraction. The extracts were concentrated by evaporation prior to analysis by GC-PFPD.

All instruments were approved by the Royal Australian Air Force, for use in the aircraft with respect to electromagnetic interference, according to whether the equipment was used in-flight or during ground testing.

Long duration air sampling for TCP. In-flight and ground-based air sampling (long duration) was carried out using sorption tubes and a metring pump (e.g. Aircheck model 2000) operating at 2 l min^{-1} . Glass-lined stainless-steel tubes (90 \times 6 mm outside diameter) were packed with \sim 0.06 g Porapak Q and held in place with glass wool. The packed tubes were conditioned by washing with hexane (6 ml) and heated at 220°C in an oven while purged with helium (70 ml min^{-1}) for 2 h. The tubes were then cooled and capped with in-house polymeric end-caps before and after air sampling.

Short duration air sampling for TCP. For most ground engine runs, high volume short duration (5–20 min) air sampling was carried out using PALL Corporation Metrical membrane filters (0.8 μm) GN used open faced with the filter directed downwards. A battery (12 V) powered diaphragm pump (Gardner Denver, Thomas 107 series) was operated at 36 l min^{-1} . This protocol was used for static engine test runs with the aircraft in a fixed location on the ground. Air samples were taken by the ground crew with the engines at high throttle (\sim 80%).

Air sampling pumps were calibrated at sea level, with the filter (or tube) attached, using a high precision gas metre, Toyo Gasmeter Co., Japan, model ML-2500 (Kittler *et al.*, 1992).

Extraction of TCP from sorbents and filters. After sampling the sorbent tubes containing the sorbent and glass wool were washed with a total iso-hexane

volume of 7 ml into 24-ml glass vials. The vials were then placed on a heating block at 60°C and the extract reduced in volume to ~1 ml by a flow of nitrogen into the vials. The extract and washings were then transferred by pipette to preweighed 1.5-ml autosampler vials, capped and reweighed.

The Metrical filters were immersed in iso-hexane (~20 ml) and sonicated for 5 min. The filters were then removed and the solution was evaporated to ~1 ml under a stream of air. The extracts and vials were then placed in an autosampler and analysed by GC-PFPD (*vide infra*).

TCP recovery studies using Porapak sorbent and Metrical membrane filters

Recovery of TCP from Porapak Q sorbent and Metrical filters. Recovery studies from sorbents were carried out by spiking the Porapak Q sorbent with a solution of the TCP and ATO followed by subsequent extraction with iso-hexane and dichloromethane after a predetermined amount of air had been passed through the sorbents. Air was passed through the samples to simulate sampling conditions and to identify break-through. Solutions were used rather than a vapour because of the difficulty of generating TCP or ATO vapour of a known and stable concentration.

Loading. The sorbent tubes used were 6.35-mm diameter; stainless steel, glass-lined (Restek Silcosteel tube, 86 mm long). They were packed with sorbent and prepared as described above. TCP, containing *m*-, *p*-, and *o*-isomers (Fluka) was diluted with iso-hexane and the sorbent tubes were loaded with 5 µl (0.12 µg) and 10 µl (0.46 µg) of the working solutions. ATO was diluted with iso-hexane and assumed to contain ~2.5% TCP. The sorbent tubes

were loaded with 5 µl (~0.1 µg TCP) and 10 µl (~0.6 µg TCP) of the prepared solutions (Table 1). The tubes were connected to an SKC AirChek 2000 pump and air was passed through the tubes at 2 l min⁻¹ to simulate airflow during sample collection (Table 1).

Metrical filters were loaded with 29.5 µl (~0.6 µg TCP) and 50 µl (~32 µg TCP) of TCP working solutions and 35.0 µl (0.72 µg TCP) and 50 µl (30 µg TCP) of the ATO working solutions containing 820 µg/ml and 2400 µg/ml of ATO, respectively (Table 1). The filters were supported by the edge so that no sample was lost through surface contact and were then allowed to stand for 5 min before they were assembled into the 37-mm air sampling cassettes. The filters were then connected to a pump (KNF UN726.3ANI) and air was drawn through the filters in order to simulate airflow during sample collection of cockpit air (at 36 l min⁻¹; Table 1). Sampling times for cockpit air were 5–20 min, corresponding to 180–720 l of air being drawn through the filters.

The tubes and filters were extracted in the same way as the aircraft samples (*vide supra*) using iso-hexane and dichloromethane. Filters were sonicated in solvent for 20 min.

Analysis of TCP

Calibration and analytical limits. A calibration plot was derived using six calibration standards of *o*-TCP; 5, 10, 20, 50, 100, and 500 µg l⁻¹; $y = 103.9x$, $r^2 = 0.99$, relative standard deviation = 5.2. Prior to analysis, an internal standard of 5 µl of 8.95 µg l⁻¹ and 44.7 µg l⁻¹ of *o*-TCP was added to samples extracted from the Porapak sorbents and Metrical filters, respectively. The standards and

