Australian Government
Department of Defence
Defence Science and
Technology Organisation

Organophosphate and Amine Contamination of Cockpit Air in the Hawk, F-111 and Hercules C-130 Aircraft

P.J. Hanhela, J. Kibby[*]*, G. DeNola and W. Mazurek*

Maritime Platforms Division
Platforms Sciences Laboratory

[*]On Contract to DSTO

DSTO-RR-0303

ABSTRACT

A survey of cockpit air contamination by organophosphates and amines in the Hawk, F-111 and Hercules C-130 aircraft was undertaken. The air contamination occurred via the engine bleed air supply. The source of tricresyl phosphates, phenyl-α-naphthylamine and dioctyldiphenylamine was jet engine oil while hydraulic fluids are suspected of contributing to the presence of trialkyl phosphates.

The concentrations of all contaminants measured were generally very low. Tricresyl phosphate concentrations were below 4 $\mu g/m^3$ with two exceptions (21.7, 49 $\mu g/m^3$, Hawk) compared to the maximum permissible concentrations (100 $\mu g/m^3$). Ground engine starts, at high power, gave rise to the highest concentrations.

Phenyl-α-naphthylamine and dioctyldiphenylamine concentrations were also very low (<0.06 $\mu g/m^3$) in the Hercules C-130 and the absence of exposure limits for the two compounds reflects on their apparent low toxicity. Trialkyl phosphates were also found in the F-111 and Hercules C-130 aircraft at concentrations (<6 $\mu g/m^3$) similar to tricresyl phosphates. They are of lower toxicity than the latter compounds and are not expected to present a health risk.

RELEASE LIMITATION

Approved for public release

Published by

DSTO Defence Science and Technology Organisation
506 Lorimer St
Fishermans Bend, Victoria 3207   Australia

Telephone: (03) 9626 7000
Fax: (03) 9626 7999

AR-013-323
October 2005

APPROVED FOR PUBLIC RELEASE

Organophosphate and Amine Contamination of Cockpit Air in the Hawk, F-111 and Hercules C-130 Aircraft

Executive Summary

Cockpit/cabin air supply, in most jet aircraft, is drawn from the compressor stage of the engine through the Environmental Control System (ECS) where the air is cooled by passage through the air/air and air/water heat-exchangers. The air is then passed through a synthetic wax impregnated (coalescer) bag which removes condensed water. The engine bleed air is prone to contamination from engine oil in the event of leaky oil seals and/or intake of contaminants such as oil and hydraulic fluids by the engine.

During the 1990s air contamination incidents aboard the BAe 146 passenger aircraft were widely publicised in the media. Some passengers and crew exposed to those incidents have subsequently claimed to be suffering from chronic health problems. In 1999, an Australian Senate inquiry into aircraft safety investigated these incidents and claims. Submissions were made by some academics that the health effects were due to contamination of the bleed air by tricresyl phosphate (TCP) additive present in the jet engine oil as an anti-wear agent. Although air samples were taken by Ansett airlines, the presence of TCP could not be quantified. However, the air sampling procedure, as described in the Senate inquiry, was flawed. It was also claimed that contamination by the anti-oxidant amine additive, phenyl-α-naphthylamine, may also occur and it has been suggested that the compound causes sensitisation and may be carcinogenic. Despite the speculation, the cabin air concentrations of these potential air contaminants have never been reported.

The engine bleed air (ECS) is also common to Australian Defence Force aircraft and therefore there may be adverse health effects arising from contamination of the engine bleed air supply. There is a history of incidents of smoke in the cockpits of the Hawk and F-111 aircraft and there have been reports of "smelly" bleed air in the Hercules C-130 aircraft. As a result, the Directorate of Air Force Safety initiated a RAAF sponsored DSTO task to investigate bleed air contamination in ADF aircraft.

Three aircraft types have been surveyed, Hawk, F-111 and Hercules C-130. Air sampling of the cockpit air in the Hawk was performed on the ground when the Auxiliary Power Unit was operated, since the main engine does not appear to cause smoke in the cockpit. The highest concentrations of TCP measured were 21.7 and 49 $\mu g/m^3$, but the remainder of the 15 Hawk air samples showed $<1.5\ \mu g/m^3$ of TCP. In the case of the F-111 and Hercules C-130 aircraft, cockpit air was sampled during ground engine power runs and in flight. The concentrations of TCP measured during ground power runs for the F-111 and Hercules C-130 were $<3.5\ \mu g/m^3$ and $<0.3\ \mu g/m^3$ respectively. Those obtained during flights were $<1\ \mu g/m^3$ and $<0.2\ \mu g/m^3$ respectively.

These concentrations are very low compared with the maximum permissible time-weighted 8 hour average (TWA) exposure of 100 μg/m^3 for TCP which is based on the tri-*o*-cresyl phosphate component. In most cases the most toxic components of TCP (mono-*o*-cresyl phosphate isomers) calculated to be present in the cockpit air corresponded to less than *ca.* 1/200 of the TCP TWA allowing for the fact that these are 10 times more toxic than tri-*o*-cresyl phosphate.

Two air samples taken from the cockpit of the Hawk indicated relatively high concentrations of TCP. One sample (49 μg/m^3) was associated with an oil spill in the vicinity of the engine (APU) air intake. As the air sample was taken with the cockpit canopy opened, excessive TCP concentrations (> 100 μg/m^3) may have occurred if the canopy had been closed.

As a general rule it is recommended that the ADF consider total TCP air concentrations <1 μg/m^3 as a *desirable* target rather than the statutory exposure limits of 100 μg/m^3. This recommendation is based on the uncertainty of toxicity data, the absence of economic imperatives (which provide a rationale for establishing a high exposure level in industry) and the potential for cognitive effects on the flight crews. The target levels appear to be readily achievable and are indicative of the satisfactory condition of the compressor oil seals.

In addition to TCPs, trialkyl phosphates were found to be present in the cockpit air of the F-111 and Hercules C-130 aircraft. These are probably due to hydraulic fluid contamination of the engine bleed air and they are present at concentrations slightly higher than TCP. However, because of their low toxicity they are unlikely to pose a health risk.

Similarly, the concentrations of phenyl-α-naphthylamine and dioctyldiphenylamine in the flight deck air of the Hercules C-130 aircraft were found to be very low (< 0.1 μg/m^3) and are likely to be inconsequential due to the low toxicity of these compounds.

