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Cabin Air – surface residue study Report

Judith Lamb, Carolyn McGonagle, Hilary Cowie and
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There has been concern that occasional leaks of aircraft engine oils or hydraulic fluid may contaminate cabin or cockpit areas; i.e. “fume events”. These oils may contain organophosphate compounds. Previous research has shown that short peak concentrations of ultrafine aerosols were occasionally found in aircraft, along with increased tri-n-butyl phosphate (TBP) and tricresyl phosphate (TCP) air concentrations. The present research measures residues on the internal surfaces of aircraft and control environments to further investigate fume events.

We developed a methodology to wipe residues from surfaces using the ethanol-moistened filters. The residues were analysed by gas chromatography/mass spectrometry for TCP, TBP, butyl diphenyl phosphate (BDPP) and dibutyl phenyl phosphate (DBPP). Samples were obtained from different aircraft types, ground vehicles and offices. A total of 86 sample sets were collected. The surface residues in the passenger compartments were generally lower than in the cockpit. The mean amounts of TBP, DBPP and BDPP detected in the aircraft were similar to those in the control vehicles. For TCP the contamination in the control vehicles and the office locations were similar, and slightly lower than found on the aircraft. Estimates of air concentrations consistent with these surface residues were in agreement with other published data.

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EXECUTIVE SUMMARY

Synthetic aircraft engine oils and hydraulic fluids contain a wide range of additives, including substances that improve anti-wear and aid high pressure performance characteristics. In certain circumstances it is possible for oil mist in engine-fed air supplies to contaminate the aircraft cabin. Aircrew and passengers have raised concerns about the potential for contamination of the cabin environment by oil and hydraulic fluid mists containing organophosphate additives. These episodes are known as “fume” or “cabin air quality” events.

This study was commissioned by the Aviation Health Working Group of the Department for Transport to complement contemporary research on cabin air quality, by providing information on chemical surface residues in aircraft as a potential indicator of previous fume events. A small number of control environments were also included in the study: both at airports and elsewhere.

The project aimed to collect, characterise and quantify these residues. Whilst there are many compounds potentially contained within surface deposits, four organophosphates were chosen as index compounds for oil fume deposition- tri-n-butyl phosphate (TBP), tricresyl phosphate (TCP), butyl diphenyl phosphate (BDPP) and dibutyl phenyl phosphate (DBPP). These are common, semi-volatile additives of aircraft lubricants and fluids, and have been a source of particular concern to aircrews regarding their potential health effects. Wipe sampling and analytical methods for collecting and evaluating residues were developed and validated. Airlines and other participant organisations were recruited and sampling was undertaken on a range of aircraft, together with airport-based and office control sites. Sampling was carried out before and after a set time interval with the aim of determining initial levels of surface contamination and collecting any residues deposited in the interim period.

A total of seventeen aircraft, five airport-based vehicles and two offices were evaluated, with a total of eighty six locations sampled. TBP, BDPP and DBPP measured in the surface deposits from the cockpits of aircraft were in general higher than those from the passenger areas, with the exception of one plane type. The amounts of TBP, BDPP and DBPP were higher in aircraft and airport-based vehicles than in offices. Factors potentially contributing to these differences include proximity to oil sources, the presence of electronic equipment, cleaning regimes, external sources of organophosphates and lighting levels, which may promote the decomposition of the organophosphate compounds. The amount of TCP measured was higher in planes than in other locations, suggesting that this substance originated from aircraft sources.

Estimates were made of the theoretical maximum airborne concentrations of TCP and TBP from which the residues may have originated. These estimated concentrations were low and comparable to those found in other research studies considering airborne cabin contaminants, which suggests that the findings of this study have provided a valid and useful addition to the current cabin air quality research body of knowledge.

1 INTRODUCTION

Synthetic aircraft engine oils and hydraulic fluids contain a wide range of function-specific additives, including substances that improve anti-wear and aid the high-pressure performance characteristics of the oil.

Of these additives, a number of organophosphate compounds have been of interest to researchers, who have studied their potential to cause health effects in aircraft crew and passengers through contamination of the cabin environment by oil mist in engine-fed air. These episodes are known as “fume” or “cabin air quality” events.

There has been widespread industry and public interest in this topic and, in 2000, the House of Lords Select Committee on Science and Technology reported on “Air Travel and Health”. Whilst this inquiry did not find evidence of harmful airborne contaminants in cabin air, it was recommended that further assessments of aircraft air quality should be undertaken.

In 2004, the Safety Regulation Group of the United Kingdom Civil Aviation Authority (CAA) published a detailed study of the toxicology of pyrolised aircraft engine oil and the results of measurements of contamination on cabin air supply ducts. Following the toxicology review, the CAA noted that there were no identifiable components of pyrolised engine oil which had the potential to the cause the symptoms reported by crews. Analysis of duct material indicated the presence of a range of organic compounds including detectable quantities of tri-ortho-cresyl phosphate (TOCP). Further to this research, the CAA issued guidance to manufacturers and operators on monitoring, cleaning and replacement of ducts on one aircraft type, together with updated flight and cabin crew procedures for dealing with suspected fume events.

In 2007 the United Kingdom Committee on Toxicity (COT) was asked by the Department for Transport (DfT) to undertake an independent scientific review of data submitted by the British Airline Pilots Association (BALPA) relating to concerns of its members about the possible health effects from oil fume contamination on commercial jet aircraft. The COT estimated that cabin air quality events occur on roughly 0.05% of flights (~1 in 2000). It concluded that whilst a causal association between cabin air contamination by oil mists and ill-health in commercial air crews could not be identified, a number of incidents where there was a temporal relationship between reports of oil/fume exposure and acute ill-health effects indicated that such an association was plausible. The COT recognised that further study of air quality events should therefore be undertaken to determine the types and concentrations of substances present in cabin air.

The DfT Aviation Health Working Group (AHWG) commissioned Cranfield University to carry out cabin air monitoring for a range of potential chemical contaminants, as an initial pilot project to determine the relevant sampling and analytical methodologies, followed by a larger study.

The results of the Cranfield University pilot investigation in a BAe-146 aircraft on the ground found tri-n-butyl phosphate (TBP) and tricresyl phosphate (TCP) in air samples along with a range of other volatile or semi-volatile organic compounds (Muir, 2008). In a second test, a fume event was observed during a test flight in a Boeing 757, and the data from a particle monitoring device showed that during the fume event there was a very high number concentration of a very small aerosol, although overall these represented a small mass concentration of oil. Slightly elevated levels of TBP and TCP were again measured.

The main Cranfield study involved further characterisation and measurement of various volatile (VOCs) and semi-volatile organic compounds (S-VOCs), carbon monoxide and ultrafine aerosol during a number of different flight phases on a range of aircraft types. This work showed mean ultrafine aerosol number concentrations across all flight sectors in the range 1,000-100,000 particles cm^{-3} with five instances of peak concentrations > 500,000 particles cm^{-3}. Mean total VOC and maximum carbon monoxide concentrations were mostly below 2 ppm. The most commonly measured VOCs were limonene and toluene, which were attributed to the use of these substances in cleaning/air freshener products and fuels, respectively. Airborne TBP and TCP were also detected during various flight phases on a range of aircraft. (Cranfield University, 2011)

To complement the Cranfield University work, the AHWG recognised that additional information on potential contaminant residues on internal surfaces could also be informative of possible fume events. The current IOM study was therefore commissioned to address this requirement.

2 AIM AND SCOPE OF THE PROJECT

The aim of this project was to measure and characterise residues on the internal surfaces of aircraft and other comparable control environments, and to interpret the significance of data obtained in relation to the possible sources of contamination, including the potential impact of episodic oil fume events.

In achieving this aim, the following objectives were identified.

2.1 OBJECTIVES

- To develop suitable sampling and analytical methods for obtaining, and where possible quantifying, cabin surface deposits containing a number of organophosphate compounds.

- To validate the sampling and analytical methodologies and associated quality assurance procedures and where possible, ensure data compatibility with the contemporary Cranfield University research into cabin air quality.

- To recruit a suitable range of aircraft operators and appropriate control organisations for inclusion in the study.

- To carry out surface sampling tests in the study and control groups and complete chemical analyses of the samples.

- To evaluate and report on the results of the sampling exercise to the Department for Transport.

3 BACKGROUND INFORMATION

3.1 ORGANOPHOSPHATE COMPOUNDS- USES AND PREVALENCE

This study aimed to determine the amounts of organophosphate compounds deposited within aircraft and other environments. As such, for comparative purposes, it was of use to identify and evaluate the general uses of these compounds, which are found in a range of applications across industrial and domestic settings. Some of these applications are highlighted below.

3.1.1 Flame Retardants

Organophosphates are used as flame retardants in a number of materials, including textiles, foams, resins, polymers and plastics. TCP-based flame retardant coatings are commercially available, as are TBP-based materials (Chemtura, 2011).

In most of these applications the organophosphate additives are not chemically bonded to the base material, and so over the lifetime of the product, they can enter the atmosphere via volatilisation, leaching or surface abrasion (Marklund et al, 2003). A number of studies have detected organophosphates emitted via these mechanisms on surfaces and in air and dusts within household and non-domestic premises.

Marklund et al (2003) found TBP concentrations of 70 ng m^{-2} in surface wipe samples taken from office computer covers and 30 ng m^{-2} in those taken from computer screens. TBP was also detected in dust samples from a radio shop (1.8 mg kg^{-1}) and at similar levels in an aircraft (2.2 mg kg^{-1}). The most prevalent organophosphate found in this study was tris-2-butoxyethyl phosphate (TBEP), which was detected in all of the samples, including the ones from the aircraft (18 mg kg^{-1}).

Marklund et al (2005) found average airborne levels of TBP in a variety of premises ranging from 0.0005- 0.12 µg m^{-3}, with the levels in public buildings such as shops, hospitals and prisons tending to be higher than those in domestic premises. The highest concentration of TBP was however detected in a house where renovations were being carried out, and this contamination was assumed to have come from TBP-containing concrete, glues and putty. In general, the differences in airborne organophosphate concentrations between locations were attributed to variation in the flame retardancy requirements and hence the different furniture, consumer products and interior fittings from which the compounds were emitted.

Van den Eede et al (2011) detected levels of tri-iso-butyl phosphate (TiBP) in household dusts ranging from 0.70 – 15.6 mg kg^{-1} - (mean 4.20 mg kg^{-1}). Levels of TBP ranged from 0.03- 2.70 mg kg^{-1} (mean 0.25 mg kg^{-1}), whilst TCP was detected at <0.04–5.07 mg kg^{-1} (mean 0.44 mg kg^{-1}). They also sampled dust from non-domestic workplace premises including furniture, electronics and mattress stores, carpentry workshops and analytical laboratories. TiBP (0.67 – 4.40 mg kg^{-1}; mean 1.45 mg kg^{-1}), TBP (0.05 – 6.01 mg kg^{-1}; mean 0.63 mg kg^{-1}) and TCP (<0.04 – 12.5 mg kg^{-1}; mean 1.53 mg kg^{-1}) were detected.

During sample analyses, van den Eede observed that the presence of TiBP in the general laboratory environment significantly contaminated blank samples. This contamination was identified as coming from laboratory fume hoods and prevented the full determination of very low levels of TiBP on some study samples.

Van den Eede also referenced work by Weschler and Nazaroff from 2008, which had suggested that organophosphate flame retardants released in indoor air distribute between the gaseous phase and various organic films and airborne particulate matter. In situations where the primary source is removed from the room, the organic film layers may then act as secondary emitting sources for the substances.

Makinen et al (2009), detected organophosphorus-based flame retardants in a range of workplaces, and found TCP and TBP in electronic equipment manufacturing/dismantling facilities and in a furniture workshop. During this study, measurements were taken of the concentrations in air, together with an assessment of employees' dermal exposure. The highest amount of TCP detected in air was found in personal samples taken in an electronics dismantling factory (<0.003 – 0.81 μgm^{-3}; mean 0.110 μgm^{-3}), whilst the highest TBP concentrations in air were identified in background samples in the sewing areas of the furniture manufacturer (0.11- 1.2 μgm^{-3}; mean 0.56 μgm^{-3}).

The concentrations in air of TCP and TBP, and a range of other organophosphate flame retardants were also measured by Hartmann (2004), in a study of indoor air contaminants within vehicles and premises. The measured concentrations of TBP ranged from 0.0017 – 0.029 μgm^{-3} with the highest concentration found in a public theatre. Hartmann also noted analytical interference from other unknown organophosphates present in the actual samples taken, which was assumed came from plastics and other surfaces.

Carlsson et al (1997) measured the concentrations in air of a number of organophosphates in various indoor workplace environments. Within schools, the mean airborne concentrations of TBP ranged from 0.0098- 0.064 μgm^{-3}, whilst within a children's daycare centre and office, the mean concentrations were 0.013 μgm^{-3} and 0.018 μgm^{-3} respectively. Samples were also taken outside one of the schools and the office block, to allow comparison of the concentrations of organophosphates in internal and external environments. All of the external samples were below the limits of detection for the various compounds. During a pilot sampling exercise for this study, Carlsson also noted the difficulties that ambient background concentrations of many organophosphates posed during laboratory analyses of trace amounts of the compounds.

Carlsson concluded that the relative concentration in air of individual organophosphate flame retardants was in part related to their volatility, with lower boiling point compounds, for example TBP and chlorinated trialkyl phosphates, being released more readily from substrate materials than additives with higher boiling points. The study postulated that each indoor environment has its own unique concentration profile for organophosphates, dependent on the particular mix of furniture, building fabric and electronic equipment therein.

It is therefore possible that organophosphate compounds may be present inside aircraft because of their presence as flame retardants in fabric and electronic equipment.

3.1.2 Plasticisers and Other Uses

Organophosphates are used commonly as plasticisers to improve the fluidity of materials, for example; TBP is used as a plasticiser in polyester resins, cellulose acetate and acrylonitrile-butadiene styrene (ABS). TCP isomers are used for this purpose in polyvinyl chloride, cellulosic polymers and synthetic rubbers (Chemtura, 2011). There is therefore the potential for TBP and TCP to be present in plastic and polymer-based aircraft and vehicle fasciae and other fixtures and fittings.

TBP is used as a solvent in the manufacture of inks, resins, adhesives and pesticide products. It is also used as an antifoam agent for textile, pulp, paper, concrete and oil drilling mud, and as a levelling agent (Chemtura, 2011).

3.1.3 Engineering/Aviation-related Applications

Organophosphate compounds are used as anti-wear and high temperature additives in aviation engine oils and hydraulic fluids. These additives improve the flame retardancy of the oils and fluids, as well as enhancing their lubricant and anti-corrosion properties.

The compounds are also used in other engineering situations that require these properties, for example marine systems, the electrohydraulic control systems of steam turbines and wherever any leak of fluid may present an ignition source (US Dept of Health, 1997).

TCP has also been used as a lubricant in refrigeration oils (Sporlan, 2007), with concentrations given as TCP (1-5%) with the tri-ortho-isomers (TOCP) being <0.06%.