Table 1. Recovery of TCP from sorbents and filters

Sample	Iso-hexane					Dichloromethane				
	Flow rate (l min ⁻¹); Vol. (l)	Mean TCP Loading (µg)	Equiv. Air Conc. (µg m ⁻³)	Recovery % (n)	RSD %	Flow rate (l min ⁻¹); Vol. (l)	Mean loading (µg)	Equiv. Air Conc. (µg m ⁻³)	Recovery % (n)	RSD %
Tubes										
TCP	2; 900	0.120	0.133	79.0 (5)	8.5	2; 900	0.120	0.133	96.6 (3)	2.7
	2; 720	0.458	0.636	94.5 (10)	4.0					
ATO	2; 900	0.100	0.111	102.3 (5)	2.5					
	2; 720	0.605	0.861	93.4 (10)	2.9					
Filters										
TCP	14; 600	0.60	1.00	76.4 (5)	9.8	14; 600	0.60	1.00	95.3 (2)	4.3
	32; 720	27.51	38.18	95.6 (10)	4.8	32; 720	26.1	36.27	98.4 (10)	3.3
ATO	14; 600	0.72	1.20	63.6 (4)	5.8	14; 600	0.72	1.20	98.1 (3)	5.5
	32; 720	31.45	43.68	97.3 (10)	2.3	32; 720	29.2	40.48	96.0 (10)	1.3

RSD, relative standard deviation for the replicates; *n*.

samples were then each chromatographed five times using the method applied to the aircraft samples.

For solutions (iso-hexane), the limit of detection (LOD) and the limit of quantitation (LOQ) were $3 \mu\text{g l}^{-1}$ ($n = 5$) and $10 \mu\text{g l}^{-1}$ ($n = 5$), respectively, using the criteria of $S/N = 3:1$ (LOD) and $S/N = 10:1$ (LOQ) (ICH, 2008) with respect to the chromatograms. The $\text{LOD}_{\text{instrument}}$ and $\text{LOQ}_{\text{instrument}}$ were 12 and 40 pg, respectively, (4 μl injection). LODs and LOQs were also determined for each aircraft air sample based on the S/N of the TCP response in the chromatograms (*vide supra*) and presented as micrograms per cubic metre after adjustment for air volumes used in the sample collection.

Instrumentation. Aircraft samples containing organophosphate species were routinely analyzed by gas chromatography on a Varian CP-3800 equipped with a PFPD, and CP-8400 autosampler. Separation was conducted with a Varian CP-Sil 8 MS (30 m \times 0.32 mm \times 0.25 μm) column with a carrier gas (high purity helium) flow rate of 1.2 ml min^{-1} . The injector temperature was set to 320°C and the injector operated in a splitless mode for 0.7 s, then in a split (100:1) mode. The initial oven temperature was 120°C and held for 2 min, then ramped at 20°C min^{-1} to 300°C and held at this temperature for 5 min.

The PFPD was operated at 325°C with a phosphorous filter, a gate delay of 4.0 ms, a gate width of 10.0 ms, and a trigger level of 200 mV. The Air(1) flow was set to 15.0 ml min^{-1} , the Air(2) flow at 10.0 ml min^{-1} , and hydrogen flow at 14.0 ml min^{-1} . TCP was determined as the four *m/p* isomers (*mmm*, *pmm*, *ppm*, and *ppp*) from the 10 possible structural isomers (De Nola *et al.*, 2008). Quantitative calibration was based on the four *m/p* isomers.

RESULTS AND DISCUSSION

TCP was detected but not quantified from acetone washings of the ECS heat exchangers. It was also detected in the coalescer bags from FB and CT aircraft after soxhlet extraction with acetone (Hanhela *et al.*, 2005). Its presence at these locations was indicative of TCP entering the cockpit/flight deck and hence it constituted justification for air sampling in the cockpit/flight deck during ground engine runs and in-flight.

Sample recovery

Porapak Q recovery. Iso-hexane and dichloromethane solvents were selected for extraction because of their volatility and good solvency. The recovery

of TCP from TCP-loaded tubes containing Porapak Q sorbent was 79.0–94.8% and 96.6% when extracted with iso-hexane and dichloromethane, respectively (Table 1). Each extraction was replicated. High recoveries of TCP (93–102%) from tubes loaded with ATO were also observed when extracted with iso-hexane. No significant TCP break-through was observed for either TCP or ATO with TCP loadings up to 0.61 μg and air volumes of 720 l as indicated by the high recoveries.

Metrical filter recovery. As in the case of Porapak Q, no significant TCP break-through was observed for either TCP or ATO at TCP loadings of up to 31.5 μg and a volume of 720 l. When extracting with iso-hexane, recovery of TCP and ATO from the cellulose Metrical filters was found to be slightly lower at lower loadings compared with dichloromethane (Table 1). However, iso-hexane was preferred over dichloromethane in the subsequent GC analysis of the extracts because it produced a linear baseline compared with the large baseline drift exhibited by the dichloromethane extracts. It also allowed a larger (twice) volume to be injected compared with dichloromethane.