Although the concentrations of these bleed air contaminants were very low and unlikely to produce any adverse health effects, washing the ECS heat exchangers with a solvent such as acetone, when maintenance permits, could further reduce the levels. Furthermore, the coalescer bags serve to trap some of the TCP (and most likely the amines and trialkyl phosphates) and frequent replacement of these would also reduce the cockpit air contamination.

However, these measures will not affect smoke incidents in the F-111 (and Hawk aircraft). This may best be achieved by the installation of a HEPA (high efficiency particulate air) filter in the ECS ducting.

It is also recommended that further research be carried out to identify and quantify the air contaminants arising from the thermal decomposition of the oil base which characterise the smoke and odour during episodes of engine bleed air contamination.

Contents

1. INTRODUCTION 1
  1.1 Toxicity of Organophosphate Esters 3
    1.1.1 Tricresyl Phosphates 3
    1.1.2 Trialkyl Phosphate Esters. 4
  1.2 Toxicity of Amine Additives 5
  1.3 Aim 6

2. EXPERIMENTAL 6
  2.1 Cockpit Air Sampling 6
    2.1.1 Ground-based Cockpit Air Sampling and Measurements from the Hawk Trainer 6
    2.1.2 Long Duration Sampling for TCP 7
    2.1.3 Short Duration Sampling for TCP 7
  2.2 Extraction of TCP from Sorbents and Filters. 7
  2.3 Analysis of Organophosphate Esters. 7
  2.4 Analysis of Amines 8
  2.5 Chemical Reference Standards 8

3. RESULTS AND DISCUSSION 8
  3.1 Tricresyl Phosphate Concentrations 8
    3.1.1 Hawk Trainer 9
    3.1.2 F-111 Aircraft 10
    3.1.3 Hercules C-130 10
    3.1.4 *o*-Cresyl Isomers 10
  3.2 Trialkyl Phosphate Concentrations in F-111 and Hercules C-130 Aircraft .. 11
  3.3 Phenyl-α-Naphthylamine and Dioctyldiphenylamine Concentrations in Hercules C-130 Aircraft 11

4. CONCLUSIONS 12
5. RECOMMENDATIONS 12

6. REFERENCES 14

APPENDIX A: COCKPIT/CABIN AIR SAMPLES 17
  A.1. Hawk Trainer Aircraft 17
  A.2. F-111 18
  A.3. Hercules C-130 19
  A.4. Air Sampling Devices 21

1. Introduction

Cockpit/cabin air contamination in both military and commercial jet aircraft has a number of sources. In recent years engine oil contamination from the Environmental Control System (ECS), which uses engine bleed air to supply the cockpit and cabin, has been of foremost concern. This is due to the presence of potentially neurotoxic tricresyl phosphate (TCP) anti-wear additive in jet engine oil and amine anti-oxidants which have been claimed to be potential irritants [1,3]. During the 1990s a series of widely publicised incidents occurred when passengers and crew suffered acute and chronic health effects after exposure to smoke and fumes in the BAe 146 passenger aircraft. Although there was much speculation about the role of TCP the absence of relevant air analysis data failed to substantiate this claim. In 1999 the Australian Senate and Regional Affairs and Transport References Committee held an inquiry into safety issues related to the cabin air contamination in this aircraft [1].

Table 1. Incidences (ASORs) of Smoke and Fumes, in ADF aircraft, per 1000 hours of flying during the period 1998-2003.

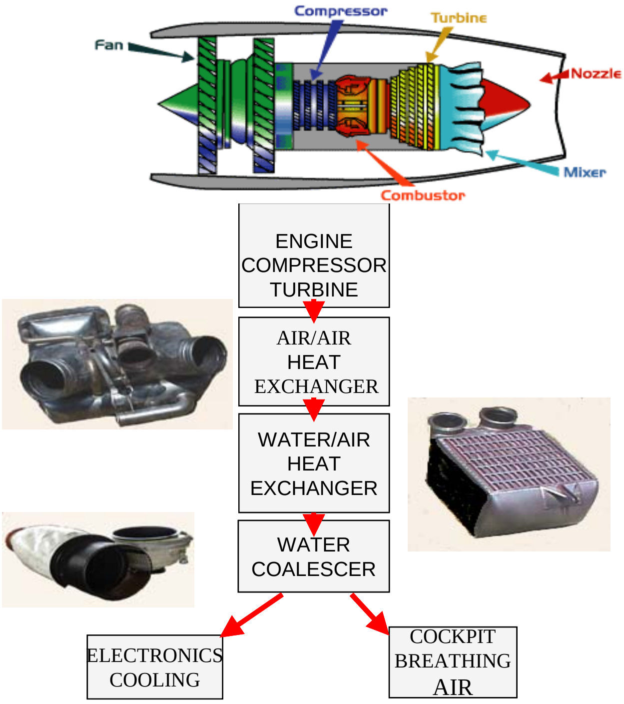
Rank	**Aircraft Type**	**Incidents**
1	CL604 Challenger*	2.498
2	Sea King	1.599
3	P3C Orion	1.588
4	HS748	1.196
5	CT4B	1.012
6	F111	0.941
7	Hawk127	0.879
8	Caribou	0.813
9	Falcon900	0.726
10	B200 King Air (AF)	0.671
11	Iroquois	0.668
12	B707	0.660
13	Squirrel	0.628
14	C130	0.521
15	DHC6 Twin Otter	0.431
16	PC9	0.428
17	Black Hawk	0.385
18	Sea Hawk	0.381
19	F/A18 Hornet	0.352
20	Chinook	0.162
21	Kiowa	0.113
22	B200 King Air (Army)	0.077

**CL604 Challenger data since 2002/03*

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 the past 5 years has catalogued incidences (Aviation Safety Occurrence Reports) of smoke and fumes in the cockpit/cabin [5] (*Table 1*).

The current procedure is for the aircrew to don oxygen masks during an air contamination incident [6]. In severe cases aircraft have had to make emergency landings and the crews have undergone medical examination. However, as the nature of the air contamination was unknown there has been no clinical treatment and the flight crews have been allowed to resume their flying duties after an overnight rest [6].

In most jet aircraft the ECS uses air from the compressor stage of the engine, where temperatures may exceed 500°C. The air is cooled by passage through an air/air and air/water heat-exchanger and then through a water coalescer consisting of a fabric bag impregnated with a synthetic wax (Fig. 1). In addition to supplying cockpit/cabin, the air is also used to cool the avionics. In the case of the F-111 aircraft, the bulk of the air is used for the latter purpose.



<u>Figure 1</u>. Schematic diagram of the F-111 Environmental Control System and its components: air/air heat-exchanger, air/water heat-exchanger and water coalescer.