The type and concentrations of different organophosphates within fluids varies depending on the manufacturers' specifications. Common compositions for hydraulic fluids include mixtures of tri-aryl, tri-alkyl and alkyl/aryl phosphate esters for example TBP (20-80%); DBPP (40-70%) and BDPP (10-30%) (Solutia, 2008; ExxonMobil 2009). This variety in stated composition reflects in part the manufacturing process for certain organophosphates whereby the required compound is manufactured as part of a mixture of chemically-similar materials rather than individually.

Whilst aviation engine oil composition also varies with manufacturer, it is often a mixture of synthetic ester base stock with specialised additives, for example alkylated diphenylamines, n-phenyl-1-napthylamine and TCP (ExxonMobil, 2008; Shell UK Ltd. 2011). TCP concentrations are around 1-3%.

References to the inclusion of organophosphate compounds (e.g. TBP) as anti-foaming and wetting additives in aircraft and runway de-icers have also been noted within patent applications (Samuels et al, 2006), however no current manufacturers' health and safety datasheets containing this information were identified.

3.1.4 Environmental Organophosphate Contamination

Carlsson et al (1997) found that concentrations of various organophosphates in outdoor air were lower than within premises, indicating that the main sources were located indoors.

The common uses of organophosphates as described above have however led to their detection in precipitation. Levels of 0.023-0.025 mg kg^{-1} of TBP have been detected in snow sampled from airport runways and 0.0021 mg kg^{-1} in aircraft parking areas. These were around 100 to 1000 times higher than in the reference snow samples taken from remote sites (1.9×10^{-5} mg kg^{-1}) and were attributed to aircraft hydraulic fluids and oils (Marklund et al, 2003).

3.2 HEALTH EFFECTS OF ORGANOPHOSPHATES

The term "organophosphates" encompasses a large group of chemical compounds, with a similarly broad range of related human toxicity. Occupational and domestic exposure to these compounds can occur via inhalation, dermal and ingestion pathways.

The neurotoxicity of the TOCP has been observed in a number of studies, with many of the reported exposures occurring via ingestion. Reports of such events in the United States, India, China and South Africa date back to the 1930s when TOCP was either inadvertently mixed with cooking oils, used as an adulterant of an alcohol-containing ginger extract or contaminated a food production process. A limited number of fatalities have been reported in relation to these incidents, with polyneuritis and paralysis also commonly observed in these cases. (WHO, 1990).

The potential of chronic exposures to low levels of TCP via ingestion, inhalation and skin absorption to cause delayed neurotoxicity have also been studied. Reported symptoms of organophosphate induced delayed neuropathy (OPIDN) include weakness, ataxia and paralysis. The symptoms of OPIDN include pain and paraesthesia in the lower extremities. Mild impairment of cutaneous sensations and muscle weakness progressing to paralysis of the lower extremities have been reported (WHO, 1990).

A number of researchers have noted that modern production processes routinely remove the majority of TOCP. For example, TCP products are typically manufactured to contain over 98% meta- and para- isomers with no detectable TOCP (United States of America Department of Health and Human Services, ATSDR, 1997).

A recent review of the health effects of phosphate tri-esters used as flame retardants (Sjögren et al, 2009) estimated that aviation oil contains 3% TCP, comprising a blend of ten TCP isomers including TOCP plus other structurally similar compounds. They conservatively estimated the percentage of TOCP within the total TCP figure as 0.1-1%, suggesting that a bulk oil containing 3 % TCP would contain about 0.003-0.03 % TOCP.

On the basis of toxicological work carried out by Henschler from 1958 relating to the relative toxicities of the different isomeric forms of TCP, it has been postulated by some recent researchers that the mono-ortho and di-ortho isomers of TCP are significantly more toxic than the tri-ortho form.

Denola et al (2011) estimated the mono-ortho- cresyl phosphate isomer concentration in typical aircraft turbine oils at approximately three times the amount of the tri-ortho-isomer. These authors also calculated that an airborne concentration of 5 μgm^{-3} of TCP would be expected to contain 0.0002 μgm^{-3} of the mono-o-di-m/p isomers.

With reference to Henschler, Denola assumed that the mono-o-m/p cresyl phosphate isomer is 10 times more toxic than the tri-o-cresyl phosphate form, therefore exposure to 0.0002 μgm^{-3} of the mono-ortho variant would be equivalent to exposure to 0.002 μgm^{-3} of the tri-ortho isomer.

3.3 OCCUPATIONAL EXPOSURE LIMITS FOR ORGANOPHOSPHATES

Occupational exposure limits have been set for TBP, DBPP and the ortho-isomer of TCP in a number of countries and are shown below in Table 1 as 8 hour and/or 15 minute time weighted averages (TWA). No exposure limit values for BDPP could be found in the literature (IFA, 2011).

Table 1: International Occupational Exposure Limits for Organophosphates

Substance	**Tributyl phosphate (all isomers)**		**Tricresyl phosphate (ortho-isomer)**		**Dibutyl phenyl phosphate**	
Country	Long term/8hr TWA/ mgm^{-3}	Short term/15 min TWA/ mgm^{-3}	Long term/8hr TWA/ mgm^{-3}	Short term/ 15 min TWA/ mgm^{-3}	Long term/8hr TWA/ mgm^{-3}	Short term/15 min TWA/ mgm^{-3}
Austria	2.5	5	0.1	0.2	3.5	-
Belgium	2.2	-	0.1	-	3.6	-
Canada	2.2	-	0.1	-	3.5	-
Denmark	2.5	5	0.1	0.2	3.5	7
France	2.5	-	0.1	-	-	-
Germany	11	22	-	-	-	-
Hungary	-	-	0.1	-	-	-
Poland	-	-	0.1	0.3	-	-
Singapore	2.2		0.1	-	3.5	-
Spain	2.2		0.1	-	3.6	-
Sweden	-	-	-	-	-	-
Switzerland	2.5	10	0.1	-	-	-
USA-NIOSH	2.5	-	0.1	-	-	-
USA- OSHA	5	-	0.1	-	-	-
United Kingdom	5	5	0.1	0.3	-	-

The limits for TOCP have in the main been set on the basis of its neurotoxic properties, whilst those for DBPP and TBP have been set because of their potential for irritation of the eyes and respiratory system.

3.4 THE AIRCRAFT CABIN ENVIRONMENT

The air within the cockpits and passenger areas of jet aircraft is supplied as a mixture of air from the outside environment and air drawn from the engine (bleed air). The bleed air supply is taken from the compressor stage of the engine, then cooled and passed through heat exchangers and fabric coalescer bags within the environmental control systems (ECS). It is then combined with a similar amount of re-circulated, filtered air from the cabin and fed back into the aircraft environment. In general, the supply to the cockpit is taken from a separate air handling system to that of the passenger cabin. The bleed air supply is also used to cool avionics equipment.

As noted in a National Research Council report on commercial airliner cabin air quality (2002), the quality of the non-bleed air component of the cabin environment is affected by the composition of the external environment, both when the aircraft is on the airport apron and in flight. As such, contaminants may enter the cabin environment from external sources, for example other planes, site vehicles, ambient air pollution in urban settings and atmospheric ozone at higher altitudes.

Van Netten (2005) noted that the environment within the aircraft cabin can be affected by the exhaust emissions of other aircraft whilst on the tarmac. Similarly, Solbu et al (2011) detected

DBPP from hydraulic fluids in air and wipe samples across a range of aircraft and helicopter types, including those where it was not used on the particular craft sampled. This was attributed to the sampling techniques capturing air from the exhausts of adjacent aircraft whilst on the ground.

For situations when the main engines are not running or are not providing sufficient power, for example when at the gate, most aircraft operate an auxiliary power unit (APU). This supplies electric and hydraulic power and can also be used to provide bleed and other air during ground time. The APU can also serve as a backup in-flight power system.

The House of Lords Select Committee on Science and Technology (2000) noted that the majority of aircraft operate at a cabin fresh air supply rate of 5 l s^{-1} (10 cubic feet per minute - cfm) or more per person, which is in accordance with the certification specification from the European Aviation Safety Agency (EASA). The average rate of supply is affected by the density of seating: one manufacturer reported to the Committee that in a standard aircraft configured to allow the maximum number of seated passengers, the fresh air flow would be between 3.1- 3.8 l s^{-1} (6.5 - 8.0 cfm) per passenger.

The Select Committee report states that the typical cabin mixed fresh/re-circulated air flow of 9.5 l s^{-1} (20 cfm) of air per occupant equates to a full change of cabin air every 2 to 3 minutes, i.e. 20 to 30 times per hour. Taking into account the 50:50 ratio of re-circulated air: fresh air, this is equivalent to an entire exchange of cabin air 10 to 15 times per hour.

With the flight deck being supplied with fresh air separately from that supplied to the cabin, there is a consequent increase in the number of air changes per hour because of the smaller cockpit volume.

A number of researchers have monitored airborne concentrations of organophosphates and other compounds in aircraft.

Whilst sampling cabin air on 5 different aircraft (over 100 flights), Cranfield University (2011) detected a range of volatile and semi-volatile organic compounds, including tri-ortho-cresyl phosphate (TOCP); other TCP isomers; TBP; toluene, meta- and para-xylenes, limonene, tetrachloroethylene and undecane.

Cranfield's methodology and strategy involved taking a series of routine samples at defined points on each flights, together with real-time samples during any fume events that were suspected to have occurred either because of a change in air quality detected via instrumentation, or because of a report by anyone on board. A total of 30 air quality event sorbent tube samples were collected during the study. Cranfield did not detect higher amounts of their selected analytes during these events compared with the contemporary routine samples taken in that flight phase.

In the Cranfield study, no detectable amounts of TOCP or other TCPs were reported for the majority of samples taken (>95%). Of the samples where TOCP was detected, a maximum airborne concentration of 22.8 µg m^{-3} of TOCP (arithmetic mean 0.07 µg m^{-3}) was measured, with a maximum of 28.5 µg m^{-3}, (arithmetic mean 0.14 µg m^{-3}) determined for the total of all other TCP isomers. TBP was detected in a number of samples, with the highest recorded amount (21.8 µg m^{-3}, overall mean 1.07 µg m^{-3}) obtained during the first start-up of the aircraft's engines.

4 METHODOLOGY

4.1 DEVELOPMENT OF QUANTITATIVE SURFACE SAMPLING AND CONTAMINANT ANALYSIS METHODS

Development and validation of the sampling and analytical methods was undertaken. A detailed account of the analytical development and validation processes is given in Appendices 1 and 2, with a short summary of the various stages provided below.

All analyses noted below for the compounds of interest were carried out using a Shimadzu QP2010S gas chromatograph/mass spectrometer (GC-MS). The instrument was set up using parameters used previously in the determination of organophosphate compounds. As standards for DBPP and BDPP could not be sourced, Skydrol hydraulic fluid was chosen as a calibration standard as it contains both these compounds, and is commonly used by many airline companies. The relative concentrations of these two substances in the bulk material were taken from the manufacturer's safety data sheet.

4.1.1 Determination of Residual Organophosphate Contamination of Sample Media, Collection Equipment and Analytical Reagents

Literature searches of methods for the determination of organophosphates were carried out and identified that there was the potential for contamination of sample media and analytical reagents from the general environment. The concentrations of TCP, TBP, DBPP and BDPP in the analytical reagents, sample collection/storage equipment and gloves were therefore determined. During this assessment, no organophosphates were determined in the analytical reagents, filter storage/transportation equipment, templates or gloves, however it was noted that certain batches of glass fibre filters to be used in the sampling exercise contained low levels of TBP. All batches of filters were therefore subsequently prepared for sampling by washing with ethyl acetate and drying prior to placing them in clean Petri dishes for transportation to site.

4.1.2 Removal Efficiency of Sampling Method

The term *removal efficiency* refers to the ability of a sampling medium, in this case the ethanol-moistened glass fibre filter, to absorb, or otherwise capture, an acceptable amount of the desired surface contaminants when it is applied across the test surface.

A number of spiked samples were prepared by micro-syringing different masses of the compounds of interest onto clean glass plates and then wiping off the deposited material using a standard and consistent pattern. The sampling method removal efficiency was calculated as a percentage of material recovered compared with the initial spiked amount. Removal efficiencies obtained were in the range 85-95% for TBP, 82-100% for DBPP, 91-100% for BDPP and 87-92% for TCP.

Removal efficiencies from a variety of plastic surfaces, assumed to be similar in composition to those found in aircraft fasciae were also determined. For these samples, the removal efficiencies ranged from 14-100% for TBP, 14-100% for DBPP, 24-100% for BDPP and 17-100% for TCP. The lowest values quoted in these ranges relate to one particular plastic, on which there was visible evidence of photodegradation of the surface prior to spiking and wiping. It is likely that this damage will have increased its surface porosity and thus prevented effective removal of the applied organophosphate solutions. (see Appendix 5- Scanning Electron Microscope Images of Trial Surfaces).

4.1.3 Desorption Efficiency of Analytical Method

The desorption efficiency for the analysis from the sampling medium was determined by spiking samples of the relevant substances onto the filter then leaving them for 20 minutes until the ethanol evaporated then analysing them via gas chromatography. Following this, the samples were analysed and the desorption efficiency calculated as the percentage of recovered analyte compared with the original spiked concentrations. Analytical recoveries obtained were in the range 59%-84% for TBP, 59-89% for DBPP, 85-100% for BDPP and 90-97% for TCP.

4.1.4 Sample Stability Test- Standardised Using Vials

Organophosphates are not completely stable and over time there will be slow decomposition to alcohols and inorganic phosphates. A method was developed to identify if any organophosphates captured during sampling would be subject to such decomposition.

Tests of the stability of spiked samples indicated that the substances of interest were still present in significant quantities after a period of 21 days when stored in sealed vials that were not exposed to light.

Tests on sealed clear vials exposed to sunlight indicated that there was some loss of TBP, potentially due to photodegradation, indicating that brown sample collection vials should be used for the main study to minimise losses of this nature post sampling.

Samples and materials throughout the project were transported by rail or by road to minimise the potential for evaporation of organophosphates in the lowered pressure of an aircraft hold.

4.1.5 Determination of Organophosphate Stability on Different Surfaces

In addition to the sealed vial tests mentioned above, samples of the organophosphates of interest were also spiked onto both watchglasses and a variety of different plastic surfaces to provide information on the residence time of the materials. The plastic surfaces were chosen for their similarity to aircraft fascia and their resistance to the ethyl acetate carrier solvent. A full description of these tests is given in Appendix 2.

In general, there were small but detectable amounts of organophosphates detected in the samples analysed following intervals of 14 days, with much less being found at 21 days, i.e. typically less than about 10%.

The highest amounts of TBP. DBPP and BDPP were detected on the porous plastic surface (rather than those with an impermeable finish), suggesting that these more volatile substances were perhaps trapped in the matrix of the material. Scanning electron microscope images of a selection of the surfaces, which illustrate these differences in porosity, are shown in Appendix 5.

4.2 ANALYSIS OF DUPLICATE SAMPLES BY AN EXTERNAL LABORATORY

To ensure that as full a picture of the cabin air environment as possible could be obtained, it was necessary to determine and achieve comparability of the analytical methods in this project with those used by the laboratory that carried out the analysis for the Cranfield University study mentioned previously (Cranfield University, 2011).

To this end, agreement on the analytical method to be used was reached with the relevant laboratory and a selection of spiked and "duplicate" real samples prepared and sent for analysis during the validation and on-site sampling periods of the project.