When monitoring during ground engine runs in the FT and FB aircraft, due to the short operating times, air sampling was undertaken over a period of 6–20 min. This necessitated a high sampling volume, which could be best achieved with a filter (e.g. 0.8 μm) rather than a sorbent. Hence, in these cases, TCP concentrations were determined as an aerosol and it was assumed that the contribution from the vapour was insignificant. This is consistent with a recent study of air monitoring of TCP-containing oils, which showed that airborne TCP is present as the oil aerosol rather than the vapour phase. Air samples were taken in both the work place and in the laboratory (generated oil aerosols) using a filter and sorbent sampling train. It was found that the TCP was retained on the filters and quantifiable amounts were not present on the sorbent (Solbu *et al.*, 2007). When sampling air concentrations of the oil at 5000 $\mu\text{g m}^{-3}$ (1% TCP), no break-through was observed over a period of 250 min and at 50 000 $\mu\text{g m}^{-3}$ (500 $\mu\text{g m}^{-3}$ TCP) for 30 min (at 1.5 l min^{-1}). The NIOSH method 5026 recommends a sample volume in the range 20–500 l at 1–3 l min^{-1} . In the present study, filter sampling was undertaken over a maximum period of 20 min (at 36 l min^{-1}).

Aircraft air samples

FT Aircraft. GC-PFPD analysis of air samples showed the presence of four of the most abundant

TCP isomers (*mmm*, *mmp*, *mpp*, and *ppp*; (D), Fig. 2a). The remaining six isomers were below the LOD. In addition, other peaks were present in the gas chromatograms, three of which had similar retention times as triisobutyl phosphate (A), tributyl phosphate (B), and triphenyl phosphate (C) (Fig. 2a) (also see supplementary material in online edition). The remaining phosphorus compounds could not be identified. These compounds were probably derived from hydraulic fluids and other sources, possibly plasticisers from polymers used in the aircraft. Hydraulic fluids are also a source of organophosphates (as fire retardants and anti-wear agents, ATSDR, 1997) but TCP appears to be no longer used for this purpose. Less toxic organophosphates such as tributyl phosphate, butyl diphenyl phosphate, and dibutyl phenyl phosphate appear to be prevalent hydraulic fluids (NRC, 2002, Muir *et al.*, 2008). The advantage of a phosphorus-specific detector was the transparency of a myriad of other compounds, which are present in commercial products and may complicate the identification of the organophosphates.

The results of the TCP monitoring are reported in Table 2 (also see supplementary material in online edition) while Fig. 3 is a graphical presentation of the TCP concentrations measured in aircraft cockpit air. TCP concentrations were plotted against method LOQs in order to show the variations in the LOQs between samples, which depended on the airborne TCP concentrations and volume of air sampled. The latter was governed by the sampling time and depended on the length of the sortie. For example, a small volume of air sampled may have a high air concentration of TCP but the amount of analyte collected may be small. Although the $\text{LOD}_{\text{instrument}}$ is constant, in such a case, the $\text{LOD}_{\text{method}}$ would be large. The two parallel lines represent the LOQ and LOD for the measurements. Quantitative values were above the LOQ line and semi-quantitative values were between the LOQ and LOD lines.

With the exception of two samples (51.3 and $21.7 \mu\text{g m}^{-3}$), TCP concentrations in the cockpits of the FT aircraft were found to be $<1.5 \mu\text{g m}^{-3}$ (Table 2, Fig. 3). Of the 16 different FT aircraft sampled (one sample per aircraft), 6 showed TCP concentrations above the LOD. The ground crew reported only two occurrences of visually detected 'smoke' corresponding to a TCP concentration of $51.3 \mu\text{g m}^{-3}$ while the other occurrence coincided with loss of sorbent (and sample). In the case of the highest TCP measurement, sampling occurred at a time when there was a spill of ATO near the APU air intake. On this particular occasion, the air was sampled with the canopy opened (to allow the smoke to

dissipate). Higher TCP concentrations may have been expected if the canopy had been completely closed.

Although only six FT concentrations are shown in Fig. 3, both the filter samples and the tube samples were in the same range, indicating no obvious bias for the two methods despite the difference in sampling geometry and sampling media.

CT aircraft. The CT aircraft is more closely related to commercial passenger aircraft in the sense that its operations are point to point involving take-off, landing and cruise and the size of the flight decks are similar to long-range commercial aircraft. Bleed air contamination in the CT aircraft was generally referred to as 'smelly' bleed air and was not associated with 'smoke'. The air samples were taken on the flight deck and mainly in-flight using Porapak Q tubes. It appeared that the flight crews may have become sensitized to the odours as on one occasion the odour was detected by the crew without being apparent to two of the authors (P.J.H. and W.M.) present. An air sample was not recorded at the time. During another incident of 'smelly bleed air', a sorbent air sample was taken but the TCP concentration was undetectable. The phosphorus compounds found in the air samples from the CT flight deck were dominated by the presence of triisobutyl phosphate with comparatively little of the other organophosphates present (Fig. 2c). These were quantifiable even when the TCP concentrations were $<\text{LOD}$. (Hanhela *et al.*, 2005a).

Nine different aircraft were sampled providing a total of 32 samples with only 5 showing levels of $\text{TCP} > \text{LOD}$. TCP air concentrations were highest in the CT aircraft during ground engine runs (max. $0.26 \mu\text{g m}^{-3}$, Table 2, Fig. 3) compared with in-flight concentrations (max. $0.05 \mu\text{g m}^{-3}$) taken during cruising. This is consistent with the general observation by crew that the bleed air contamination is most evident during high engine power in the case of the FB and CT aircraft. During ground engine runs, tube samples taken from the same aircraft over periods of 6 and 2 h produced comparatively similar TCP concentrations (0.255 and $0.123 \mu\text{g m}^{-3}$, respectively). Overall, the TCP concentrations were lower than those found in the FT aircraft.