Depending on the aircraft type, air contamination is perceived by crews as smoke or fumes (odour). The F-111 and Hawk aircraft are associated with smoke contamination while the C-130 aircraft has been reported to produce "smelly" bleed air. The aircraft use jet engine oil made to military specification MIL-PRF-23699 (for example, Mobil Jet Oil II). In the C-130 and F-111 aircraft, smoke and odour incidents were observed by crews to occur at high engine thrusts. These conditions were most likely to arise during take-off and ground engine runs at high power. The source of air contamination in the Hawk aircraft was the auxiliary power unit (APU). In addition to bleed air contamination from within the engine, external sources such as oils and hydraulic fluids can also contribute to bleed air contamination by entering the engine air intake.

TCP had been previously detected in the engine bleed air system of a Hercules C-130 aircraft [7] and in an Ansett Airlines BAe 146 passenger aircraft [1] but not quantified. There was also an attempt by private consultants (SIMTARS) to characterise the air contaminants during "cockpit smoke" incidents in the F-111 but the air monitoring failed to detect the presence of TCP [8]

The RAAF sponsored DSTO Task "Aircraft Cockpit/Cabin Air Habitation" (AIR 02/295) was initiated in September 2002 to develop air monitoring and analytical procedures for airborne TCP with the object of surveying the ADF fleet for TCP contamination.

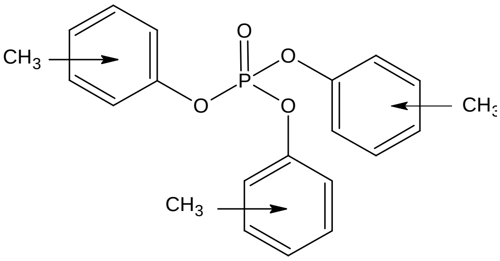
1.1 Toxicity of Organophosphate Esters

1.1.1 Tricresyl Phosphates

Most organophosphates exert their acute toxicity 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 neurodegenerative condition known as organophosphate-induced delayed neuropathy (OPIDN), which affects both the central and peripheral nerves of birds and mammals [9].

The relationship between the chemical structure of many pure triaryl phosphates and potency in causing OPIDN has been extensively studied and the relative neurotoxic activities of these compounds are well known. It has been recognised for at least forty years that alkyl substituents at the ortho positions of the aromatic rings are responsible for the neurotoxic activity of TCP. Material synthesised from only *m*–cresol and *p*-cresol does not cause OPIDN [4] but the possibility of chronic toxicity of this isomeric mix cannot be dismissed.

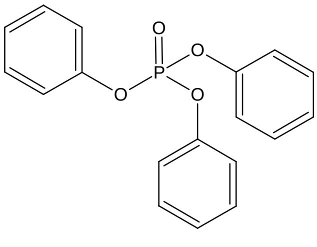
Of all the 10 possible TCP isomers the mono-*o*-cresyl isomers are regarded as the most toxic; 10 times more toxic than the tri-*o*-cresyl isomers and 2 times more toxic than the di-*o*-isomers. Hence the toxicity of TCP is related to the *o*-cresyl isomer content with the *m*- and *p*-cresyl isomers having low toxicity [10].



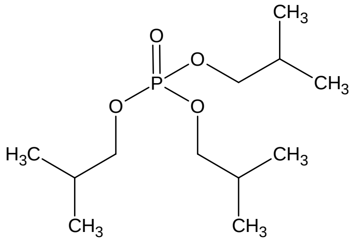
(1)
Tricresyl Phosphate (TCP)

1.1.2 Trialkyl Phosphate Esters.

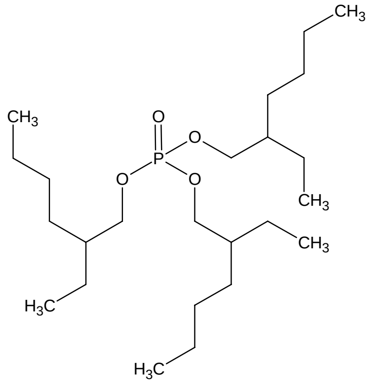
Aviation hydraulic fluids are known to contain phosphate esters as fire retardants [11]. They include triphenyl phosphate and trialkyl phosphates [12]. There are Australian occupational exposure standards (TWA) for triphenyl phosphate (3 mg/m^3) and tributyl phosphate (2.2 mg/m^3) but not for tris(2-ethylhexyl) phosphate and triisobutyl phosphate [13]. Triisobutyl phosphate is considered to be of low toxicity, showing no signs of neurotoxicity at high dose levels when given orally to chickens. Nevertheless, it is listed by the German Commission for the Investigation of Hazards in the Workplace (MAK-Kommission) as a skin sensitising substance based on dermal exposure to rabbits [14,15]. However, there have been no reports of human skin sensitisation associated with the manufacture and handling of the compound [14]. Similarly, tris(2-ethylhexyl) phosphate is considered to be of low toxicity and not skin sensitising [16]. It is also used as a fire retardant plasticiser for automotive PVC wiring [17].



(2)
Triphenyl Phosphate



(3)
Triisobutyl Phosphate



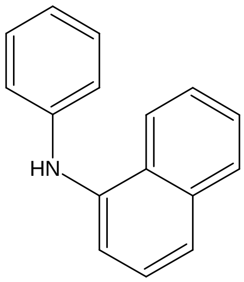
(4)
Tris(2-ethylhexyl) Phosphate

1.2 Toxicity of Amine Additives

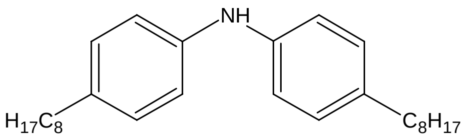
As previously reported jet engine oils used in the ADF aircraft contain amine anti-oxidants [18] and there has been some concern expressed over the potential health effects of these compounds [1,3]. Phenyl-α-naphthylamine (PAN) and the isomeric compound, N-phenyl-β-naphthylamine, have been found to produce an increase in the incidence of lung and kidney cancers following subcutaneous administration to mice. A high incidence of various forms of cancer was also found amongst workers exposed to antirust oil containing PAN [19].

However, in a review published in 1993 by the German Chemical Society the acute toxicity of PAN is low as shown by tests conducted on laboratory animals. Although it has been associated with cases of allergic contact dermatitis, PAN is not regarded as a skin irritant in humans, [20].