4.3 RECRUITMENT OF PARTICIPANT ORGANISATIONS

4.3.1 Aircraft Operating Companies

Aircraft companies were recruited with the assistance of the DfT, which provided contact details for commercial airline carriers. Initial contact was made with the company representatives via telephone and email.

During discussions with the DfT and airline carrier participants, it was determined that changes to the proposed types of aircraft to be sampled were necessary, because of changing fleet composition over time. In particular, there were difficulties in obtaining samples on the BAE146e craft because of its limited present-day commercial use in the UK. To allow for a larger spread of samples, the decision was taken to broaden the scope of the study to include a selection of aircraft which are currently used within the UK. The study was therefore extended to include samples on the Boeing 737 and 767 airframes, which are both operated widely across the UK by a number of carriers, as well as the Boeing 757 and Airbus 320/321 series craft which were proposed initially.

Only one BAe 146-type aircraft was identified and included within the study. This was of a unique and entirely non-standard design in terms of its internal layout and ventilation system configuration. The aircraft carried a large amount of scientific equipment within its rear compartment, with a maximum of around 20 scientists being transported at any one time. It was therefore considered unrepresentative of the standard passenger-carrying BAe 146 type which was originally sought, however was included to provide additional data.

4.3.2 Control Locations

The IOM undertook to recruit suitable control groups for the study, using internet searches of engine oil and hydraulic fluid manufacturers' information to identify potential end users of organophosphate-containing substances.

These potential groups were divided into transport-related and non-transport-related. A further division of the transport-related group was made into aviation and non-aviation.

4.3.2.1 Aviation-related Transport Controls

Aviation transport controls were identified as either using organophosphate containing lubricants or in the vicinity of their use, for example airport-based maintenance and service vehicles. These controls were recruited with help from the airline carriers involved in the aircraft sampling exercise.

4.3.2.2 Non-aviation Transport Controls

Potential non-aviation transport controls with operational similarity to commercial aircraft were identified during the initial desk-based phase of the study. This group included bus and rail operating companies, who use vehicles with distinct passenger and crew areas, thus potentially providing a close comparison with aircraft flight decks and passenger cabins

In practice, however, there were significant difficulties in recruiting directly-comparable participants from train and bus companies, as none of the companies with whom successful contact was made used fluids or oils containing organophosphates.

The search was therefore widened to include other organisations using heavy-duty engines, for example the fire and ambulance services and ferry companies using marine oils. However; those organisations which did respond used fluids of similar composition to train and bus operators, with zinc dialkyl dithiophosphate additives generally being used in place of organophosphates.

The oil manufacturers confirmed that this alternative composition was commonplace for general automotive oils. In the absence of available transport-related controls, it was therefore decided to concentrate the sampling programme on an extended range of aircraft types as noted above.

4.3.2.3 Non-transport Controls

Organophosphate esters have been added to various building materials, electric appliances, upholstery and floor polishes for their flame retardant and plasticising properties. Indoor levels are therefore typically higher than those found outside, indicating their presence in many everyday materials. Office environments were therefore recruited as non-transport-related controls to allow determination of the ambient levels of surface contamination from these potential sources.

Potential control group participants were contacted by telephone and email and were provided with information about the study. It was established whether or not organophosphate-containing lubricants were used within the company. For the office environments, the absence of additional organophosphate generating processes or fluids containing the compounds was confirmed.

4.4 FIELD SURVEY

On-site sample collection was organised and undertaken as detailed below. All sampling was undertaken over the spring and early summer period.

4.4.1 SAMPLING STRATEGY

4.4.1.1 Aircraft/Aviation Controls

Sampling was undertaken opportunistically depending on the available aircraft and vehicles at each location. Samples were taken in the flight deck and passenger cabin areas of each aircraft. The locations chosen were relatively smooth and in areas where surface contact by the crew or passengers was considered unlikely. The particle size of any aerosols generated during cabin air quality events is such that deposition is likely to occur via diffusion, i.e. based on the research by Cranfield University < 1µm. Therefore it was considered acceptable to choose vertical surfaces in preference to horizontal areas, which were thought more likely to be accessed by crew and/or passengers, for sample collection. All plane samples were taken whilst the aircraft were stationary on the apron with the majority carried out during sixty or ninety minute flight turnaround periods.

4.4.1.2 Non-Aviation Controls

As for the aircraft and other vehicle locations, the surfaces chosen for sampling in the non-aviation control office environments were relatively smooth and in areas where there was unlikely to be any disturbance by the room occupants.

4.4.2 SAMPLING METHOD

Following consultation with on-site staff, samples were collected as described below, before and after a number of flights and at agreed flight deck/cabin locations that were representative of typical surfaces. An identical process was followed for the vehicle and non-vehicle control sites. Duplicate samples for analysis by the external laboratory were taken using the same method at positions adjacent to the IOM sample.

A clear acetate template incorporating a 0.1m x 0.1m square aperture was applied to the sample site and held in place using adhesive tape. The corners of the template were marked using a graphite pencil to allow repositioning of the template during the follow-up sampling run.

Nitrile disposable gloves were donned before removing the filter from its case, with gloves being changed on completion of each stage of the sampling process to minimise the risk of sample cross-contamination.

A glass fibre filter was moistened with a small quantity of ethanol (approximately 10 drops) using a clean glass pipette dropper. The filter was then used to wipe the area within the aperture in a set pattern to ensure consistent and effective removal of any surface contamination. The filter was folded between each segment of the pattern to provide a clean collection surface. The wiping pattern consisted of one wipe clockwise round the four edges of the aperture in sequence, followed by five vertical wipes across the width of the aperture, with a final pass of ten horizontal wipes covering the vertical aspect of the aperture.

An additional sampling method was also undertaken on several sites, whereby multiple wipes were taken from the same location to determine on-site removal efficiencies from different surfaces, and so provide a comparison with those obtained in the laboratory setting. These samples were taken using an identical method to that described above.

A reference photograph of the sample location was taken using a digital camera.

The filter was then returned immediately to a numbered brown autosampler vial (4ml capacity), sealed and transported to the IOM laboratory in Edinburgh for analysis. Details of the location of each sample were noted on sample record sheets for each site to ensure traceability.

Following an agreed time period, (around 7-14 days, depending on aircraft scheduling), the sampling process was repeated at each of the original locations to collect any contamination that may have occurred in the interim period.

For quality assurance purposes, field blanks were obtained at each sampling location, with at least one field blank collected on each day of sampling. These samples were handled in an identical manner to the other samples with the exception that the surface was not wiped.

4.4.3 CONTEXTUAL INFORMATION

To assist in interpretation and reporting of the results obtained, where possible contextual information was gathered on the aircraft, their operation and flight schedules, for example engine type, number of sectors flown between samples etc. Similar information was collected for control vehicles and locations as appropriate. Enquiries were also made regarding any flight and engineering crew reports of any cockpit/cabin odours, oil/fluid leaks and general air quality issues that had occurred in the interim period.

Reference samples of the hydraulic fluids and engine oils used were collected at each site to assist in sample analysis.

4.4.4 SAMPLE ANALYSIS

A modified version of an analytical method developed by the US National Institute for Occupational Safety and Health (NIOSH, 1994) was used for the analyses of the organophosphates of interest. The analyses were carried out using a Shimadzu 2010 gas chromatograph equipped with an AOC-20i autosampler, a split/splitless injector and a Shimadzu QP2010S quadrupole mass spectrometer. A ZB-5MS capillary column was used to separate each organophosphate. The organophosphates were quantified in the single ion monitoring (SIM) mode, using the most abundant fragment for each organophosphate.

4.4.5 STATISTICAL ANALYSIS METHODS

The data were examined in detail using tables and graphs as appropriate. Statistical regression methods were used to examine associations between levels of TBP, DBPP, BDPP and TCP and type of aircraft or control site, and locations within aircraft (cockpit or rear).

The distributions of these measurements were highly skewed as is typical of exposure data of this kind, and preliminary regression analysis on the actual measurement scale showed a systematic lack of fit to the data. Regression analyses were therefore carried out on data transformed to the log scale, with negative and zero values recoded as half of the relevant limit of detection to allow their inclusion in the analyses. The use of a substitution method such as this can lead to some distortion of the distribution of values at the low end of the scale of measurement, and subsequent results from any formal statistical analyses may be less reliable. Non-parametric analyses, which do not rely on any distributional assumptions were also carried out for the key analyses (with findings very similar to those of the parametric analyses), and the results reported below encompass both sets of analyses.

Comparisons of results between laboratories were carried out using paired t-tests, and statistical regression methods.

The statistical analyses were carried out using the Minitab and Genstat statistical software packages.

5 RESULTS

5.1 SAMPLES ANALYSED BY IOM LABORATORY

5.1.1 Data

Data were available from 6 sites – 4 airports and 2 control sites; and from aircraft (5 different plane types), vehicles (2 different types) and offices (2 buildings).

A total of 86 samples were collected with measurements of four substances TBP, DBPP, BDPP and TCP. As Skydrol was used for calibration of DBPP and BDPP results, the amounts of these substances were calculated from their maximum stated concentration in bulk fluid (70% and 30% respectively). It was noted that there was potentially contamination of some samples from sites A, C and F and so statistical analyses of TCP measurements were carried out with and without these samples included.

Statistical analysis was carried out in two ways – firstly, using the first wipe of each sample and, secondly, using the total of each substance measured on all wipes taken in a particular location for those samples taken using the multiple wipe method.

On most aircraft, samples were taken on two occasions, usually two weeks apart. Additional analyses were carried out on the second set of samples only, as these represent the amount of the substance amassed over the 2-week period, whereas the first set of samples represent the amount of substance amassed over an unknown length of time prior to the study taking place.

In addition, the number of sectors flown between the two sampling periods was known for most of the planes and, for these aircraft, a further analysis was carried out on the total amount of substance per unit area amassed between sampling periods expressed as an 'amount per sector'.

The results shown below illustrate the amounts of TBP, DBPP, BDPP and TCP determined for the different aircraft types, together with data from the vehicular and building control sites.

Whilst the statistical analyses were carried out using the analytically-determined values, which may include negative numbers, the data are presented in tables and figures with reference to the following limits of detection (LOD): TBP (3.3 x10^3 ngm^{-2}); DBPP (1.4 x10^4 ngm^{-2}); BDPP (5.9 x10^3 ngm^{-2}); TCP (1.8 x10^4 ngm^{-2}).

5.1.2 Inter-aircraft and Inter-site Comparison

The 86 samples were distributed as shown in Table 2.

Table 2: Distribution of samples by site and aircraft/control type

			Aircraft			Vehicle	Building	Total
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**			
A	0	0	0	0	10	0	0	10
B	5	10	6	4	0	2	0	27
C	0	4	4	0	0	6	0	14
D	0	16	0	7	0	2	0	25
E	0	0	0	0	0	0	4	4
F	0	0	0	0	0	0	6	6
All samples	5	30	10	11	10	10	10	86

There was some evidence of correlation between the substances measured, particularly between TBP, DBPP and BDPP, and so results from these substances tend to show similar patterns. Measurements of TCP were less correlated with the other substances and tended to be low with 52 of the 86 samples (60%) either the same as or lower than the measurements from the blank media.

5.1.2.1 Mean amounts of TBP by Aircraft Type/Control Type

The average mass of TBP on the first wipe per area made for each of the 86 samples is shown in Table 3 and the distribution of TBP (on the log scale) by aircraft/control type shown in Figure 1.

Table 3: Mean Amounts of TBP (ngm^{-2}) by Site and Aircraft/Control type (standard deviation)

			Aircraft			**Vehicle**	**Building**
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	9.3 x10^{4} (8.2 x10^{4})	-	-
B	< LOD	4.9 x 10^{3} (4.5 x10$^{3)}$	2.0 x10^{4} (2.5 x10^{4}	1.1 x10^{4} (1.3x10^{4})	-	<LOD	-
C	-	4.0 x 10^{4} (6.3 x10 $^{4)}$	<LOD	-	-	7.4 x10^{4} (7.8 x10^{4})	-
D	-	1.9 x 10^{4} (2.6 x10^{4})	-	5.1 x10^{4} (5.3x10^{4})	-	2.7 x10^{4} (4.5 x10^{3})	-
E	--	-	--	-	-	-	< LOD
F	--	-	-	-	-	-	<LOD

(Limit of detection = 3.3 x10^{3} ngm^{-2})

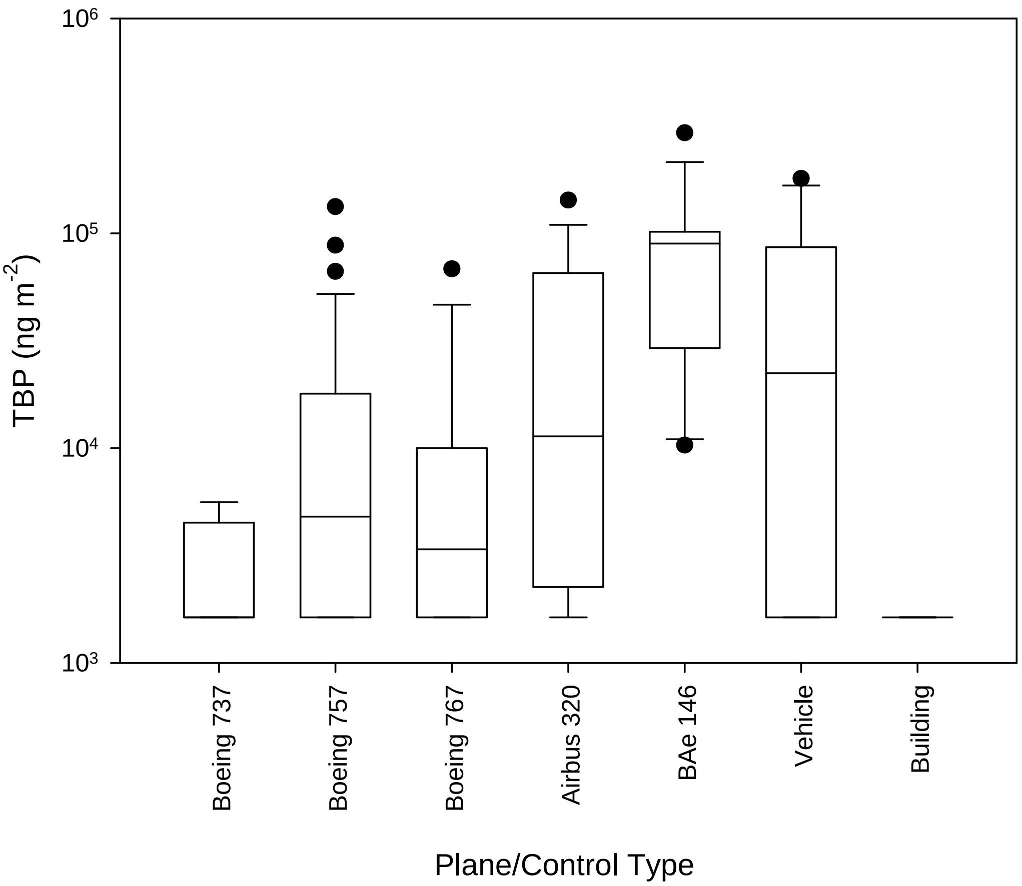

Figure 1: Distribution of TBP by aircraft/control type

It can be seen that the levels of TBP are highest for the BAe 146 plane at site A, and are low at the building control sites. Because the BAe 146 was only seen at one site and site A had only this type of plane, it is not possible to attribute this high level to the plane type or to the site.