FB aircraft. Air samples from the FB cockpit showed the presence of similar organophosphates to the FT aircraft with tributyl phosphate (Fig. 2b, B) being a significant component in the sample. Table 2 and Figure 3 contain a summary of the TCP concentrations in the cockpit air of the FB aircraft. A total of 30 samples were measured from 24 different aircraft of which 19 samples were above the

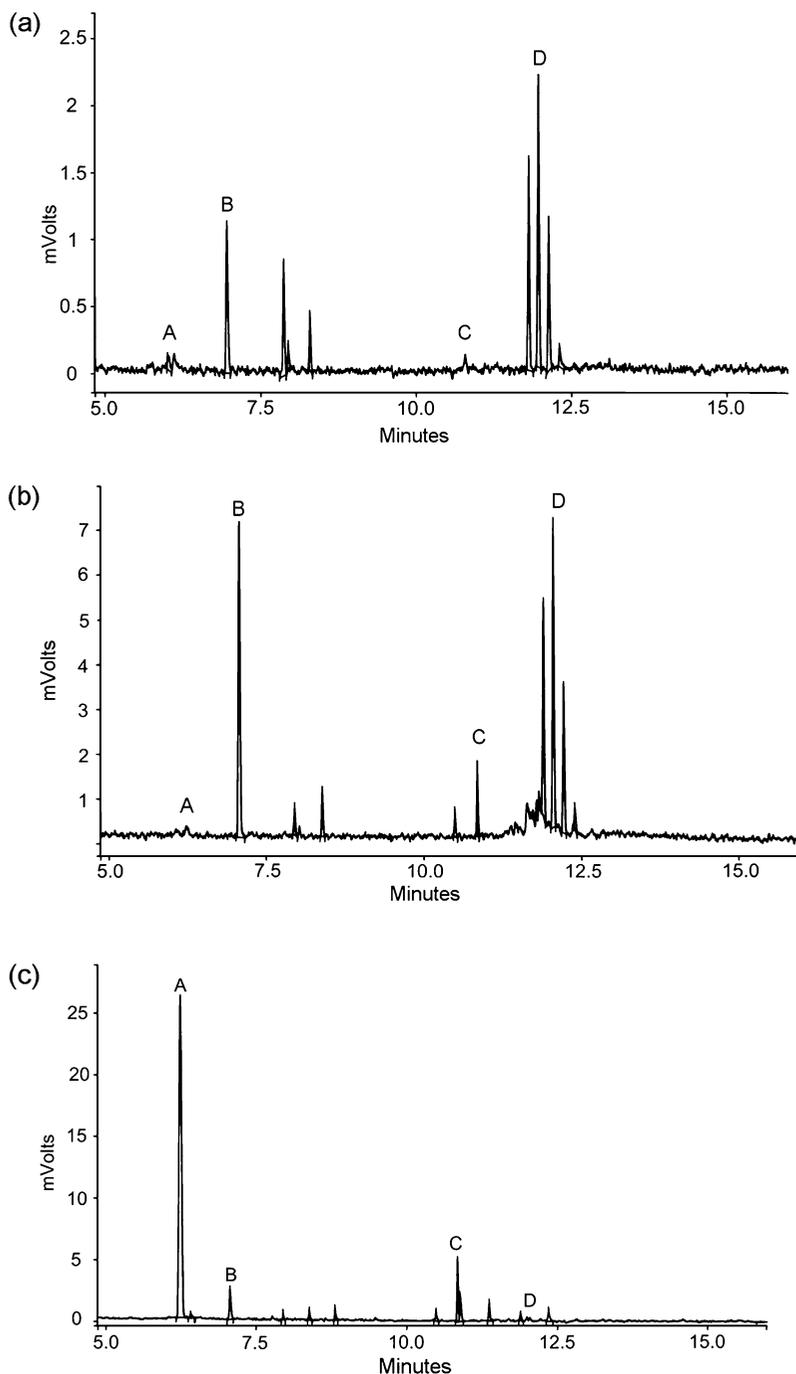


Fig. 2. GC (PFPD) of an air sample taken from a (a) FT, (b) FB and (c) CT aircraft cockpits showing the presence of triisobutyl phosphate (A), tributyl phosphate (B), triphenyl phosphate (C), and the four most abundant TCP structural isomers, *mmm*, *mmp*, *mpp*, and *ppp*, in order of elution (D).

LOD. Generally, the highest TCP concentrations measured were during ground engine runs when the engines were operated at ~80% full power.