Dioctyldiphenylamine (DODPA) is also considered to be of low acute toxicity as indicated by studies with laboratory animals. There have been no reports of adverse health effects on humans. Neither DODPA nor PAN is registered on the National Occupational Health and Safety Commission (NOHSC) *Designated List of Hazardous Substances* [20] and hence airborne concentrations are not regulated in the work place.



(5)
Phenyl-α-Naphthylamine (PAN)



(6)
Dioctyldiphenylamine (DODPA)

1.3 Aim

The aim of this study was to determine the concentrations of TCPs in the aircraft cockpit cabin air and consequently the potential health risk to flight crew and ground crew from exposure to the contaminated air. Air concentrations of amine additives were also measured in the Hercules C-130 aircraft. Although they are generally not regarded as being hazardous, reports in the scientific literature have raised concerns.

This report describes the air sampling, analytical procedures and the results of a survey of airborne concentrations of TCP in the Hawk trainer, the Hercules C-130 and the F-111 aircraft. In the case of the Hercules, trialkyl phosphates were also detected and their concentrations are also reported together with amine oil additives.

2. Experimental

2.1 Cockpit Air Sampling

2.1.1 Ground-based Cockpit Air Sampling and Measurements from the Hawk Trainer

Ground based cockpit air monitoring was conducted in the Hawk trainer using a Dust-Trak (TSI) Model 8520 aerosol monitor with a sampling time of 1 sec.

Air grab samples were taken with an Entech passive air sampling canister (1 L, 01-29-MC1000SV). The air samples were subsequently analysed using a Micromass GCT TOF mass spectrometer coupled to an Agilent 6890N gas chromatograph. The samples were introduced via an Entech 7100 preconcentrator.

Prior to use, canisters were cleaned on an Entech Canister Cleaner 3000SL with heating bands attached. This cleaning cycle entailed evacuating to 2 Pa with a high vacuum pump followed by pressurizing to 275 kPa with filtered, humidified nitrogen. This was repeated 10 times. The canisters were capped after the final evacuation of 2 Pa and ready for use.

The preconcentrator employed a Cold Trap Dehydration method with a heated block. The GC sample transfer line was set to 100°C and the sample transfer lines set to 80°C. The preconcentrator has three traps, trap one having a glass bead trap, trap two a sorbent trap and trap three being blank (GC transfer line only). During the introduction of the 100 mL in-house prepared 10 ppb toluene-d_8 standard (at 50 mL/min), 400 mL sample (at 50 mL/min) and 100 mL helium sweep purge (at 50 mL/min) trap one was set to -10°C and trap two to -50°C. For transfer to trap two, trap one was preheated to 10°C and desorbed for 1 minute (10 mL/min). Trap three was cooled to -150°C before trap two was preheated to 50°C and then heated to 180°C before the column helium supply was passed through for 3.5 minutes. At completion, trap three was heated rapidly to 180°C and the GC-MS run started.

The chromatography was carried out using a DB-5 60 m x 0.32 mm x 1 μm column using helium as the carrier gas at 1.5ml/min. The injector was set to split mode at 10:1 and a temperature of 220°C. The temperature profile of the oven was 35°C held for 2 min., ramped to 110°C at 10°C/min., then 150°C at 5°C/min, then at 10°C/min. and finally held at 200°C for 10 min. (a total run time of 52.5 min.).

The mass spectrometer was operated for 52.5 minutes with a solvent delay of 3.9 minutes collecting masses 33 to 330 m/z EI+. Centroid data was collected with 0.25 sec. scan time and 0.05 sec. interscan delay.

2.1.2 Long Duration Sampling for TCP

Long duration air sampling was carried out using sorption tubes and a metering pump (e.g. Aircheck model 2000) operating at 2 L/min (Appendix, Fig.1). Glass-lined stainless-steel tubes (90mm x 6mm o.d.) were packed with approximately 0.06 g Porapak Q and held in place with glass wool. The packed tubes were washed with hexane (6 mL) and heated at 220° C in an oven while purged with helium (70 mL/min.) for 2 hours. The tubes were then cooled and capped with in-house polymeric end-caps before and after air sampling.

The air sampling was carried out in the cockpit/flight deck during operational flights with the sorbent tube located as close as possible to an air vent. The sampling period varied between 2-6 hours depending on the aircraft type and sortie.

2.1.3 Short Duration Sampling for TCP

High volume short duration (5 - 20 min.) air sampling was carried out using Pall Corporation Metricel membrane filters (0.8 μm) GN. A battery (12V) powered diaphragm pump (Thomas 107 series) was operated at 36 L/min. (Appendix, Fig.2). 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 (~80%).

2.2 Extraction of TCP from Sorbents and Filters.

The sorbent tubes were washed with hexane (7 mL) and the washings were evaporated to approximately 1 mL. The Metricel filters were immersed in hexane (approx. 20 mL) and sonicated for 5 min. The filters were then removed and the solution was evaporated to approx. 1 mL.

2.3 Analysis of Organophosphate Esters.

Samples containing organophosphate species were routinely analysed by gas chromatography using a Varian CP-3800 equipped with a pulsed flame photometric detector (PFPD), flame ionization detector (FID) and CP-8400 autosampler. Separation was conducted with a Varian CP-Sil 8 MS (30 m x 0.32 mm x 0.25 μm) column with a carrier gas (high purity helium) flow rate of 1.2 mL/min. The injector temperature was set to 320°C and the injector operated in a splitless mode for 0.7 sec., then in a split mode (100:1). The initial oven temperature was 120°C and held for 2 minutes, then ramped at 20°C/min to 300°C and held at this temperature for 5 min.

The Pulsed Flame Photometric Detector (PFPD) was operated at 325°C with a phosphorous filter, a gate delay of 4.0 msec, a gate width of 10.0 msec and a trigger level of 200 mV. The Air 1 flow was set to 15.0 mL/min, the Air 2 flow at 10.0 mL/min and hydrogen flow at 14.0 mL/min.

2.4 Analysis of Amines

Dioctyldiphenylamine (DODPA) and phenyl-α-naphthylamine (PAN) were analysed using a Varian CP-3800 gas chromatograph coupled to a Varian Saturn 2000 ion trap mass detector. The mass spectrometer was operated in the ms/ms mode. Gas chromatographic conditions were similar to those used for the analysis of TCPs. The scan range was 33-250 *m/z* (PAN), 33-330 *m/z* (DODPA) with a scan time of 0.38 sec/scan (PAN) and 0.40 sec/scan (DODPA). The emission currents were 50 μA, the excitation storage levels were 75 *m/z* and the excitation amplitudes were 52V. The parent ions occurred at 219 *m/z* (PAN) and 322 *m/z* (DODPA).The trap temperature was 160°C, the transfer line temperature was 170°C and the manifold temperature was 80° C.