Results of the regression analyses showed that levels among aircraft and vehicles were significantly higher than in buildings. The differences between aircraft types were statistically significant with the amounts detected on samples from the BAe 146 highest followed by levels from the Airbus 320.

5.1.2.2 Mean Amounts of DBPP and BDPP by Aircraft Type/Control Type

The results for DBPP and BDPP showed similar patterns to those for TBP (Tables 4 and 5; Figures 2 and 3). Higher levels were detected in samples taken from aircraft than in vehicles and buildings, with the difference between aircraft and buildings being statistically significant. The amounts of DBPP and BDPP detected on samples from the BAe 146 were higher than from other aircraft models.

Table 4: Mean Levels of DBPP/(ngm^{-2}) by Site and Aircraft/Control Type (standard deviation)

	Aircraft					Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	7.4 x10^5 (5.9 x10^5)	-	-
B	<LOD	<LOD	1.9 x10^4 (2.4 x10^4)	4.1 x10^4 (4.9 x10^4)	-	<LOD	-
C	-	<LOD	<LOD	-	-	1.8 x10^4 (1.1 x10^4)	-
D	-	1.9 x10^4 (2.2 x10^4)	-	1.2 x10^5 (1.2 x10^5)	-	<LOD	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection= 1.4 x10^4 ngm^{-2})

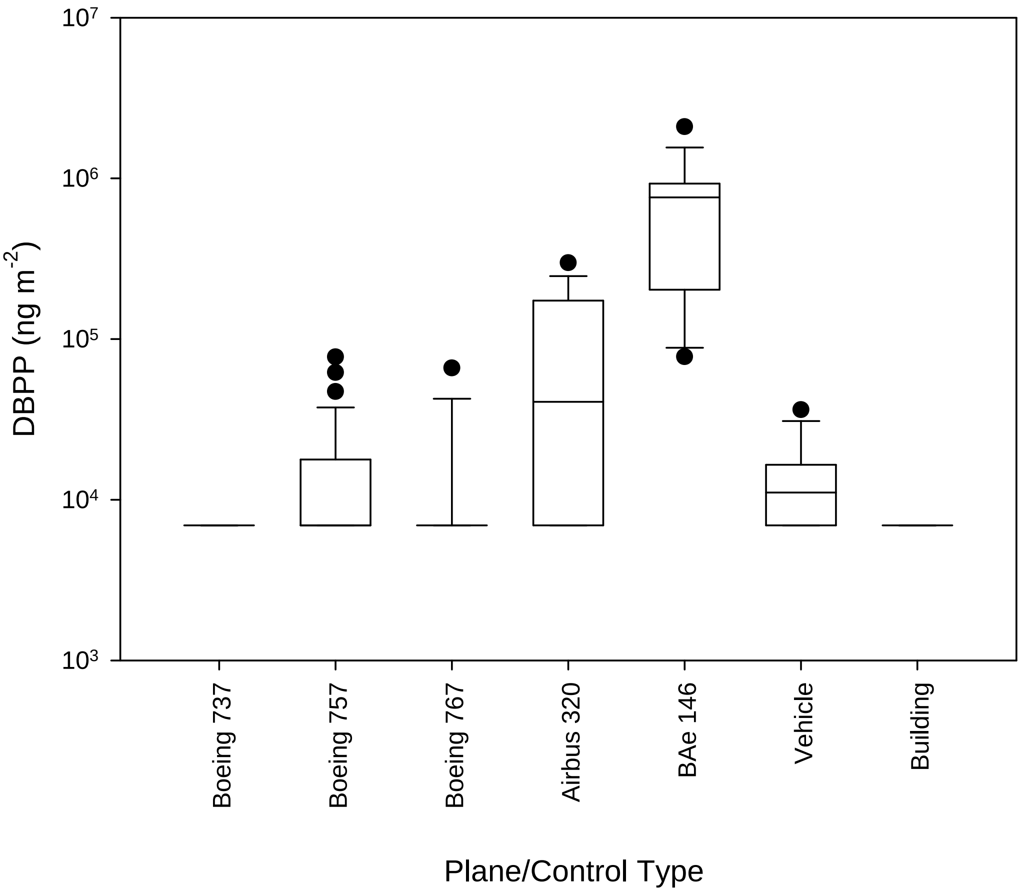

Figure 2: Distribution of DBPP by aircraft/control type

Table 5: Mean Levels of BDPP/(ngm^{-2}) by Site and Aircraft/Control Type (standard deviation)

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	1.3 x10^{5} (9.9x 10^{4})	-	-
B	8.1 x10^{3} (7.0 x10^{3})	1.0 x10^{4} (2.0 x10^{4})	1.0 x10^{4} (8.3 x10^{3})	1.9 x10^{4} (2.1 x10^{4})	-	<LOD	-
C	-	8.0 x10^{3} (6.7 x10^{3})	<LOD	-	-	2.0 x10^{4} (1.6 x10^{4})	-
D	-	2.5 x10^{4} (3.5 x10^{4})	-	6.8 x10^{4} (7.9 x10^{4})	-	7.6 x10^{3} (1.7 x10^{3})	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	6.7 x10^{3} (9.1 x10^{3})

(Limit of detection = 5.9 x10^{3} ngm^{-2})

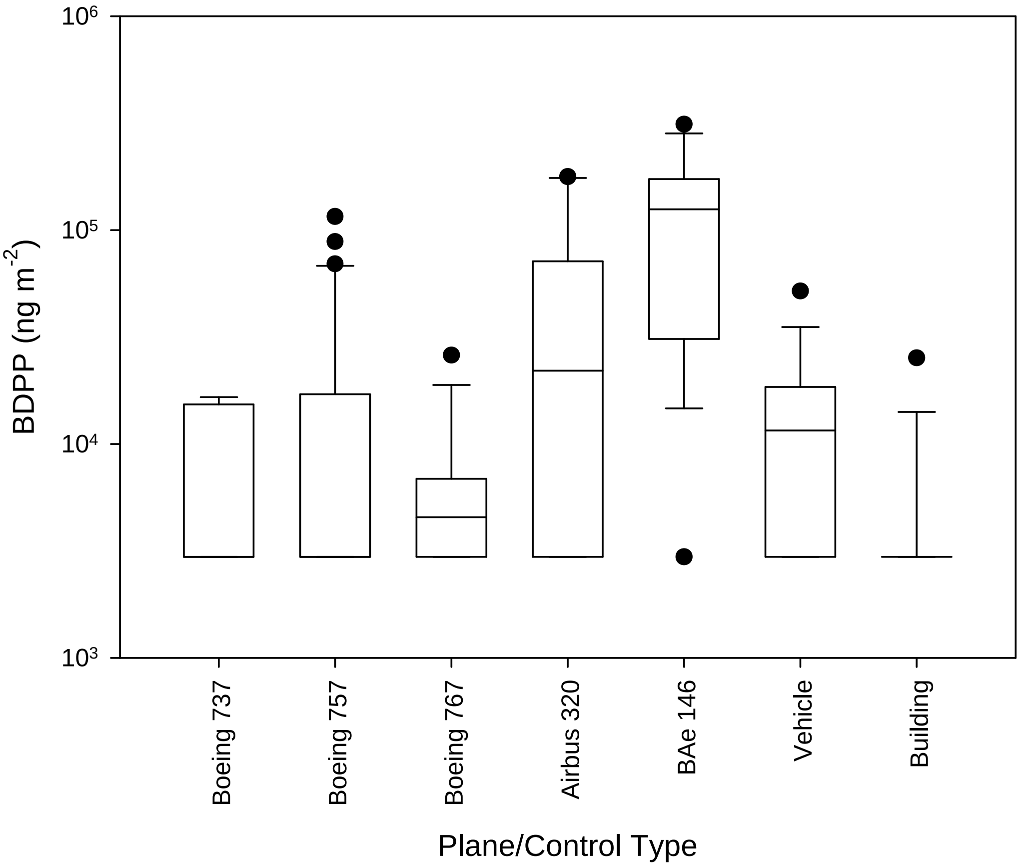

Figure 3: Distribution of BDPP by aircraft/control type

5.1.2.3 Mean Amounts of TCP by Aircraft Type/Control Type

For TCP, the amounts measured were similar in buildings and vehicles, and slightly higher in aircraft (Table 6), however the differences were not statistically significant. There was no significant difference in the amounts of TCP between different types of aircraft, though the levels in B757s were slightly higher than other airframes. When the less reliable results were excluded, there remained no significant differences between the levels of TCP detected in aircraft, vehicles and buildings, however there was evidence that levels in B757s were significantly higher than in other types of aircraft.

Table 6: Mean Levels of TCP/(ngm^{-2}) by Site and Aircraft/Control Type (standard deviation)

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	2.0 x10^{4} (3.0 x10^{4})	-	-
B	<LOD	2.3 x10^{4} (2.7 x10^{4})	<LOD	<LOD	-	<LOD	-
C	-	<LOD	<LOD	-	-	<LOD	-
D	-	3.9 x10^{4} (3.2 x10^{4})	-	<LOD	-	3.0 x10^{4} (3.0 x10^{4})	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection = 1.8 x10^{4} ngm^{-2})

5.1.3 Comparison of Different Locations within Aircraft

For all four substances, the samples taken from the passenger compartment of the Boeing and Airbus aircraft were significantly lower than in the cockpit area, though the reduction was less significant for TCP (Tables 7 to 10).

For TBP, a larger difference between the cockpit and rear was observed for the Airbus, as compared to the Boeing aircraft.

For DBPP and BDPP, there was evidence from the regression analyses that these differences were highest among Airbus followed by the Boeing 757 aircraft.

For TCP, there were no statistically significant differences between plane types, for the whole data set and with the less reliable data excluded (no measurements were available for the BAe 146 in the latter case).

For TBP, DBPP and BDPP levels in the BAe 146 were higher in the rear of the aircraft than in the cockpit.

Table 7: Mean levels of TBP/(ngm^{-2}) by location within aircraft (standard deviation)

Location			Aircraft		
	B 737	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	3.7 x10^{3} (2.0 x10^{3})	3.1 x10^{4} (3.7 x10^{4})	2.1 x10^{4} (2.8 x10^{4})	6.4 x10^{4} (4.8 x10^{4})	3.0 x10^{4} (2.8 x10^{4})
Rear	<LOD	3.8 x10^{3} (6.0 x10^{3})	3.7 x10^{3} (3.0 x10^{3})	<LOD	1.4 x10^{5} (7.9 x10^{4})
All samples	<LOD	3.8 x10^{3} (3.0 x10^{4})	1.2 x10^{4} (2.0 x10^{4})	3.6 x10^{4} (4.6 x10^{4})	9.3 x10^{4} (8.2 x10^{4})

(Limit of detection = 3.3 x10^{3} ngm^{-2})

Table 8: Mean levels of DBPP/(ngm^{-2}) (assumed concentration 70%) by location within aircraft (standard deviation)

Location			Aircraft		
	B 737	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	2.4 x10^{4} (2.1 x10^{4})	2.1 x10^{4} (2.6 x10^{4})	1.6 x10^{5} (8.8 x10^{4})	2.4 x10^{5} (2.3 x10^{5})
Rear	<LOD	<LOD	<LOD	<LOD	1.1 x10^{6} (5.1 x10^{5})
All samples	<LOD	1.5 x10^{4} (1.7 x10^{4})	1.4 x10^{4} (1.8 x10^{4})	9.3 x10^{4} (1.0 x10^{5})	7.4 x10^{5} (5.9 x10^{5})

(Limit of detection= 1.4 x10^{4} ngm^{-2})

Table 9: Mean levels of BDPP/(ngm^{-2}) (assumed concentration 30%) by location within aircraft (standard deviation)

Location			Aircraft		
	B 737	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	6.9 x10^{3} (6.9 x10^{3})	3.6 x10^{4} (3.5 x10^{4})	9.3 x10^{3} (1.0 x10^{4})	8.8 x10^{4} (7.0 x10^{4})	1.1 x10^{6} (1.1 x10^{6})
Rear	9.8 x10^{3} (9.6 x10^{3})	<LOD	<LOD	<LOD	1.4 x10^{6} (1.0 x10^{6})
All samples	8.1 x10^{3} (7.0 x10^{3})	1.8 x10^{4} (2.9 x10^{4})	7.2 x10^{3} (7.2 x10^{3})	5.0 x10^{4} (6.7 x10^{4})	1.3 x10^{6} (9.9 x10^{4})

(Limit of detection = 5.9 x10^{3} ngm^{-2})

Table 10: Mean levels of TCP/(ngm^{-2}) by location within aircraft (standard deviation)

Location			Aircraft		
	B 737	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	4.2 x10^{4} (3.5 x10^{4})	1.2 x10^{4} (7.6 x10^{3})	<LOD	3.7 x10^{4} (4.6 x10^{4})
Rear	<LOD	1.7 x10^{4} (1.5 x10^{4})	<LOD	<LOD	<LOD
All samples	<LOD	3.0 x10^{4} (3.0 x10^{5})	<LOD	<LOD	2.0 x10^{4} 3.0 x10^{4}

(Limit of detection = 1.8 x10^{4} ngm^{-2})

Table 11: Mean levels of TCP/(ngm^{-2}) by location within aircraft (standard deviation) (with contaminated/less reliable samples excluded)

Location	**Aircraft**				
	B 737	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	4.7 x10^4 (3.5 x10^4)	<LOD	<LOD	-
Rear	<LOD	1.9 x10^4 (1.6 x10^4)	<LOD	<LOD	-
All	<LOD	3.3 x10^4 (3.0 x10^4)	<LOD	<LOD	-

(Limit of detection = 1.8 x10^4 ngm^{-2})

5.1.4 Analysis of Second (“after”) Samples

When the analysis was restricted to the second set of samples only (the ‘after’/follow-up samples, i.e. those taken on the second site visit following a known time interval), for TBP, BDPP and TCP, no statistically significant differences were seen between aircraft, vehicles and buildings. For DBPP there was evidence from the non-parametric analyses of a significant difference between locations of sample, with levels in aircraft higher than those in buildings. Differences between types of aircraft were similar to those seen in the analysis of all samples for TBP, DBPP and BDPP. (Appendix 4, Tables A1 to A4).

Differences between the cockpit and rear of the aircraft varied significantly by aircraft type for TBP, DBPP and BDPP, with reduction in levels in the rear of the plane significantly greater in the Airbus planes. (Appendix 4, Tables A5 to A8).

The amounts detected of all substances were higher in the rear of the BAe 146 than in the cockpit.

5.1.5 Analysis of Total Amount for All Wipes per Sample

Analyses were also carried out on the total amount of organophosphates measured across multiple wipes, where taken. The patterns between aircraft types and location within aircraft were broadly consistent with those seen in analyses of the first wipe only. There were no observable systematic decreases in amounts determined between the first and subsequent wipes in the sequences. This differed from the laboratory removal efficiency trials, whereby there was a steady decrease over sequential wipes from the same area.