Under these conditions, the highest recorded value was $\sim 5 \mu\text{g m}^{-3}$. The TCP concentrations measured in-flight were $< 2.1 \mu\text{g m}^{-3}$. Six incidents of smoke

Table 2. Summary of TCP measurements from the FT, CT and FB aircraft

Aircraft	Smoke odour	Sampling time (<i>t</i>)	Mean TCP Air Conc. ($\mu\text{g m}^{-3}$)	LOD ($\mu\text{g m}^{-3}$)	LOQ ($\mu\text{g m}^{-3}$)	RSD %
FT tube samples ground engine runs						
		0.15	21.71	0.854	2.848	6.42
		0.17	1.460	0.718	2.393	5.98
		0.18	0.760	0.692	2.308	45.2
FT filter samples ground engine runs						
NS	Smoke	0.11	51.34	0.158	0.529	3.98
NS		0.08	1.284	0.161	0.538	—
NS		0.33	0.845	0.085	0.282	3.80
CT tube samples ground engine runs						
#		6.0	0.255	0.009	0.031	6.33
#		2.0	0.123	0.032	0.106	10.62
CT tube samples in-flight						
		5.1	0.052	0.017	0.055	0.78
		7.0	0.019	0.012	0.039	9.52
		6.4	0.010	0.010	0.034	9.41
	odour	10.2	0.000	—	—	—
FB tube samples in-flight						
	Smoke	0.42	2.068	0.107	0.356	—
		0.33	0.243	0.137	0.455	—
a		1.68	0.211	0.142	0.472	17.31
a		1.93	0.192	0.143	0.476	7.58
b		0.70	0.181	0.042	0.139	12.42
	Smoke	1.42	0.180	0.057	0.189	—
	Smoke and odour	0.80	0.150	0.038	0.127	8.19
		1.80	0.138	0.023	0.077	—
		1.55	0.052	0.029	0.098	—
b		1.82	0.047	0.038	0.125	1.50
		2.23	0.028	0.027	0.091	51.36
b	Smoke	2.00	0.025	0.016	0.054	5.88
	Smoke	0.72	0.000	—	—	—
FB filter samples ground engine runs						
		0.33	4.986	0.010	0.033	0.86
		0.03	4.205	0.561	1.869	—
	Smoke	0.02	1.694	1.059	3.530	—
		0.33	0.236	0.010	0.032	2.96
		0.20	0.052	0.033	0.109	4.55
		0.33	0.019	0.013	0.043	13.96
		0.33	0.015	0.010	0.034	5.56

LOD = Limit of detection, LOQ = Limit of quantitation, N = Number of measurements of each air sample, SD = Standard of deviation, RSD = Relative standard of deviation, NS = not specified, like letters (a,b) designate common aircraft. Shaded areas represent measurements which lie between LOD and LOQ. LOD was estimated corresponding to an S/N = 3:1 and for LOQ S/N = 10:1. (ICH, 2008). Two measurements which were <LOD but coincided with smoke/odour incidents are shown. Measurements were corrected for recovery.

were reported during the study of the FB aircraft. Five corresponded to TCP concentrations >LOD the sixth occurred when the TCP was undetectable. However, none of the samples were taken during the most severe smoke incidents which have been

known to occur and therefore it is unlikely that these results represent the highest possible TCP concentrations for this aircraft type.

Of the samples in Table 2, two samples taken from the one aircraft in flight gave very similar results

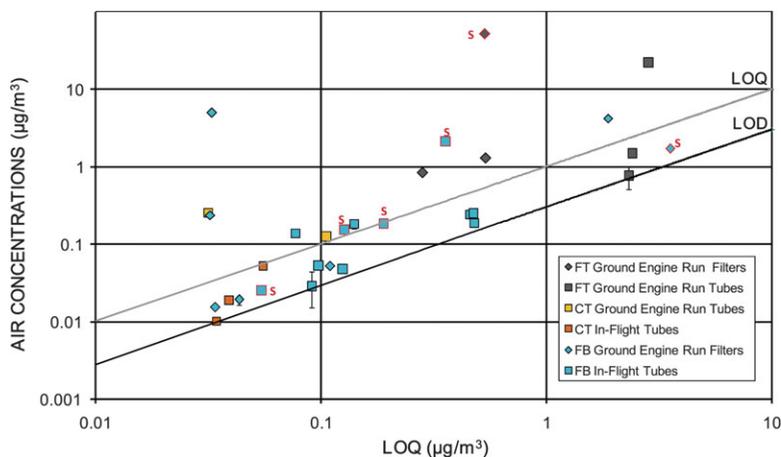


Fig. 3. Airborne TCP concentrations in the cockpit of the FT, CT, and the FB aircraft, and corrected for TCP recovery and plotted against the level of quantitation (LOQ). A total of 6/16, 5/32, and 19/30 air samples taken from the FT, CT, and FB aircraft respectively, had TCP concentrations above the LOD and are shown in the table. Data points outlined in red (with an 'S' beside them) represent air samples where odour and/or smoke were noted by the ground/flight crew who took the samples. Only those with TCP concentrations above the limit of detection (LOD) are shown. Error bars are shown for replicate measurements; most are obscured by data markers.

(0.255 and 0.123 $\mu\text{g m}^{-3}$), while three samples taken from another aircraft, also in flight, varied considerably (0.025–0.181 $\mu\text{g m}^{-3}$) with a smoke incident corresponding to the lower TCP air concentration. The latter results indicated the extent of variability of airborne TCP concentrations in any one aircraft of this type.

Unlike commercial aircraft, the fighter aircraft undertake various exercises under variable engine power and thus it is more difficult to relate the flying conditions of these aircraft with those of commercial aircraft.