2.5 Chemical Reference Standards

Phenyl-α-naphthylamine (98%) and tricresyl phosphates (>96%) were purchased from Aldrich Chemicals. The R.T. Vanderbilt Company, Inc. (Norwalk, CN) kindly supplied a sample of dioctyldiphenylamine (octylated diphenylamines, Vanlube® 81). Trialky phosphate esters were quantified relative to tricresyl phosphate concentrations.

3. Results and Discussion

3.1 Tricresyl Phosphate Concentrations

Initially, TCP was detected in the ECS heat exchangers, (particularly the water/air heat exchanger) and coalescer bags from Hercules and F-111 aircraft. Their contamination with TCP was indicative of TCP entering the cockpit/cabin air. Subsequently, air sampling and analyses indicated that approximately half of the aircraft tested had quantifiable concentrations of TCPs in the cockpit/cabin air.

The results of retrospective air monitoring for total TCPs in 3 types of ADF aircraft are presented in the Appendix while a summary is shown in *Table 2*. The smoke and odour incidents reported were rare and the few air samples taken during such incidents did not correlate with elevated TCP concentrations.

Table 2. TCP Concentrations in Cockpit Air

Aircraft Type	**TCP Concentration (μg/m^3) (Sampling Time)**				**Samples (In-flight, Ground)**
	Inflight		**Ground Engine Runs**		
	Mean	**Maximum**	**Mean**	**Maximum**	
Hawk*		-	2.1 (9-46 min)	49 (15 min)	-,15
F-111	0.02 (1-2 h)	2.1 (25 min)	0.80 (10-20 min)	3.2 (20 min)	20,12
C-130	0.006 (2-8 h)	0.052 (5.2 h)	0.19 (2-6 h)	0.26 (2 h)	31,2

*Air samples taken during the operation of the Auxiliary Power Unit (APU).

3.1.1 Hawk Trainer

Air monitoring in the cockpit of the Hawk trainer was initiated after complaints of "smoke" in the cockpit during the operation of the Auxiliary Power Unit (APU). The APU supplies power and cockpit cooling air while the aircraft is on the ground and the main engine is not operating. This may take up to 0.5 hours.

In order to confirm the contribution of the APU to cockpit air contamination, air sampling for TCP was carried out over a period of 6 minutes and volatile organic compounds (VOCs) were determined from canister air samples (~5 sec.). Respirable aerosol (<10 μm dia.) concentrations were measured in real-time to assess the smoke intensity. The air sampling and aerosol monitoring were executed with the APU operating and the main engine disabled. The process was then repeated for the reverse case. The results showed no detectable increase in aerosols (including smoke) but a small increase in VOC concentrations from the APU (*Table 3*). More significant was the increase in TCP concentration although it did not exceed the 8 hour Time-weighted Average (TWA) concentration for TCP (100μg/m^3) based on the tri-*o*-TCP isomer [13].

Table 3. Results of Cockpit Air Testing HAWK Trainer (A27-07) Williamtown, 27 May, 2003

Engine Operation	Total TCP	Smoke	VOCs
APU on, Engine off	1 μg/m^3	Ambient levels	0.3 ppm
APU off, Engine on	0.01 μg/m^3	Ambient levels	0.04 ppm

A TCP air monitoring program was implemented for the Hawk trainer and the results are shown in the Appendix and summarised in *Table* 2. With the exception of two samples (21.7, 49 μg/m^3, Appendix) TCP concentrations in the cockpit were found to be < 1.5 μg/m^3. Of the 15 air samples taken, the ground crew reported two occurrences of visually detected "smoke". The air sample which contained 49 μg/m^3 TCP was associated with an oil spill in the vicinity of the air intake to the APU and visible smoke present during the sampling period. The air was sampled with the cockpit canopy opened. Higher TCP air concentrations would have been expected if the canopy had been closed.

3.1.2 F-111 Aircraft

Table 2 contains a summary of the analyses of cockpit air samples taken from the F-111 aircraft while the complete data can be found in the Appendix. Earlier samples were analysed for TCPs only but later samples were also analysed for other organophosphates (*vide infra*).

Generally, the highest TCP concentrations measured were during ground engine runs when the engines were operated at about 80% full power. The highest recorded value was 3.2 $\mu g/m^3$ under these conditions. The TCP concentrations measured in-flight were below 0.3 $\mu g/m^3$ and approximately 1/3 of the samples had TCP concentrations below the level of detection ($< 0.001\ \mu g/m^3$).

3.1.3 Hercules C-130

Bleed air contamination in the Hercules aircraft, at Richmond Air Force Base, is generally referred to as “smelly bleed air” and is not associated with “smoke”. The air samples were taken on the flight deck and mainly in-flight. It appeared that the flight crews may have become sensitised to the odours as on one occasion the odour was detected by the crew without being apparent to two of the authors (PJH, WM) present.

As with the Hawk and the F-111 aircraft, TCP air concentrations were highest in the Hercules during ground engine runs (max. 0.26 $\mu g/m^3$, *Table 2* and Appendix) compared with in-flight concentrations (max. 0.05 $\mu g/m^3$.). Overall, they were lower than those found in the other aircraft types.

In addition to the TCPs, trialkyl phosphates were also found to be present in the flight deck air of the Hercules. These were mainly triphenyl phosphate, triisobutyl phosphate and tris(2-ethylhexyl) phosphate and their source(s) is unknown. However, organophosphates are used in hydraulic fluids and as plasticisers in plastics.

3.1.4 *o*-Cresyl Isomers

The toxicity of TCP is based on the concentration of the tri-*o*-cresyl phosphate isomer. The highest recorded TCP concentration was well below the TWA of 100 $\mu g/m^3$ [13]. A recent study of the jet engine oil used in these aircraft has revealed that the concentrations of *o*-cresyl TCP isomers in recent batches of oil are very low (<50 ppm). At these low concentrations the *o*-cresyl isomers are present almost exclusively in the form of the mono-*o*-cresyl-di-*m*/*p*-cresyl phosphate [18].

With the exception of two air samples, the total TCP concentrations were below 3.5 μg/m^3. This corresponds to ~0.05 μg/m^3 mono-*o*-di-*m*/*p*-cresyl phosphate based on mono-*o*-di-*m*/*p*-cresyl phosphate in the TCP (~1400ppm) found in the oil. The highest TCP concentration measured was 49 μg/m^3 , corresponding to ~1 μg/m^3 mono-*o*-di-*m*/*p*-cresyl phosphate.