5.2 SAMPLES ANALYSED BY EXTERNAL LABORATORY

For 27 samples, analyses of each of the four substances were carried out by the IOM and an external laboratory. A comparison of the results from the two laboratories is presented here. Full information and results provided by the external laboratory are given in Appendix 3- Inter-laboratory Comparison.

The 27 samples covered 3 sites and both locations within aircraft. Thirteen samples were from the cockpit, 12 samples from the rear of the plane and 2 samples from vehicles. Ten of the duplicate samples were field blanks.

A paired t-test on the sample results showed that for all substances the results for BRE were higher than for IOM and that these differences were statistically significant for TBP and BDPP (Table 12)

Table 12: Paired t-test for comparison between IOM and BRE Laboratories

Substance	Difference/ (ug in sample)	p-value
TBP	1.48	<0.001
DBPP	0.94	0.17
BDPP	1.26	0.003
TCP	1.46	0.12

Differences between the laboratories did not differ significantly between locations (cockpit, rear of plane, vehicles) with the exception of TBP where the differences were significantly higher in the 2 samples from vehicles than in the samples taken from planes.

Results from the regression analyses of the results (on the original and on the log-scale) from the two laboratories also showed that results from BRE were higher than those for IOM, and that there was a lack of linear association between the two sets of results.

There was no difference between laboratories in the comparisons of results from ‘Blank’ samples and other samples.

6 DISCUSSION

6.1 GENERAL OBSERVATIONS

The amounts of TBP, DBPP and BDPP detected in the initial samples were on average higher than those collected on the subsequent site visit. The initial samples provided an indication of surface residues that have accumulated over time, in some cases possibly since aircraft commissioning or last refit, and will reflect all sources including, for example, engine combustion products.

Over the whole period of on-site sampling, it is estimated that around 450 flight sectors (one sector = one take off/flight/landing) were flown in total by the chosen aircraft.

During discussions with on-site staff and observation of logged aircraft maintenance and repair information, it was noted that no air quality events (fume events) had been reported in the period between the first and second set of samples. A number of events describing odours had been recorded but all of these had been traced to on-board ovens, electrical faults, lavatories or other non-engine/hydraulics' related issues.

The second (after/follow-up) set of samples taken may therefore at least partly reflect general deposition of particulate that occurs in aircraft and on-site vehicles, rather than a specific episode of contamination. The potential for ingress of particulate matter from the external airport environment has been documented by a number of researchers.

In addition, as a method of determining on-site sampling recoveries from the many different surfaces found in aircraft and other locations could not be fully developed, it is possible that some of the materials gathered in the second set of samples were residues that had not been completely been removed by the first sample.

Samples taken using the multiple wipe technique tested in some locations did not show a systematic decrease in amounts of substance measured through the sequence of first to subsequent wipes. Statistical analyses of the total amount collected over the full set of these multiple samples, i.e. all sequential wipes from a particular area, showed the same general patterns as identified during examination of the first wipe samples only.

Taking the multiple samples only, there was no longer a significant overall difference between aircraft, vehicles and buildings except for TBP.

The multiple wipe sample analyses also showed that the mean levels in the rear of the aircraft were, with the exception of the BAe 146, lower than those in the cockpit. The decrease in levels between the cockpit and passenger areas was greater in the Airbus aircraft than in the Boeing planes. The levels of all four substances were higher in the rear compartment of the BAe 146 compared with those from its cockpit. This was however an unusual aeroplane that carried a large amount of scientific equipment in the cabin.

6.2 DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS FOR THE COLLECTION AND DETERMINATION OF SURFACE RESIDUES IN AIRCRAFT

6.2.1 Development and Validation of the Wipe Sampling Method

The chosen wipe sampling method achieved satisfactory recoveries during the laboratory-based validation process. These were undertaken in a standardised manner, with a known amount of analyte in ethyl acetate solution spiked onto a glass plate, removed by wiping in a set pattern, then analysed by GC/MS as detailed previously. This is a standard approach to determining removal efficiencies as detailed in OSHA guidance for the evaluation of surface sampling methods (OSHA, 2007).

As the surfaces within aircraft cabins and vehicles vary in composition, with the majority formed from plastics or polymers, determination of sampling recoveries from non-glass surfaces was also attempted. Unfortunately, because of the aggressive nature of the ethyl acetate carrier solution used for diluting the spikes, performance of realistic sampling over a full range of plastic surfaces was very challenging, as there were obvious signs of surface damage noted during these assessments on many of the plastics trialled~~.~~

For those surfaces where the material remained intact, there was a steady decrease in the amounts collected from the area over the sequential wipes, indicating that the method was effective in removal of surface residues.

It was hoped that some quantification of on-site removal efficiencies could be determined from analysis of the data obtained from the multiple samples, however the absence of a systematic decrease in measured amounts from first to last in the series of wipes precluded such quantification.

6.2.2 Stability of Organophosphates on Surfaces

6.2.2.1 Stability on Glass Surfaces

The stability tests carried out on open impermeable watchglasses indicated that there were higher amounts of TCP remaining at 7, 14 and 21 days after application than TBP, DBPP or BDPP. This may in part be related to the comparatively lower volatility of TCP, however could also reflect the increased photodegradability of TBP compared with the other substances.

Where the spike solution was applied to a glass fibre filter on a watchglass, it was noted that the percentage recoveries at 7, 14 and 21 days were generally higher for all four substances compared with the samples where the solution had been introduced directly onto the glass itself.

This may have been caused by binding of the substances to the filter material, thus reducing the effective volatility. In addition, the presence of the filter may have reduced the amount of TBP photodegradation, again resulting in higher percentage recoveries compared with the equivalent watchglass-only samples.

6.2.2.1 Stability on Plastic Surfaces

The stability tests carried out on plastic surfaces indicated that there were differences between porous surfaces compared with impermeable finishes at intervals of 14 and 21 days following spike application.

For the more volatile compounds, as for the glassfibre filters above, the porous-surfaced plastic may be acting as a sink for the materials, reducing their effective volatility. In contrast, the recoveries for TCP at 14 and 21 days were similar for all of the plastics used.

The results suggest that the sampling method would detect any deposits from fume which had occurred during the previous 14 days, however that after 21 days, the recoverable amounts would be very low. As the initial and follow-up on-site samples were taken at a maximum of 14 days apart, it is therefore felt that the capture method was appropriate.

6.2.3 Analytical Method - Interferences

A number of researchers have noted difficulties in the determination of very low levels of organophosphates in air, dust and filter samples (Carlsson 1997; van den Eede 2011; Hartmann 2004). In these studies, interference from background levels of organophosphates detectable from the many uses of the compounds as flame retardants, plasticisers and general product additives made achieving very low limits of detection challenging. Analyses of the current study samples were complicated by the presence of identified sources of organophosphates within the general environment and IOM's laboratory environment which had the potential to cause similar difficulties. For example, during the analytical method validation process, significant levels of TCP, TBP, DBPP and BDPP were detected in marker pens used widely in many laboratories for marking on glassware, and as such additional precautions to avoid contact with the ink were required.

A number of different filter types have been used previously to collect organophosphates and oil mists in air and on surfaces, including filters made from glass fibre and other filters made from mixed cellulose esters. In this study, glass fibre filters were chosen for sampling because of their inherent sturdiness compared to cellulose ester filters, which meant that they were less likely to abrade during surface wiping. During the validation process, TBP was detected in several batches of glass fibre filters. A number of potential sources of contamination in the manufacture and supply chain for the filters were postulated, however these were outside the control of the laboratory. As the problem occurred randomly rather than systematically, it was necessary to clean all filters with ethyl acetate prior to sampling.

In the course of the analyses of the actual samples, contamination of the laboratory blank filters was found with low levels of TBP, DBPP, BDPP and TCP similar to or greater than those found in previous samples. As such, for these batches there were significant difficulties in differentiating between blank contamination and material gathered during on-site sampling. The source of the contamination could not be identified, and, as it was not systematic in nature, it could not be corrected for using data from the blank samples.

Contamination of laboratory blanks was observed for sites A, C and F only.

The contamination of samples with TCP was considered most significant, and so a decision was made to carry out separate statistical analyses excluding the TCP results from these contaminated batches of filters to identify any differences this could have made to the overall interpretation of results. When these less reliable values of TCP were excluded from the analysis, differences in amounts measured between locations in the different plane types became statistically significant, with lower levels in the rear of the plane for the Boeing 737 and 757, and higher levels in the rear for the Boeing 767 and Airbus (no measurements were available for the BAe146) compared with the cockpit. Overall, the exclusion of these samples did not result in a statistically significant difference between aircraft types, which matched the original finding for the whole data set.

It was therefore proposed that a worst case situation would be that the actual amounts of TCP and TBP sampled were identical to those in the most contaminated multiple wipe sample. This approach erred greatly on the side of caution, but allowed a theoretical calculation of a maximum airborne concentration for comparison with the literature, as outlined in Section 6.4.

6.3 DETERMINATION OF ORGANOPHOSPHATE CONTAMINANTS IN AIRCRAFT

A number of researchers have investigated airborne contaminants and surface residues in aircraft cabin environments. A summary and comparison of these previous studies with the current project findings are outlined below.

6.3.1 Tributyl Phosphate, Dibutyl Phenyl Phosphate and Butyl Diphenyl Phosphate

TBP, DBPP and BDPP are commonly found as co-constituents of aviation hydraulic fluids. The results obtained for aircraft samples in the current study showed that there was a correlation between the amounts of each of these substances determined. These compounds are therefore considered together below.

Solbu et al (2011) reported that the TBP levels detected were different in one type of aircraft depending on the location where the samples were taken. TBP concentrations in air samples taken in the cockpit were significantly higher than those in the galley area, which was attributed to the differences in proximity to the emission source and variations in the ventilation/air exchange rates between different areas.

This is consistent with the findings in the current study, where it was noted that for the Boeing and Airbus aircraft, the mean amounts of TBP detected in surface deposits were higher in the aircraft cockpits compared with the passenger areas. However, for the BAe 146 aircraft, the mean amount of TBP in the rear of the plane was higher than in the cockpit. The amounts of TBP, DBPP and BDPP detected in the BAe 146 were in general higher than those from the other plane types, and this aircraft was unusual in that it was used for scientific experiments rather than as a passenger aircraft.

Aside from deposition of surface residues during cabin air quality events which is the main focus of this project, because of the very low levels of organophosphates detected, and in the absence of an identified event taking place, it is useful to consider other factors that may have contributed to these between-sample location (i.e. cockpit or passenger area) and between-plane differences.

(i) Presence of electronic equipment

Marklund et al (2003) detected TBP in surface wipes taken from office computer covers (mean 70 ngm^{-2}) and screens (30 ngm^{-2}). Makinen (2009) also detected airborne TBP in electronics dismantling and repair facilities (<0.006-0.1 µg m^{-3}). These studies highlight the potential for detectable amounts of airborne and surface TBP to be emitted from electronic/computer sources, where the organophosphates are not chemically bound to the bulk material. Carlsson (1997) noted that more volatile organophosphates, for example TBP, are more easily released from their parent material than substances with higher boiling points.

Aircraft cockpits contain a wide range of electronic equipment, much of which is contained within plastic and polymer fasciae. It is therefore possible that there is a contribution to the TBP levels determined on the cockpit surfaces from emissions from this equipment and its casing, which would not be separable analytically from any TBP deposited from hydraulic fluids.

Within the BAe 146 samples, where the TBP levels determined in the rear of the plane (equivalent to the passenger cabin on the other airframes) were higher than in the cockpit, the presence of a large amount of scientific and analytical equipment is likely to have made a contribution to the total amount of TBP per unit area, as this was housed in similar materials to those found in computer casings, and itself contained numerous electronic components.

Solbu (2011) found that aircraft air may also contain other organophosphates (for example TiBP) from non-oil/hydraulic fluid sources. These were attributed to the commonplace use of this substance as a flame retardant and plasticiser, and the potential for related emissions into cabin air. This is in agreement with the findings of Hartmann (2004) who noted that there were a number of non-identified, interfering organophosphate peaks during MS analysis of air samples from a variety of locations.

It was not possible to validate the wipe sampling method on plastic/polymer surfaces and thus identify if substrate decomposition could contribute to the amount of non-hydraulic fluid/oil organophosphates measured. There was also therefore the potential for organophosphates contained within these materials to be dissolved and captured during sampling with the ethanol-moistened filter. Because of the wide variety of surfaces sampled, for which there was no compositional information available, this potential contribution could not be quantified in this research.

It was noted from the materials' compatibility chart from one hydraulic fluid manufacturer that many plastics and polymers are not resistant to phosphate ester fluids for example ABS, polycarbonate and polyvinyl chloride (Solutia, 2011). These materials have been shown to contain TBP and TCP (Chemtura, 2011) and may be found in aircraft fasciae. It is therefore possible that there was some dissolution of surfaces within the aircraft from contact with any surface deposits of the fluid.

(ii) Cleaning regimes

Aircraft cockpits are not cleaned routinely, with the exception of litter removal and cleaning of the captain and first officer seats. This approach is taken to minimise the obvious safety risk of ingress of water or other cleaning materials into electrical and electronic cockpit equipment.

Any surface deposits are therefore less likely to be removed from the cockpit surfaces than from the passenger areas, which are cleaned regularly. This was evident during the sampling exercise when one of the passenger cabin sample locations could not be resampled because the orientation marks had been removed by cleaners in the interim period.

It was also noted that on some aircraft, the wipe sampling left "cleaner" patches on the cockpit surfaces. This effect was not generally observed following sampling in the passenger areas, suggesting that a fine layer of surface residue was present in the cockpit. This cleaning-effect was also noted in the sampling undertaken on the airport-based vehicle controls, where similar evidence of fine surface residues in the crew cabs was observed.

A notable and consistent exception to this pattern was evident in the samples from the BAe 146 rear compartment, where because of the nature of the scientific activities carried out and equipment present, surface cleaning was not routinely done.

As indicated in the study by Van den Eede (2011) surface films containing organophosphates such as TBP can act as secondary sources releasing the substance after an initial deposit has occurred. Uncleaned surfaces within the cockpit and vehicles could therefore act as reservoirs allowing a slow release of TBP over time. A similar release of TBP from the surfaces in the rear of the BAe 146 could also occur.

(iii) Contribution to organophosphate residues from external sources

The mean amounts of TBP, DBPP and BDPP detected in the aircraft across all types were similar to those determined in the airport-apron based control vehicles. This was consistent with the findings of Solbu (2011) and van Netten (2005), which found that there was a contribution to the air within aircraft from the exhaust emissions of other aircraft taxiing and sitting at gate. Ingress of aircraft exhaust emissions is therefore also likely to occur in vehicles operating in close proximity to aircraft.

Within the current study, it was noted that, with the exception of the BAe 146, the manufacturers' safety data sheet for the hydraulic fluid used in the planes did not mention DBPP or BDPP, however both of these compounds were detected in the majority of the samples taken, and correlated with the TBP levels obtained. This is also consistent with the comparatively higher levels of TBP, DBPP and BDPP found on the BAe 146, which uses a hydraulic fluid containing all three of these substances.

This agrees with a study by Solbu (2011) who also detected DBPP, attributed to hydraulic fluids across a range of aircraft and helicopter types, including those where it was not used on the particular craft sampled. This was reported as being caused by inadvertent capture of air from other aircraft during continuous on-ground sampling runs.