Summary of TCP measurements. The TCP concentrations reported for the FT aircraft are the highest for any aircraft to date (cf. 0.04–1.3 $\mu\text{g m}^{-3}$; Muir *et al.*, 2008; van Netten, 2009) and are relevant to the smoke incidents involving the BAe-146 where there was an association between the operation of the APU and smoke contamination (Australian Parliament Senate, 2000, Muir *et al.*, 2008; van Netten, 2009). However, the small size of the FT cockpit compared with the cabin of the BAe-146 was most likely to exacerbate the problem in the FT aircraft.

The results reflect the sporadic occurrence of bleed air contamination coupled with the relatively short duration of these events. Anecdotal evidence suggested that the bleed air contamination was most likely to occur during high engine thrusts. This appears to be consistent with the highest TCP concentrations coinciding with ground engine runs at ~80% engine power. The coincidence of these events with

sampling times can provide a true indication of peak TCP concentrations, while sampling periods beyond these events tend to reflect average air concentrations. Statistical cluster analysis of the data was not possible due to the small number of samples in each group (aircraft type, ground engine runs, and sorbent/filter).

In this study, few TCP concentrations exceeded the LOQ. There was only one case (51.3 $\mu\text{g m}^{-3}$), where the airborne TCP concentration was ≥ 10 times the LOQ. Although smoke was observed in this case, the reporting of smoke and odour did not necessarily correlate with TCP concentrations in other incidences. Only six samples with measurable TCP concentrations were associated with smoke/odour occurrences as reported by the ground/flight crews (Table 2). Two additional samples with undetectable amounts of TCP were also taken during smoke incidences.

o-Cresyl isomer concentrations. The exposure limit to TCP (TWA, 100 $\mu\text{g m}^{-3}$) is based on the toxicology of tri-*o*-cresyl phosphate (NIOSH, 2005; ACGIH, 2010). It is recognized that while in this study, occupational standards may be relevant to the employees, in the context of the commercial passenger airlines adjustments need to be made for the flying public (Nagda *et al.*, 2000).

With the exception of two samples, the TCP concentrations in the aircraft air samples were $< 5 \mu\text{g m}^{-3}$. The total mono-*o*-di-*m/p*-cresyl phosphates content of TCP has been previously determined (De Nola *et al.*, 2008) to be ~0.004%

($\sim 40 \text{ mg kg}^{-1}$) in modern ATO used throughout the ADF, although earlier oils appeared to have had higher concentrations (0.015%) (Kibby *et al.*, 2005; De Nola *et al.*, 2008). At these concentrations, the *o*-cresyl isomers are present largely in the form of the mono-*o*-di-*m/p*-cresyl phosphate (approximately three times the concentration expected for tri-*o*-cresyl phosphate) and hence these isomers are most relevant to the toxicity of TCP. Because of their low concentrations, the *o*-cresyl phosphate isomers were not detected in the air samples. On the basis of the known composition of ATO, a TCP air concentration of $5 \mu\text{g m}^{-3}$ would be expected to contain $\sim 0.0002 \mu\text{g m}^{-3}$ mono-*o*-di-*m/p*-cresyl phosphates. However, these isomers are considered to be 10 times more toxic than tri-*o*-cresyl phosphate and therefore the levels are equivalent to $\sim 0.002 \mu\text{g m}^{-3}$ in tri-*o*-cresyl phosphate. Thus, the measurements reported here indicate a low health risk from TCP exposure on the basis of present knowledge of the toxicology of TCP and associated isomers and derivatives.

It should be pointed out, however, that dermal contact with ATO and hence TCP ($\sim 2.5\%$) is likely to occur during aircraft turbine engine maintenance. This represents another and possibly more hazardous route of exposure to TCP compared with the respiratory pathway. However, this issue is beyond the scope of the present study.

CONCLUSIONS

Low concentrations of airborne TCP can be determined in aircraft air using both Porapak Q sorbent tubes and Metricel filters at high flow rates. The obvious absence of differences between the two media implies that airborne TCP is mainly present as the aerosol rather than the vapour and there appears to be no obvious bias in the sample collection of the aerosol. High volume sampling was found to be essential in proving high quality measurements.

Only four TCP isomers could be detected (*mmm*, *mmp*, *mpp*, and *ppp*). The airborne concentrations of TCP in the cockpit/flight deck of three types of ADF aircraft with a history of engine bleed air contamination revealed generally low concentrations of TCP ($< 5 \mu\text{g m}^{-3}$) with the exception of two results (51.3 and $21.7 \mu\text{g m}^{-3}$) from the FT aircraft. Elevated TCP concentrations were not necessarily associated with smoke/odour incidents but smoke/odour incidents were associated with elevated TCP concentrations.

The results represented a low health risk for workers, based on the 8-h TWA exposure limit for tri-*o*-cresyl

phosphate ($100 \mu\text{g m}^{-3}$), and the inferred concentrations of the more toxic *ox*x TCP isomers. Higher airborne TCP concentrations may be possible under some extreme circumstances of bleed air contamination but such conditions did not arise during this survey.

SUPPLEMENTARY DATA

Supplementary data can be found at <http://annhyg.oxfordjournals.org/>.