Although these isomers are considered to be 10 times more toxic than tri-*o*-cresyl phosphate the levels are equivalent to ~0.5 -7 μg/m^3 in tri-*o*-cresyl phosphate (~ 1/200 to ~1/15 of the TCP TWA).

In addition to TCP exposure through inhalation, dermal exposure is also a valid route for TCP toxicity [13]. This is likely to be hazard for maintenance staff, bearing in mind that oil contains 3% TCP.

3.2 Trialkyl Phosphate Concentrations in F-111 and Hercules C-130 Aircraft

Trialkyl phosphate concentrations were determined in the Hercules and F-111 aircraft. The major source of these organophosphate compounds is considered to be hydraulic fluid although the PVC used to insulate electrical wiring is also known to contain tris(2-ethylhexyl) phosphate as a fire-retardant plasticiser (*vide supra*). At these concentrations they are unlikely to present a health risk given their low toxicity.

Table 4 Trialkyl Phosphate Concentrations in Cockpit/Cabin Air

Aircraft Type	**Trialkyl Phosphate Concentrations (μg/m^3)**		**Samples (Number)**
	Mean	**Maximum**	
F-111	0.64	4.0	14
C-130	0.86	5.82	30

3.3 Phenyl-α-Naphthylamine and Dioctyldiphenylamine Concentrations in Hercules C-130 Aircraft

The concentrations of PAN and DODPA sampled from the flight deck air of the C-130 aircraft are presented in *Table 5* and are of the same order as the TCP concentrations for the same aircraft type reflecting the low volatility of these compounds. The absence of an established exposure limit for the two amines is indicative of their relatively low toxicity. The concentrations measured are low even by TCP standards and hence unlikely to be a health concern.

Table 5 PAN and DODPA Concentrations in the Flight Deck of the Hercules C-130

Amine	**Amine Concentrations (μg/m³) (Sampling Time)**				**Samples (Inflight, Ground)**
	Inflight		**Ground Engine Starts**		
	Mean	**Maximum**	**Mean**	**Maximum**	
PAN	0.043 (2-7h)	0.081 (5h)	0.029 (2-6h)	0.055 (2h)	7,2
DODPA	0.006 (2-7h)	0.040 (5h)	0.026 (2-6h)	0.039 (2h)	

4. Conclusions

It needs to be emphasised that none of the species TCP, PAN and DODPA are responsible for the odours or smoke in the contaminated engine bleed air. As a matter of priority, this study has focused on what has been perceived to be the most hazardous components of engine bleed air while the malodorous thermal decomposition products of the base oil have been left for future studies.

The concentrations of the jet engine oil additives, TCP, PAN and DODPA were measured in ADF aircraft together with tris(alkyl) phosphates from hydraulic fluids The concentrations of TCP were less than *ca.*1/30 of the TWA (with two exceptions). However, the concentrations of toxic mono-*o*-di-*m*/*p*-cresyl phosphates in all but two cases, were less than the equivalent of 1/200 of the TWA of tri-*o*-cresyl phosphate This takes into consideration the higher (10 times) toxicity of the mono-*o*-di-*m*/*p*-cresyl phosphates compared with the tri-*o*-cresyl phosphate.

The two high TCP (21.7 and 49 μg/m³) samples from the Hawk indicate that air concentrations of TCP may exceed the TWA in special circumstances from sources external to the engine. With the possible exception of these conditions, the results indicate that the RAAF personnel at a greater risk from TCP exposure are the engine maintenance mechanics who come into skin contact with jet oil containing 3% TCP rather than the flight crews.

Similarly, the tris(alkyl) phosphate concentrations were very low and unlikely to be of health concern particularly in view of the lower toxicity of these compounds compared with the TCPs.

The concentrations of phenyl-α-naphthylamine and dioctyldiphenylamine were found to be less than 0.1 μg/m³ in the flight deck air of the Hercules C-130 aircraft and is not expected to be a health hazard as indicated by the absence of regulatory maximum exposure levels.

5. Recommendations

As a general rule it is recommended that the ADF consider total TCP air concentrations <1 μg/m^3 as a desirable target rather than the statutory exposure limits of 100 μg/m^3. This recommendation is based on the uncertainty of toxicity data, the absence of economic imperatives (which provide a rationale for establishing a high exposure level in industry) and the potential for cognitive effects on the flight crews. The target levels are readily achievable and probably indicative of the satisfactory condition of the compressor oil seals.

The survey of bleed air contamination was prioritised on the basis of the incidence of smoke and odour reported by air crews. Since the engine oil additives, TCP, PAN and DODPA are odourless, the criteria are not necessarily indicative of contamination by these compounds. Squadrons should be made aware of this fact.

The presence of TCP in the heat exchangers and coalescer bags, in the F-111 and Hercules C-130 aircraft, is likely to provide a background concentration of TCP in the cockpit/cabin of these aircraft even in the absence of leaky engine oil seals. Regular cleaning of the heat-exchangers (with a solvent such as acetone) and frequent replacement of the coalescer bags is likely to reduce the TCP levels in the cockpit/cabin air.

However, these measures will not affect smoke incidents in the F-111 (and Hawk aircraft). This may best be achieved by the installation of a HEPA (high efficiency particulate air) filter in the ECS ducting.

It is also recommended that further research be carried out to identify and quantify the air contaminants arising from the thermal decomposition of the oil base which characterise the smoke and odour during episodes of engine bleed air contamination.

6. References

1. Senate Rural and Regional Affairs and Transport References Committee,(1999) Report "Air Safety and Cabin Air Quality in the BAe 146 Aircraft".

2. House of Lords (UK), (2000) Select Committee on Science and Technology, Air Travel and Health.

3. Winder, C and Balouet, J-C. (2002) "The toxicity of commercial jet oils" Environ. Res. A, **89**, 146-164.

4. Mackerer, C.R., Barth, M.L., Krueger, A.J., Chawla, B. and Roy, T.A., (1999) "Comparison of Neurotoxic Effects and Potential Risks from Oral Administration or Ingestion of Tricresyl Phosphate and Jet Engine Oil containing Tricresyl Phosphate", *Journal of Toxicology and Environmental Health*, Part A, **56**, 293.