The higher amounts of TBP, DBPP and BDPP compared with TCP detected across the aviation-related sample sites reflect their much greater relative concentrations within hydraulic fluids (10-80%) than the concentration of TCP ($\leq$ 3%) in aircraft engine oils.

In addition, the hydraulic systems in aircraft operate at much higher pressures (in some larger craft > 20 MPa) than engine lubricant systems and these systems are therefore perhaps more likely to leak, with an associated increase in the amounts emitted within and outside the craft. The hydraulic system is also spread throughout the aircraft, for example the brakes, flaps and landing gear, with many more potential points of leakage than the relatively contained engine section.

The potential for environmental dispersion of liquid or mists of hydraulic fluids from aircraft within airport sites is indicated by the detection of TBP in snow from runways and aircraft parking areas by Marklund et al (2005). These contaminants may therefore become airborne via disturbance by moving aircraft and vehicles, and so provide an additional source of organophosphates in air entrained into the on-board ventilation systems. Some contribution to the amounts of organophosphates detected in snow could also have come from the use of TBP-containing de-icers for aircraft and runways. No information on the prevalence of use of these materials could be found, therefore this contribution is not quantifiable.

(iv) Photodegradation of TBP

Some photodegradation of TBP was noted during the analytical and sampling method validation processes. From on-site observation, the lighting levels within the cockpits appeared to be lower than those in the passenger areas. It is therefore possible that there was some degradation of TBP within the passenger areas because of this difference in ambient light, resulting in lower levels of TBP being detected within the rear of the planes.

6.3.2 Tricresyl Phosphate

Analysis of the initial/before samples for TCP detected similar amounts in the control vehicles as for the office locations, whilst those taken from aircraft were slightly higher. There was no significant difference in TCP levels between different types of planes, for either the whole data set, or with some data excluded.

As for the other three organophosphates, the amounts of TCP measured in the rear of the planes were significantly lower than in the cockpit, though this between-area difference was less significant for TCP than TBP, DBPP or BDPP.

Statistical analysis of the TCP results for the follow-up/after samples only showed no significant difference between the planes, vehicles or buildings. This suggests that there were no deposits of TCP in the interim period between the first and second samples being taken on the aircraft, as the follow-up samples are consistent with the concentrations found in non-aircraft locations.

The detection of TCP in aircraft surface-wipe samples agrees with the findings of Solbu et al (2011), who reported that wipe sampling techniques favoured the collection of non-volatile organophosphates such as TCP, and found that there were differences in TCP levels between different types of aircraft. No ortho-isomers of TCP were detected in any of the samples taken. Solbu detected but did not quantify TCP from acetone washings of aircraft ECS heat exchangers. TCP was also detected in coalescer bags from the ECS of fighter bomber and cargo transport aircraft (Hanhela et al, 2005).

6.4 ESTIMATION OF THEORETICAL MAXIMUM AIRBORNE CONCENTRATIONS OF TRICRESYL PHOSPHATES AND TRIBUTYL PHOSPHATE FROM MEASURED SURFACE AMOUNTS

For the calculations below, it was assumed that any residues collected from surfaces had been deposited in a single fume event, when in fact they may have accumulated over time. In addition, the amounts collected may have contained a contribution from other sources of organophosphates. The amounts deposited and the associated air concentrations are therefore likely to be overestimated.

6.4.1 Tricresyl Phosphates

Sampling undertaken by Denola (2011) identified maximum concentrations of TCP of 0.26 µg m^{-3} in cockpit air within military transport aircraft during ground engine runs, when the engines were running at their highest power. Lower concentrations of TCP were detected during flight conditions (maximum 0.05 µg m^{-3}). Denola noted that the TCP sampled was in the aerosol form rather than vapour phase, which is in accordance with the findings of Solbu (2007).

It is of note that Makinen et al (2009) detected airborne TCP (<0.003 – 0.81 µg m^{-3}, mean 0.11 µg m^{-3}) in electronic equipment manufacturing and dismantling facilities, which are comparable with those found in studies aboard aircraft. This suggests that, as for other organophosphates, there is potentially a contribution to the overall amount of TCP detected in aircraft from emissions from electronic equipment.

Muir et al (2008) measured various airborne substances during a ground trial run of a Boeing 757, TBP levels were in the range 2 – 42 µg m^{-3} and TCP levels were between 0.02 – 1.3 µg m^{-}

[3]. During this pilot study by Cranfield, very high numbers of small airborne particles were measured during a contamination event observed in the course of a test flight by a Boeing 757. TCP ($\leq$ 0.04 µg m^{-3}) and TBP (2 - 8 µg m^{-3}) were detected during this episode.

In 2011, a further Cranfield University study reported mean ultrafine particle numbers across all flight sectors as being in the range 1,000-100,000 particles cm^{-3} with five instances of peak concentrations > 500,000 particles cm^{-3}. TBP, tri-ortho-cresyl phosphates (TOCP) and other TCP isomers were also measured. The study quoted mean levels of 0.07 µg m^{-3} for TOCP and 0.22 µg m^{-3} for all TCP isomers.

Denola et al (2011) did not manage to detect any ortho-isomers of TCP within aircraft air, which was assumed to be because of the very low concentrations present during the sampling runs. However; using compositional information from aircraft oils, they estimated that an airborne total TCP concentration of 5 µg m^{-3} would contain approximately 0.2 ng m^{-3} of the mono-ortho isomer.

From the particulate results obtained in the Cranfield 2011 studies, a fume event appears to generate a sub-micron oil aerosol. In these circumstances, the main mechanism of deposition onto surfaces will occur via diffusion of the aerosol.

According to Schneider et al (1999) the deposition velocity for 0.1 µm diameter aerosol is 10^{-3} m s^{-1}. If it is assumed that during a fume event the concentration of oil mist in air is 0.1 mg m^{-3} for 5 minutes then about 30 µg of oil might deposit on a 0.1m x 0.1m square surface. Van Netten and Leung (2000) and Sjögren et al (2009) reported that aircraft jet engine lubricating oils contain up to 3% TCP. Sjögren et al (2009) conservatively estimated the percentage of TOCP within the total TCP figure as 0.1-1%, suggesting that a bulk oil containing 3 % TCP would contain about 0.003-0.03 % TOCP.

It was not possible in the current study to differentiate analytically between the various isomers of TCP. Previous air monitoring and wipe sampling studies within aircraft using similar fluids and lubricants have not identified TOCP isomers (Solbu 2011; Denola 2011), and there is no reason to suspect that they are present in the samples taken within the current study.

It is helpful however, to relate the measured surface residues to potential airborne concentrations of tri-ortho and mono-ortho TCP. To determine a hypothetical worst case situation, a theoretical maximum airborne concentration of these substances for each aircraft type was calculated using the maxima of the total of the multiple wipe samples taken and assumed amounts of tri- and mono-ortho-cresyl phosphate derived from the literature on oil composition and the work by Denola (2011). The maxima were chosen as these values were considered to more closely reflect potential concentrations resulting from a potential fume event.

The calculations were carried out using the maxima taken from the whole data set, i.e. including those samples where the TCP amounts were likely to have been reported as significantly higher than the actual amount, because of blank contamination. This approach was chosen to ensure that, in the unlikely event that all of the TCP measured was in fact from surface deposits, an assessment of the associated worst case airborne concentration could be made. These maxima are shown, together with the estimated associated airborne concentrations of the different isomers of TCP in Table 13 below.

Table 13: Table of Maximum Surface Amounts of TCP/ng and associated estimated airborne concentrations/(µgm^{-3})

			Aircraft		
	B737	**B757**	**B767**	**Airbus**	**BAe 146**
Measured TCP Maxima (all wipes per sample) by Aircraft Type/ng	930	13000	4800	260	1500
Estimated Maximum airborne concentration of TCP (all isomers)/ µgm^{-3}	3.1	44	16	0.90	4.9
Estimated Maximum airborne concentration tri-ortho cresyl phosphate/µgm^{-3}	0.00004	0.0006	0.00021	0.00001	0.00007
Estimated Maximum airborne concentration mono-ortho cresyl phosphate/µgm^{-3}	0.00012	0.0018	0.00064	0.00004	0.0002

These concentrations for total TCP are in agreement with those detected in military aircraft by Hanhela et al (2005) (0.02-49 µgm^{-3}) and those found in passenger aircraft by Cranfield University (2011) (2.1- 38 µgm^{-3}). The estimation method used is therefore considered valid.

The maximum theoretical concentrations in air of tri-ortho and mono-ortho TCP were calculated using the method described earlier, and assuming isomeric airborne concentration ratios as per Denola (2011), i.e. a concentration of 5 µg m^{-3} total TCP will contain 0.0002 µg m^{-3} of the mono-ortho isomer. Denola also postulated that the airborne concentration of mono-ortho isomer at these levels was around three times that of the tri-ortho isomer.

6.4.2 Tributyl Phosphate

Similar calculations of the maximum airborne concentrations of TBP were also made for each aircraft type, as shown in Table 14 below.

Table 14: Table of measured TBP Maxima (all wipes per sample) by Aircraft Type

			Aircraft		
	B737	**B757**	**B767**	**Airbus**	**BAe 146**
Maximum value (Total for All wipes)/ng	591	6384	3390	1423	12294
Maximum airborne TBP concentration/ µgm^{-3}	2.0	22	11	4.7	41

These maximum estimated concentrations in air of TBP are in accordance with those found previously in aircraft by Muir et al (2008) (2-42 µgm^{-3}), Cranfield University (2011) (2-22 µgm^{-3}) and Solbu (2011) (0.41- 4.1 µg m^{-3}).

6.5 COMPARISON BETWEEN IOM AND EXTERNAL LABORATORY RESULTS

A statistical comparison of the results obtained from the IOM laboratory with those from the external laboratory indicated that the amounts detected by the IOM were systematically lower across all substances and locations.

In general, the external laboratory results were around 1.5 times the IOM results. At the very low levels of substances being measured, this is not considered to be significant, and would thus not cause a fundamental change to the estimated airborne concentrations calculated previously.

It is however of interest to consider the factors which could have contributed to this difference.

(i) Sampling Method

Within any sampling exercise, there is a certain amount of natural variation in the way samples are taken, the locations and the analytical methods used.

Although duplicate samples were taken as closely to the corresponding IOM sample as possible, the locations could not be identical because of the nature of the technique which required wiping of a specific area per individual sample. There may therefore be variation in the amount of surface deposits through differences in local air movements and surface textures. However, this is unlikely to cause any systematic bias.

As noted above, the sampled surface may also vary in composition, leading to differences in the type and amount of materials collected.

To minimise any between-site difference in wipe pressure during sampling, the same scientist carried out all of the samples, in addition to carrying out the majority of the laboratory validations of the wipe method. There is still likely to have been some variation in applied pressure however, on occasion because of cramped sampling locations restricting movement.

There may also have been some inadvertent collection of fresh long-term deposited material because of slight variation in re-positioning of the template during the follow-up sample runs, which would have increased the amounts collected on these filters.

(ii) Analytical Method

A different desorption method was used by each of the laboratories, with the external laboratory using a thermal desorption technique, whilst the IOM used chemical desorption. Whilst both of these techniques are appropriate, variation in the general analytical conditions, for example run times, instrument parameters and ambient temperatures could all contribute to the differences observed.

The external laboratory also noted that there were difficulties in obtaining satisfactory calibrations for the instrumentation used, because of high and inconsistent levels of TBP and low levels of BDPP in the hydraulic fluid used for calibration. This is consistent with the IOM laboratory findings and that of other researchers regarding environmental contamination of media and reagents.

7 CONCLUSIONS

7.1 DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODS FOR CAPTURING SURFACE RESIDUES IN AIRCRAFT

The methods used for collecting and analysing residues in aircraft were considered appropriate for the project, although the very low levels encountered made the sampling and analysis challenging. In any future studies the use of multiple samples from the same area may maximise sampling efficiencies from surfaces of unknown composition and texture.

There is the significant possibility of contamination of blank and site sampling media from environmental organophosphates, therefore any future studies should therefore also include additional blank testing prior to and during site work.

The evaluations of organophosphate stability on various surfaces indicated that the substances as spiked onto the plastic materials were quantifiable up to 14 days after application, although by 21 days following the initial application there was generally only a small fraction of the original material detectable.

It should be noted that the measurable amounts of organophosphates collected from the on-site samples suggested different retention behaviour on surfaces of the substances when deposited from a fine mist than through application as discrete liquid drops as in the laboratory trials. In this case the fine particles may settle into the surface texture of the plastic, and so prolong retention compared to the laboratory tests.

During the laboratory stability tests, it was not possible to replicate application of the spike samples from an aerosol.

This deposition in surface indentations could also explain the observations from multiple wipe samples, where there was no systematic decrease in amounts collected from the same surface over sequential wipes.

The surface textures and associated differences in porosities of the trial plastics observed and illustrated in Appendix 5 support these theories.

Additional study of the behaviour and stability of organophosphates on aircraft surfaces would be of use in further characterisation of residues.

7.2 DETERMINATION OF ORGANOPHOSPHATES IN SURFACE RESIDUES WITHIN AIRCRAFT

The study detected a range of organophosphates in samples of surface residues collected from a variety of airframes. The arithmetic mean data by type of aircraft ranged up to about 3×10^4 ngm^{-2} for TCP, to 10^6 for BDPP, to 7×10^5 for DBPP and to 9×10^4 for TBP.

In addition to any organophosphates deposited during previous fume events, it was noted that there may have been a contribution to the overall amount of organophosphates within a particular aircraft from flame retardants and other additives in its fasciae or electronic equipment, and from contaminated air ingress from other aircraft in the vicinity.

The amounts of all of the organophosphates detected on surfaces within aircraft and airport vehicles during the study were higher than those collected in offices. There were differences in the amounts of organophosphates detected in residues from different areas of the aircraft, with the cockpit levels in general being higher than those in the passenger areas. This can perhaps be explained by differences in ventilation mechanisms and in cleaning routines, which were typically less rigorous in the cockpit areas.

It was not possible to determine the concentration of ortho isomers of TCP analytically during the study. The theoretical concentrations of tri-ortho cresyl phosphate and mono-ortho cresyl phosphate were therefore estimated from data in the literature.

7.3 ESTIMATED AIRBORNE CONCENTRATIONS OF TRICRESYL PHOSPHATES AND TRIBUTYL PHOSPHATE DETERMINED FROM AIRCRAFT SURFACE RESIDUES

To provide a comparison with contemporary research into airborne levels of organophosphate compounds, the maximum airborne concentrations for isomers of TCP and for TBP were estimated by calculation, on the assumption that these compounds were present in aerosol form with an expected particle diameter of 0.1 µm and that they would mainly deposit by diffusion.

Using this method, the maximum estimated airborne concentrations for TBP were low, i.e. between about 10 and 40 µgm^{-3}. The estimated maximum amounts of airborne tri-ortho-cresyl phosphate (TOCP) were very low, i.e. between about 0.0001 to 0.0006 µgm^{-3}.

These estimated concentrations are in agreement with those detected in studies of cabin air quality and therefore considered to constitute a valid assessment of organophosphate contaminants.