REFERENCES

- Abou-Donia MB. (2003) Organophosphorus ester-induced chronic neurotoxicity. *Arch Environ Health*; 58: 484–97.
- ACGIH. (2010) Threshold limit values and biological exposure indices. Cincinnati, OH: ACGIH/Signature Publications.
- Achido B. (2002) USAToday.com—Jury rejects ailing flight attendants' lawsuit. Available at: <http://www.usatoday.com/money/biztravel/2002-05-21-toxic-air-verdict.htm>. Accessed June 2009.
- ATSDR. (1997) Toxicological profile for hydraulic fluids. Atlanta, GA: Department of Health and Human Services. Public Health Service.
- Australian Parliament Senate (2000) Rural and Regional Affairs and Transport Reference Committee. Air safety and cabin air quality in the BAe 146 aircraft: report. Canberra, ACT: Commonwealth of Australia.
- Björklund J, Isetun S, Nilsson U. (2004) Selective determination of organophosphate flame retardants and plasticizers in indoor air by gas chromatography, positive-ion chemical ionization and collision-induced dissociation mass spectrometry. *Rapid Commun Mass Spectrom*; 18: 3079–83.
- CAA (Civil Aviation Authority) (2004) *Cabin air quality*: CAA Paper 2004/2. London: CAA© Civil Aviation Authority 2004. ISBN 0 86039 961 3.
- Castello G, D'Amato G. (1982) Characterization of porous polymer beads gas chromatographic columns by retention index values of ethylene, acetylene and carbon dioxide. *J Chromatogr A*; 243: 25–34.
- Craig PH, Barth ML. (1990) Project status report, MTR-21-6S-90. Princeton, NJ: Mobil Environmental and Health Science Laboratory.
- Craig PH, Barth ML. (1999) Evaluation of the hazards of industrial exposure to tricresyl phosphate: a review and interpretation of the literature. *J Toxicol Environ Health B Crit Rev*; 2: 281–300.
- Daughtrey W, Biles R, Jortner B *et al.* (1996) Subchronic delayed neurotoxicity evaluation of jet engine lubricants containing phosphorus additives. *Fundam Appl Toxicol*, 32: 244–9.
- De Nola G, Kibby J, Mazurek W. (2008) Determination of ortho-cresyl phosphate isomers of tricresyl phosphate used in aircraft turbine engine oils by gas chromatography and mass spectrometry. *J Chromogr A*; 1200: 211–6.
- Easdown G. (2010) Flight path to courts. Melbourne, Australia: Herald Sun Newspaper, p. 30.
- Fowler MJ, Flaskos J, McLean WG *et al.* (2001) Effects of neuropathic and non-neuropathic isomers of tricresyl phosphate and their microsomal activation on the production of axon-like processes by differentiating mouse N2a neuroblastoma cells. *J Neurochem*; 76: 671–8.