5. Singh, B. (2004) Institute of Aviation Medicine, Royal Australian Air Force, AVMED 1856/1/3/1/MED Pt 1 (6).

6. Singh, B. (2004) Institute of Aviation Medicine, Royal Australian Air Force, Private Communications.

7. Kelso, A.G., Charlesworth, J.M. and McVea, G.G. (1988) "Contamination of Environmental Control Systems in Hercules Aircraft", *DSTO Report* , MRL-R-1116.

8. SIMTARS (2002) "Smoke in F-111C & G Model Aircraft Cockpits, Preliminary Investigations".

9. Fowler, M.J., Flaskos, J., McLean, W.G. and Hargreaves, A. J. (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", *Journal of Neurochemistry*, **76**, (3), 671.

10. Henschler, D. (1958) "Die Trikresylphosphatvergiftung", *Klinische Wochenschrift*, **36**, 663.
11. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (1977) "Toxicological Profile for Hydraulic Fluids."

12. Healy C.E., Nair RS, Ribelin W.E. and Bechtel C.L. (1992) "Subchronic rat inhalation study with Skydrol 500B-4 fire-resistant hydraulic fluid." Am Ind Hyg Assoc J. 53(3) 175-80.

13. National Occupational Health and Safety Commission http://www.worksafe.gov.au

14. Berufsgenossenschaft der chemischen industrie, (2000) Toxicological Evaluation, No. 112 "Triisobutyl phosphate" CAS No 126-71-6.

15. Jenseit W., Bunke D., Rheinberger U., Kalberlah, Zerrin A. and Moll S. (2004) "Research, development statistical and analytical work to develop appropriate environmental indicators related to chemicals", Interim report, July, Institute for Applied Ecology, Germany

16. van Esch G.J. (2000) Environmental Health Criteria 218 "Flame retardants: tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl)phosphate and tetrakis(hydroxymethyl) phosphonium salts", World Heath Organisation, Geneva.

17. Plasticisers Information Centre , www.plasticisers.org

18. Kibby J., Hanhela P.J., DeNola G and Mazurek W. (2005) "Analysis of Jet Engine Oils" DSTO Report DSTO-RR-0292.

19. Wang H-W., Wang D. and Dzeng R.W. (1984) "Carcinogenicity of N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine in rat." Cancer Research 44 (7) 3098-3100.

20. Kristensen, S. "Mobil Jet Oil II – Overview of Available Scientific Background Information". Submission No. 12 of *Reference 1* (NICNAS).

Appendix A: Cockpit/Cabin Air Samples

A.1. Hawk Trainer Aircraft

Table 1 TCP Concentrations in the Cockpit of the Hawk Trainer Aircraft (Measured during ground runs of the APU. over the Period 27 October to 14 November, 2005)

Aircraft	**Comments (RAAF)**	**TCP Conc. (μg/m^3)**
A27-20	Clear air	<0.1
A27-13	Smokey air	<0.1
A27-10	Clear air	0.7
A27-04	Clear air	0.5
A27-16	Clear air	<0.5
A27-03	Clear air	0.7
A27-02	Clear air	1.5
A27-15	?	0.1
A27-07	Clear air	<0.1
A27-23	Clear air	21.7
A27-24	Clear air	<0.1
A27-28	Clear air	0.6
A27-30	Smoke	49

A.2. F-111

Table 2. Analyses of TCP from F-111 Cockpit Air Samples April 2003 – November 2004

Aircraft	**Comments (RAAF)**	**TCP Conc. (μg/m^3)**	**Other OPs (μg/m^3)**
In Flight			
A8-126	Reconnaissance flight - mid level transit- low level high G mission	<0.01	
A8-152	9000ft 15 min low level mix G, 11/2hr:: 13000 ft 20 min	0.24	
A8-512	smoke observed on takeoff: med. Light. Crew always flying with 100%Oxy so did not smell smoke.	0.18	
A8-134	010604A8-134 Recce flight	0.028	
A8-134	2.3 hr flight (1.3hr high level, 0.6 hr high, 0.6 low and 0.4 hr circuit)	<0.01	
A8-138		0.14	
A8-138		<0.01	
A8-140	Cockpit air. Straight and level, 1 speed. Very smoky on speed brake application	2.08	0.44
A8-140	Low high bombing simulation	<0.001	
A8-113	2 hours sortie	<0.001	
A8-277	Good. Only turned it on with 20 min to go.	0.25	
A6-132	Smoke bad at takeoff (concentrated haze). Aircrew on 100% oxygen. Residual smoke for rest of flight.	0.052	
A8-145		0.19	
A8-145		0.24	
A8-145	95% at low level, with numerous 1-4G turns	0.059	
na	Low level sortie	0.047	
A8-130	Speed brake operations 2 x 1G	0.180	0.87
A8-130	Little smoke on takeoff. Clear and clean (apparent) for rest of flight.	0.025	0.09
A8-142	Smoke smell. Not visible.	0.15	0.51
Ground Engine Runs			
na		1.1	na
na		2.9	na
A8-134		<0.001	
A8-114		<0.001	
A8-134		<0.001	
A8-142		0.033	0.10
-	Smoke Evident	1.08	
-	Nil smoke. Light smell	2.69	
A8-140	20min. Sample, Idle 80%	<0.001	0.02
A8-148	20min Engine RPM 68%-100% filter yellow	3.2	4.04
A8-143	Engine 0%-100%	0.15	0.28
A8-145		0.01	0.14

BDL= Below Detection Level

A.3. Hercules C-130

Table 3. Hercules C-130 Tricresyl Phosphate and Trialkyl Phosphates May 2004 – December 2004