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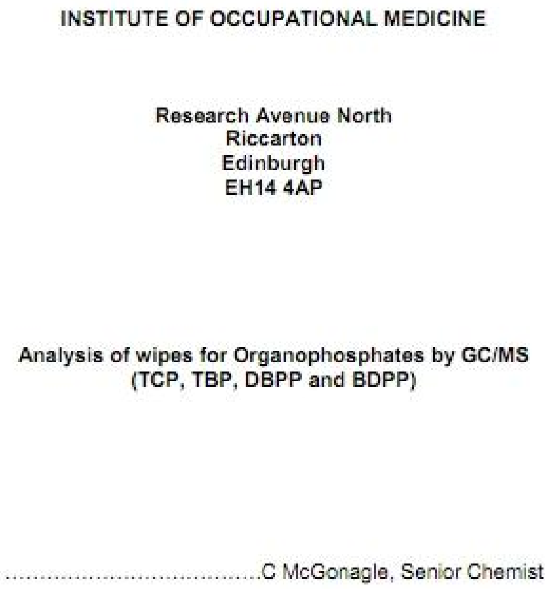
APPENDIX 1 - ANALYTICAL METHOD



INSTITUTE OF OCCUPATIONAL MEDICINE

Research Avenue North
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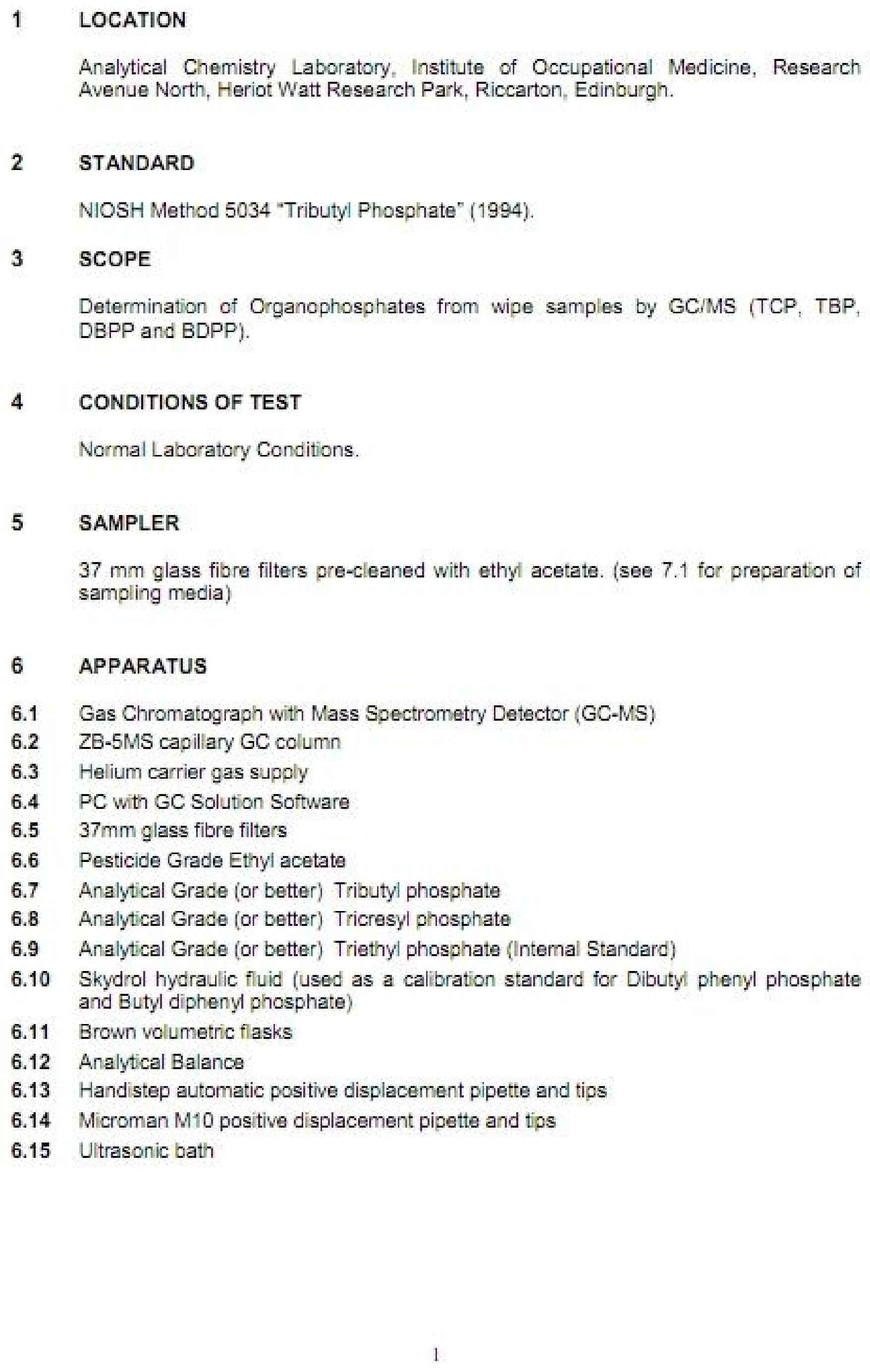
Edinburgh
EH14 4AP

Analysis of wipes for Organophosphates by GC/MS
(TCP, TBP, DBPP and BDPP)

……………………………….C McGonagle, Senior Chemist



1 LOCATION

Analytical Chemistry Laboratory, Institute of Occupational Medicine, Research Avenue North, Heriot Watt Research Park, Riccarton, Edinburgh.

2 STANDARD

NIOSH Method 5034 "Tributyl Phosphate" (1994).

3 SCOPE

Determination of Organophosphates from wipe samples by GC/MS (TCP, TBP, DBPP and BDPP).

4 CONDITIONS OF TEST

Normal Laboratory Conditions.

5 SAMPLER

37 mm glass fibre filters pre-cleaned with ethyl acetate. (see 7.1 for preparation of sampling media)

6 APPARATUS

6.1 Gas Chromatograph with Mass Spectrometry Detector (GC-MS)
6.2 ZB-5MS capillary GC column
6.3 Helium carrier gas supply
6.4 PC with GC Solution Software
6.5 37mm glass fibre filters
6.6 Pesticide Grade Ethyl acetate
6.7 Analytical Grade (or better) Tributyl phosphate
6.8 Analytical Grade (or better) Tricresyl phosphate
6.9 Analytical Grade (or better) Triethyl phosphate (Internal Standard)
6.10 Skydrol hydraulic fluid (used as a calibration standard for Dibutyl phenyl phosphate and Butyl diphenyl phosphate)
6.11 Brown volumetric flasks
6.12 Analytical Balance
6.13 Handistep automatic positive displacement pipette and tips
6.14 Microman M10 positive displacement pipette and tips
6.15 Ultrasonic bath

7 PROCEDURE

7.1 PREPARATION OF SAMPLING MEDIA

Using tweezers transfer the 37mm glass fibre filters into a beaker containing Pesticide Grade Ethyl Acetate, the beaker should be rinsed with ethyl acetate prior to use. The filters are left to stand in the ethyl acetate for approximately 1 hour then removed with tweezers and allowed to dry.

7.2 PREPARATION OF FRESH STANDARD STOCK SOLUTION

Fresh standard stock solution should be prepared for every batch of samples analysed. For TCP and TBP, weigh an appropriate amount (e.g. 0.5 g) directly into a brown glass volumetric flask (e.g. 25 mL) and make up to volume with ethyl acetate (stock solution 1). A 0.2ml aliquot of stock solution 1 is then made up to 25ml with ethyl acetate (Stock Solution 2).

Accurately weigh approximately 0.1g of Skydrol into a 100ml brown glass volumetric flask and make up to volume with ethyl acetate.

7.3 PREPARATION OF THE DESORPTION SOLUTION.

Pipette approximately 5µl of triethyl phosphate into 250 mls of ethyl acetate. Invert to mix.

7.4 PREPARATION OF WORKING STANDARDS FOR CALIBRATION

Using the Handystep automatic positive displacement pipette, transfer 1 ml of the desorption solution prepared as in 7.3 above into 1.5 ml glass vials. At least five standards should be prepared to cover the range of interest.

For TCP and TBP, using the Microman M10 positive displacement pipette add aliquots of standard Stock Solution 2 prepared as in 7.2 above to the vials containing the desorption solution. (e.g. 0.5, 1, 3, 5, 10, 20 and 40 ul).

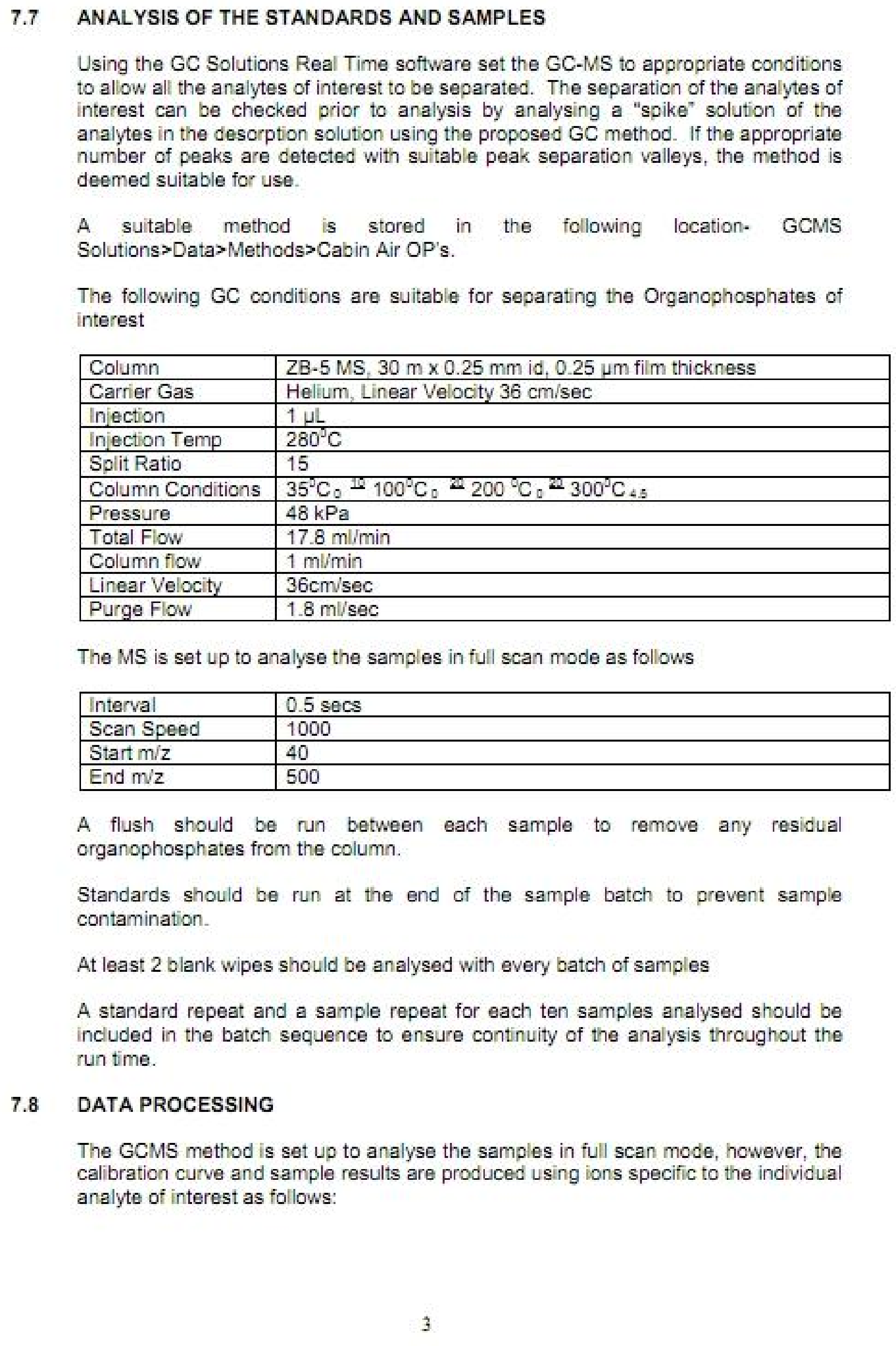
For DBPP and BDPP, using the Microman M10 positive displacement pipette add aliquots of the Skydrol standard stock solution prepared as in 7.2 above to the vials containing the desorption solution. (e.g. 1, 3, 5, 10, 20 and 40 ul).

7.5 PREPARATION OF QUALITY CONTROL SAMPLE

A QC check standard must be run with every batch of samples, containing at least 2 of the analytes of interest. The QC sample should be prepared by a separate analyst using the analytical grade solutions described in section 6.

7.6 DESORPTION OF SAMPLES

Using tweezers, place each wipe into an individual brown 4 ml glass sample vial. Using the Handystep automatic positive displacement pipette transfer 2ml of the desorption solution, prepared as in 7.3 above, to the vial containing the filter. Cap and shake the vial, allow to stand for approximately 1hr. Transfer an aliquot of the solution into a brown glass 2ml vial and cap.



7.7 ANALYSIS OF THE STANDARDS AND SAMPLES

Using the GC Solutions Real Time software set the GC-MS to appropriate conditions to allow all the analytes of interest to be separated. The separation of the analytes of interest can be checked prior to analysis by analysing a "spike" solution of the analytes in the desorption solution using the proposed GC method. If the appropriate number of peaks are detected with suitable peak separation valleys, the method is deemed suitable for use.

A suitable method is stored in the following location- GCMS Solutions>Data>Methods>Cabin Air OP's.

The following GC conditions are suitable for separating the Organophosphates of interest

Column	ZB-5 MS, 30 m x 0.25 mm id, 0.25 µm film thickness
Carrier Gas	Helium, Linear Velocity 36 cm/sec
Injection	1 µL
Injection Temp	$280^{0}C$
Split Ratio	15
Column Conditions	$35^{0}C_{0} \xrightarrow{10} 100^{0}C_{0} \xrightarrow{20} 200\ ^{0}C_{0} \xrightarrow{20} 300^{0}C_{4.5}$
Pressure	48 kPa
Total Flow	17.8 ml/min
Column flow	1 ml/min
Linear Velocity	36cm/sec
Purge Flow	1.8 ml/sec

The MS is set up to analyse the samples in full scan mode as follows

Interval	0.5 secs
Scan Speed	1000
Start m/z	40
End m/z	500

A flush should be run between each sample to remove any residual organophosphates from the column.