- Great Britain Parliament. (2000) House of Lords, Select Committee on Science and Technology. Session 1999–2000-5th Report Air Travel and Health. London: HMSO.
- Hanhela P, Kibby J, De Nola G *et al.* (2005a) Organophosphorus and amine contamination of cockpit air in the Hawk, F-111 and C-130 aircraft. Melbourne, Australia: Defence Science and Technology Organisation (DSTO) Report No.: DSTO-RR-0303.
- Hanhela P, Kibby J, De Nola G *et al.* (2005b) Engine bleed air contamination in military aircraft. In Contaminated Air Protection Conference: 20–21 April; Imperial College. London: British Airline Proceedings of the Air Safety and Cabin Air Quality International Aero Industry Conference; Pilots Association/University of New South Wales.
- Harnly M, McLaughlin R, Bradman A *et al.* (2005) Correlating agricultural use of organophosphates with outdoor air concentrations: a particular concern for children. *Environ Health Perspect*; 113: 1184–89.
- Henschler D. (1958) Die Trikresylphosphatvergiftung—Experimentelle Klärung von Problemen der Atiologie und Pathogenese. *Klin Wochschr*; 36: 663–74.
- Henschler D. (1959) Beziehungen zwischen chemischer struktur und lahmungswirkung von triarylphosphaten. *Arch Exp Path Pharm*; 237: 450–472.
- Hocking MC. (2005) Air quality in airplane cabins and similar enclosed spaces. In Air pollution part H. Berlin, Germany: Springer.
- Hood E. (2001) OPs cause bad trips? *Environ Health Perspect*; 109: A156.
- ICH. (2008) International conference on harmonisation of technical requirements for registration of pharmaceuticals for human use validation of analytical procedures text and methodology Q2(R1). Guideline. <http://www.ich.org/LOB/media/MEDIA417.pdf>.
- Johannsen FR, Wright PL, Gordon DE. *et al.* (1977) Evaluation of delayed neurotoxicity and dose-response relationships of phosphate esters in the adult hen. *Toxicol Appl Pharmacol*; 41: 291–304.
- Kittler P, Swan H, Ivey J. (1992) “An indicating oxidant scrubber for the measurement of atmospheric dimethylsulphide”, *Atmos Environ*; 26: 2661–64.
- Kelso AG, Charlesworth JM, McVea GG. (1988) Contamination of environmental control systems in Hercules aircraft. Melbourne, Australia: Materials Research Laboratory Report No.: MRL-R-1116.
- Kibby J, Hanhela P, De Nola G *et al.* (2005) Analysis of jet engine oils. Melbourne, Australia: Defence Science and Technology Organisation (DSTO) Report No.: DSTO-RR-0292.
- Lebele-Alawa BT, Hart HI, Ogaji SOT *et al.* (2008) Rotor-blades’ profile influence on a gas-turbine’s compressor effectiveness. *Appl Energy*; 85: 494–505.
- Mackerer CR, Barth ML, Krueger AJ *et al.* (1999) Comparison of neurotoxic effects and potential risks from oral administration or ingestion of tricresyl phosphate and jet engine oil containing tricresyl phosphate. *J Toxicol Environ Health A*; 57: 293–328.
- Menichini E. (1986) Sampling and analytical methods for determining oil mist concentrations. *Ann Occup Hyg*; 30: 335–48.
- Merck Index. (1976) An encyclopaedia of drugs and chemicals. 9th edn. In Windholz M, editor. Rahway, NJ: Merck and Co., Inc.
- Mortensen A, Ladefoged O. (1992) Delayed neurotoxicity of trixylenyl phosphate and a trialkyl/aryl phosphate mixture, and the modulating effect of atropine on tri-*o*-tolyl phosphate-induced neurotoxicity. *Neurotoxicology*; 13: 347–54.
- Muir B, McDonald G, Cooper DB *et al.* (2005) Optimisation of solvent desorption conditions for chemical warfare agent and simulant compounds from Porapak Q(TM) using experimental design: part 2: extraction of sulphur mustard from steel and glass Porapak (TM) tubes. *J Chromatogr A*; 1076: 1–6.
- Muir H, Walton C, McKeown R. (2008) Cabin Air Sampling Study Functionality Test. Report prepared for the UK Department for Transport. Cranfield, UK: School of Engineering, Cranfield University.
- Murawski JTL, Supplee DS. (2008) An attempt to characterize the frequency, health impact, and operational costs of oil in the cabin and flight deck supply air on US commercial aircraft. *J ASTM Int*; 5 Paper ID JAI101640.
- Nagda NL, Rector HE, Li Z *et al.* (2000) Aircraft cabin air quality: a critical review of past monitoring studies. In Nagda NL, editor. Air quality and comfort in airliner cabins. ASTM STP 1393. West Conshohocken, PA: American Society for Testing and Materials.
- Nagda NL, Rector HE, Li Z *et al.* (2001) Determine aircraft supply air contaminants in the engine bleed air supply system on commercial aircraft ENERGEN report number AS20151, prepared for American society for heating, refrigerating, and air-conditioning engineers, Atlanta, GA. Germantown, MD: ENERGEN Consulting, Inc 20874.
- NIOSH. (1996) Oil mist, mineral: method 5026, issue 2. In NIOSH manual of analytical methods (NMAM). Rev ed. Cincinnati, OH: US Department of Health and Human Services.
- NIOSH. (2005) Pocket guide to chemical hazards: NIOSH publication No. 205–149. Cincinnati, OH: US Department of Health and Human Services.
- Nomeiri AA, Abou-Donia MB. (1986) Studies on the metabolism of the neurotoxic tri-*o*-cresyl phosphate. Synthesis and identification by infrared, proton nuclear magnetic resonance and mass spectrometry of five of its metabolites. *Toxicology*; 38: 1–13.
- NRC (2002) The Airliner Cabin Environment and the Health of Passengers and Crew Committee on Air Quality in Passenger Cabins of Commercial Aircraft. Board of Environmental Studies and Toxicology, Division of Earth and Life Sciences. US National Research Council. Washington, DC: National Academy Press.
- Simpson AT, Groves JA, Unwin J *et al.* (2000) Mineral oil metal working fluids (MWFs)-development of practical criteria for mist sampling. *Ann Occup Hyg*; 44: 165–72.
- Simpson AT, Stear M, Groves JA *et al.* (2003) Occupational exposure to metalworking fluid mist and sump fluid contaminants. *Ann Occup Hyg*; 47: 17–30.
- Singh B. (2005) In-Flight Smoke and Fumes. In Winder C, editor. Proceedings of the BALPA Air Safety and Cabin Air Quality International Aero Industry Conference, Imperial College London, 20–21 Apr. Sydney, Australia: University of New South Wales, pp. 92–99.
- Solbu K, Thorud S, Hersson M, *et al.* (2007) 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. *J Chromatogr A*; 1161: 275–83.
- Staaft T, Östman C. (2005) Indoor air sampling of organophosphate triesters using solid phase extraction (SPE) adsorbents. *J Environ Monit*; 345: 344–48.
- van Netten C, Leung V. (2000) Comparison of the constituents of two jet engine lubricating oils and their volatile pyrolytic degradation products. *Appl Occup Environ Hyg*; 15: 277–83.

- van Netten C. (2009) Design of a small personal air monitor and its application in aircraft. *Sci Total Environ*; 407: 1206–10.
- Winder C, Balouet J-C. (2002) The toxicity of commercial jet oils. *Environ Res*; 89: 146–164.
- Winder C. (2006a) Air monitoring studies for aircraft cabin contamination. *Curr Top Toxicol*; 3: 33–48.
- Winder C. (2006b) Hazardous chemicals on jet aircraft: case study—jet engine and aerotoxic syndrome. *Curr Top Toxicol*; 3: 65–88.