Aircraft	**Air Sample Description (RAAF)**	**TCP Conc. (μ g/m^3)**	**Total OPs Conc. (μ g/m^3)**
In-Flight			
A97-009	010604A97-009 Standard strat. Cruise	0.052	5.874
A97-004	010604A97-004 Cruise at Fl 230-270	0.014	1.263
OO5	10604005 Standard cruise	0.018	1.249
A97-004	010604A97-004a High level cruise Richmond to Pearce	0.016	0.970
A97-004	010604A97-004b Cruise	<0.001	0.938
	010604 Blank	0.000	
OO4	030604-004a Standard cruise	<0.001	0.550
OO4	030604-004b Standard cruise	<0.001	0
A97-008	Standard cruise Richmond-Edinburgh Darwin	<0.001	0.369
A97-008	Standard cruise Tindall-Richmond	<0.01	0.507
A97-004	Std cruise 970 ceiling initial	<0.001	0.337
A97-002	Standard step climb cruise	<0.001	0.587
A97-002	Cruise fl 23.0	<0.001	1.309
A97-002	Standard cruise profile	<0.01	0.408
A97-004	Cruise FL230	0.017	0.794
A97-004	Standard climb profile setting. 970 TIT to 26000ft. Constant level 300kts cruise. Standard descent.	0.020	0.781
A97_002	#2 smelly bleed. Only open for start	<0.001	0.409
A97-	Standard cruise and opt stop	<0.001	0.382
A97-011	Cruise flt 180 lang/ t/o Fl 270 910/1010. Dn-Tn-Win-Ri.	<0.001	0.163
A97-006	Amberley-Darwin. Standard level 20000' cruise. (2200′ cabin altitude). 2x Toasted sandwich batches cooked in oven during sample.	0.002	0.859
A-97-006	Std cruise	0.002	1.346
A97-002		<0.001	0.26
A97-002		<0.001	0.24
		<0.001	0.93
		<0.001	0.30
		<0.001	0.17
		<0.001	0.25
A97-005		0.02	0.65
		<0.001	0.26
		0.01	0.63
Ground Engine Runs			
A97-002	010604A8-134 Ground Power Run, 6h	0.260	na
A97-002	010604A97-007 Ground power run.	0.123	2.914
A97-002	Ground power run 6 hours continuous. 1010C setting	0.260	0

Table 4. _Amine Concentrations in the Flight Deck Air of the Hercules C-130 Aircraft

Aircraft	**Air Sample Description (RAAF)**	**PAN Conc. (μ g/m^3)**	**DODPA Conc. (μ g/m^3)**
In-Flight			
A97-002	Ground power run 6 hours continuous. 1010C setting	0.004	0.013
A97-009	Standard strat. Cruise	0.052	0.000
A97-004	Cruise at Fl 230-270	0.081	0.040
A97-OO5	Standard cruise	0.031	0.004
A97-004	High level cruise Richmond to Pearce	0.075	0.001
A97-004	Cruise	0.061	0.000
A97-OO4	Standard cruise	<0.001	0
A97-004	Standard cruise	<0.001	0
Ground Engine Run			
A97-002	Ground power run.	0.055	0.039

A.4. Air Sampling Devices

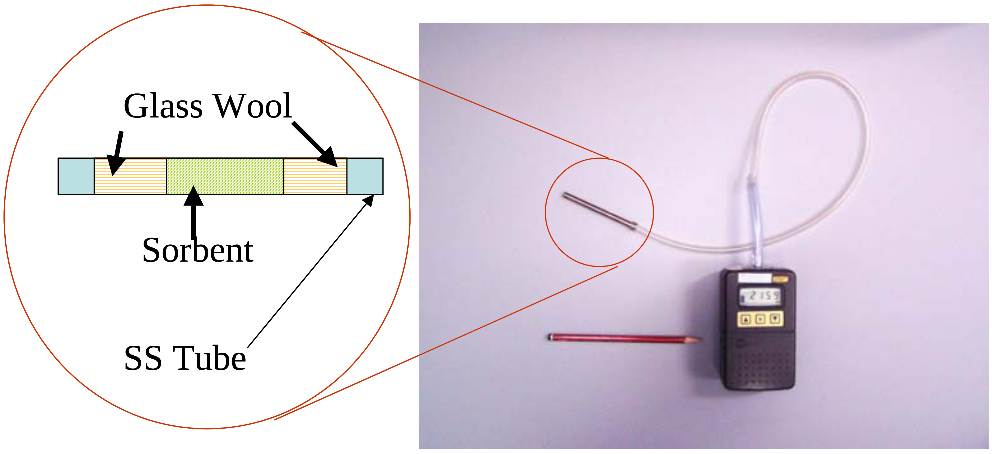


Figure 1. Long duration (>3 hour) sampling pump and sorbent tube attached

Figure 2. Short duration (10-20 min.) air sampling pump with filter attached

Page classification: UNCLASSIFIED

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
DOCUMENT CONTROL DATA

1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)

2. TITLE (U) Organophosphate and Amine Contamination of Cockpit Air in the Hawk, F-111 and C-130 Aircraft	3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION) Document (U) Title (U) Abstract (U)
4. AUTHOR(S) P.J. Hanhela, J. Kibby, G. DeNola and W. Mazurek	5. CORPORATE AUTHOR Platforms Sciences Laboratory 506 Lorimer St Fishermans Bend Victoria 3207 Australia

6a. DSTO NUMBER DSTO-RR-0303	6b. AR NUMBER AR-013-323	6c. TYPE OF REPORT Research Report	7. DOCUMENT DATE October 2005

8. FILE NUMBER 2005/1073278/1	9. TASK NUMBER AIR 05/050	10. TASK SPONSOR DFS-ADF	11. NO. OF PAGES 21	12. NO. OF REFERENCES 20

13. URL on the World Wide Web http://www.dsto.defence.gov.au/corporate/reports/DSTO-RR-0303.pdf	14. RELEASE AUTHORITY Chief, Maritime Platforms Division

15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for public release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE, PO BOX 1500, EDINBURGH, SA 5111

16. DELIBERATE ANNOUNCEMENT

No Limitations

17. CITATION IN OTHER DOCUMENTS Yes

18. DEFTEST DESCRIPTORS

Air contamination, Jet engine oil, Engine bleed air, Tricresyl phosphate, dioctyldiphenylamine, tris(alkyl) phosphate, Hercules, Hawk, F-111

19. ABSTRACT

A survey of cockpit air contamination by organophosphates and amines in the Hawk, F-111 and Hercules C-130 aircraft was undertaken. The air contamination occurred via the engine bleed air supply. The source of tricresyl phosphates, phenyl-α-naphthylamine and dioctyldiphenylamine was jet engine oil while hydraulic fluids are suspected of contributing to the presence of trialkyl phosphates.

The concentrations of all contaminants measured were generally very low. Tricresyl phosphate concentrations were below 4 µg/m3 with two exceptions (21.7, 49 µg/m3, Hawk) compared to the maximum permissible concentrations (100 µg/m3). Ground engine starts, at high power, gave rise to the highest concentrations.

Phenyl-α-naphthylamine and dioctyldiphenylamine concentrations were also very low (<0.06 µg/m3) in the Hercules C-130 and the absence of exposure limits for the two compounds reflects on their apparent low toxicity. Trialkyl phosphates were also found in the F-111 and Hercules C-130 aircraft at concentrations (<6 µg/m3) similar to tricresyl phosphates. They are of lower toxicity than the latter compounds and are not expected to present a health risk.