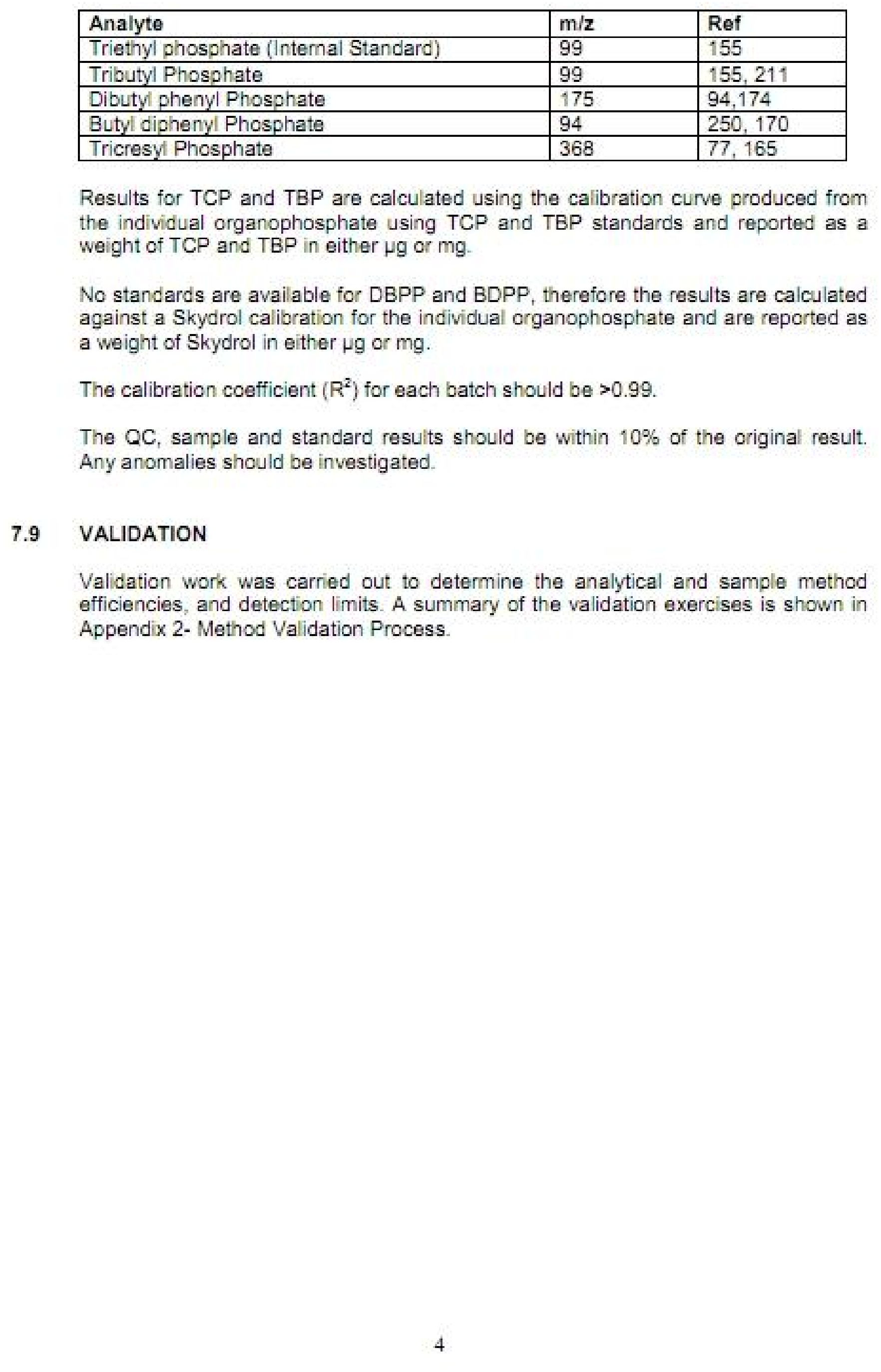
Standards should be run at the end of the sample batch to prevent sample contamination.

At least 2 blank wipes should be analysed with every batch of samples

A standard repeat and a sample repeat for each ten samples analysed should be included in the batch sequence to ensure continuity of the analysis throughout the run time.

7.8 DATA PROCESSING

The GCMS method is set up to analyse the samples in full scan mode, however, the calibration curve and sample results are produced using ions specific to the individual analyte of interest as follows:



Analyte	m/z	Ref
Triethyl phosphate (Internal Standard)	99	155
Tributyl Phosphate	99	155, 211
Dibutyl phenyl Phosphate	175	94,174
Butyl diphenyl Phosphate	94	250, 170
Tricresyl Phosphate	368	77, 165

Results for TCP and TBP are calculated using the calibration curve produced from the individual organophosphate using TCP and TBP standards and reported as a weight of TCP and TBP in either µg or mg.

No standards are available for DBPP and BDPP, therefore the results are calculated against a Skydrol calibration for the individual organophosphate and are reported as a weight of Skydrol in either µg or mg.

The calibration coefficient (R^2) for each batch should be >0.99.

The QC, sample and standard results should be within 10% of the original result. Any anomalies should be investigated.

7.9 VALIDATION

Validation work was carried out to determine the analytical and sample method efficiencies, and detection limits. A summary of the validation exercises is shown in Appendix 2- Method Validation Process.

4

APPENDIX 2 – METHOD VALIDATION PROCESS

METHOD VALIDATION PROCESS

Report prepared by: Carolyn McGonagle

Contents

1. INTRODUCTION

As part of the Cabin Air-Surface Residues project, the IOM was requested to validate an analytical method to determine the amount of organophosphates (OP's) present on cabin air surfaces. The OPs of interest were Tributyl Phosphate (TBP), Tricresyl Phosphate (TCP), Dibutyl phenyl phosphate (DBPP) and Butyl diphenyl phosphate (BDPP).

2. SCOPE

This analytical method was designed to validate a method to determine the amount of organophosphate compounds (OPs) present on wipe samples spiked with hydraulic fluids and aviation engine oil containing the OP's of interest. Preliminary work from published methods had identified that glass fibre filters would be suitable media.

The aim of the validation work was to determine the limit of detection (LOD) for the various substances, the storage stability of the OPs on glassfibre filters and the stability of OPs on a number of open surfaces, including plastics and glass.

3. ANALYTICAL PROCEDURE

After spiking, all samples were prepared and analysed using the IOM in-house method "Analysis of wipes for Organophosphates by GC/MS (TCP, TBP, DBPP and BDPP)"

Unless otherwise stated, all recovery results were determined using either Skydrol or Mobil Jet 11 hydraulic fluids as calibration standards.

4. PREPARATION OF SPIKED SAMPLES

Preparation of spiking solutions was carried out by analytical lab staff. Spiking of filters and surfaces was carried out by J Lamb.

Stock Spiking Solutions

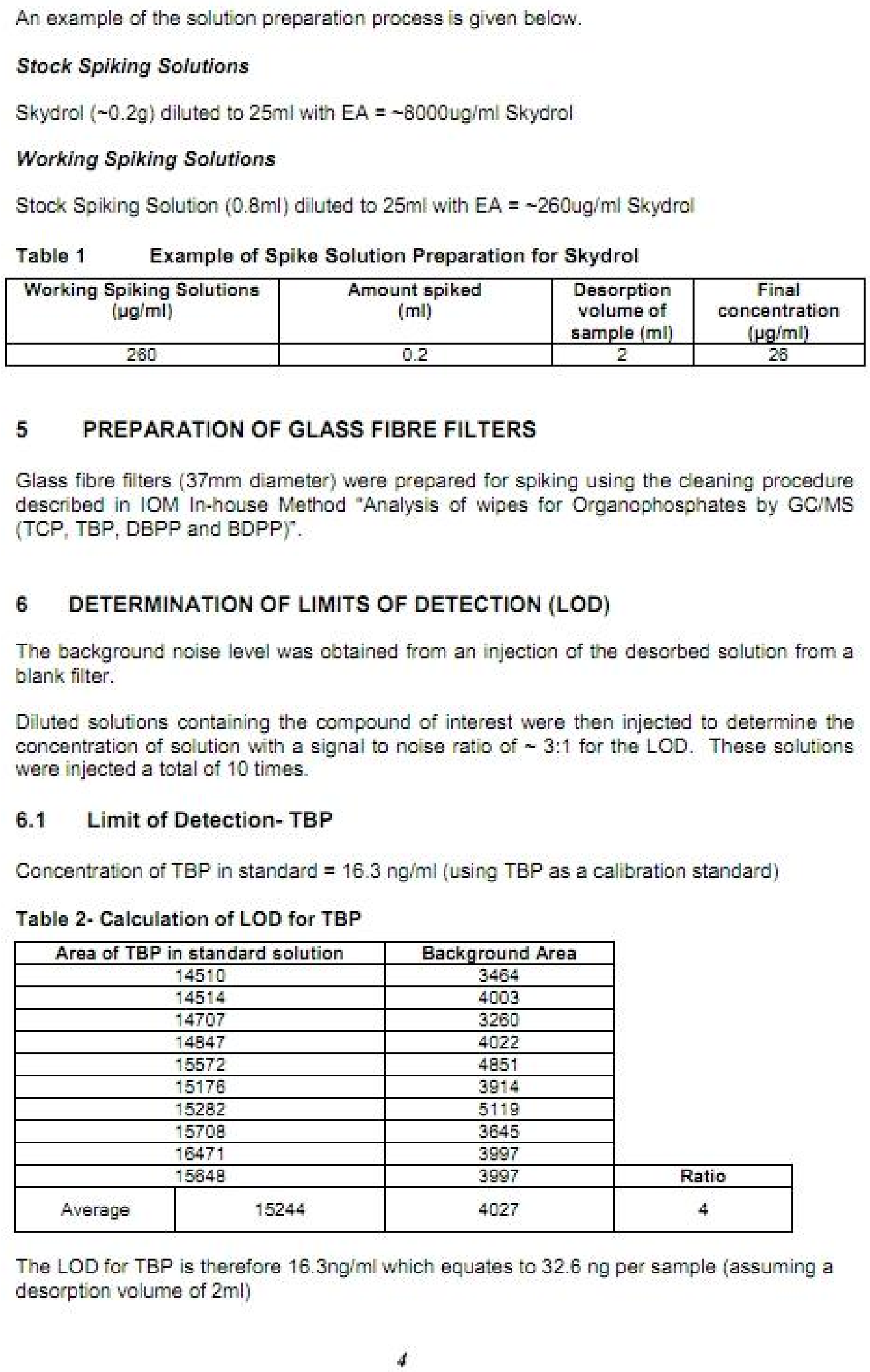
Spiking solutions were prepared for each analyte by weighing an exact amount into a volumetric flask, which was then dilutined to volume with EA.

Working Spiking Solutions

Working Spiking Solutions were prepared by transferring a known aliquot of the Working Spiking Solution into a volumetric flask and diluting to volume with EA.

Spiked Samples

Spiked samples were prepared by J Lamb by pipetting known amounts for the working spiking solution onto a variety of surfaces including glass, plastic and glass fibre filters.



An example of the solution preparation process is given below.

Stock Spiking Solutions

Skydrol (~0.2g) diluted to 25ml with EA = ~8000ug/ml Skydrol

Working Spiking Solutions

Stock Spiking Solution (0.8ml) diluted to 25ml with EA = ~260ug/ml Skydrol

Table 1 Example of Spike Solution Preparation for Skydrol

Working Spiking Solutions (µg/ml)	Amount spiked (ml)	Desorption volume of sample (ml)	Final concentration (µg/ml)
260	0.2	2	26

5 PREPARATION OF GLASS FIBRE FILTERS

Glass fibre filters (37mm diameter) were prepared for spiking using the cleaning procedure described in IOM In-house Method "Analysis of wipes for Organophosphates by GC/MS (TCP, TBP, DBPP and BDPP)".

6 DETERMINATION OF LIMITS OF DETECTION (LOD)

The background noise level was obtained from an injection of the desorbed solution from a blank filter.

Diluted solutions containing the compound of interest were then injected to determine the concentration of solution with a signal to noise ratio of ~ 3:1 for the LOD. These solutions were injected a total of 10 times.

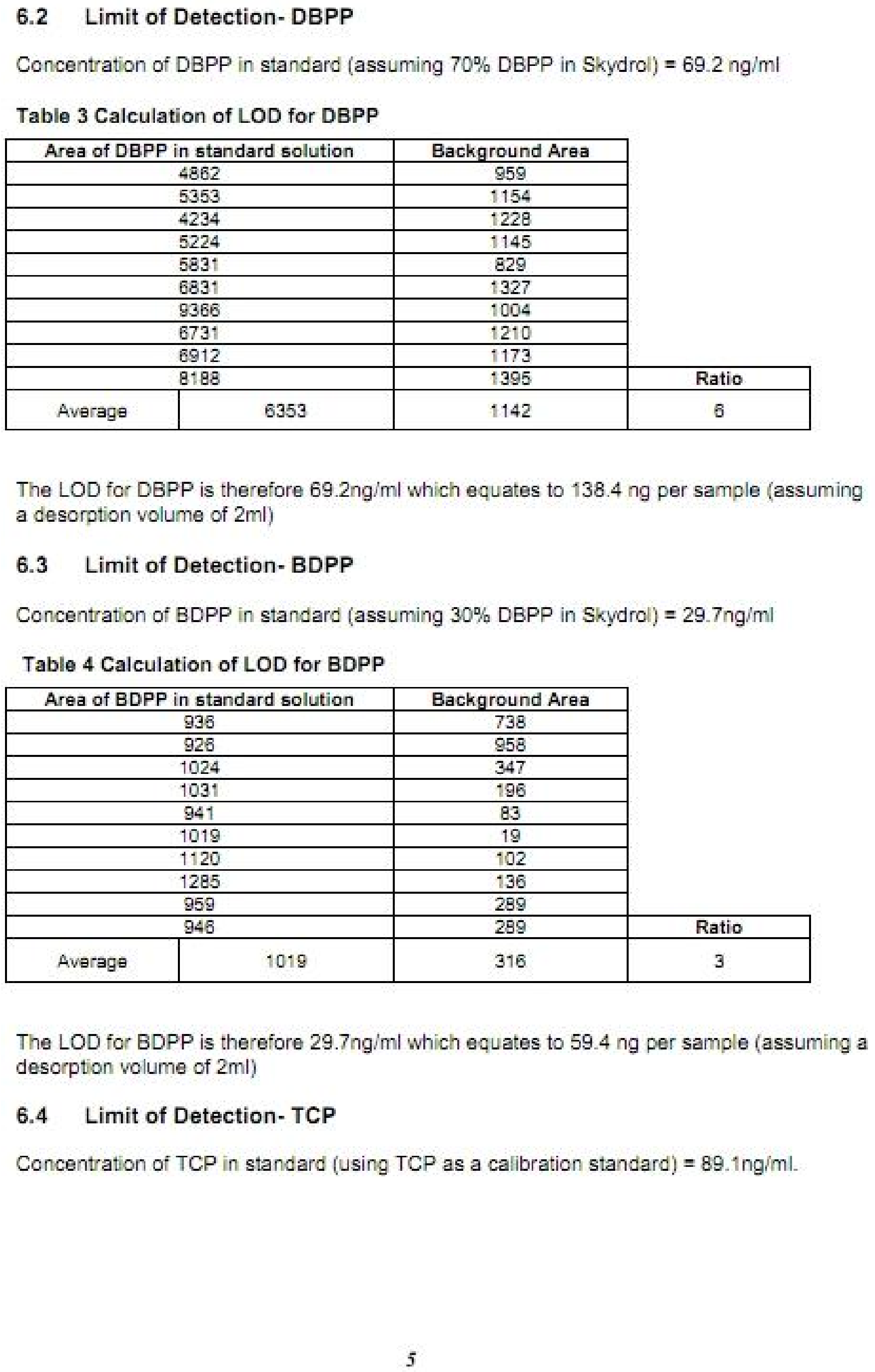
6.1 Limit of Detection- TBP

Concentration of TBP in standard = 16.3 ng/ml (using TBP as a calibration standard)

Table 2- Calculation of LOD for TBP

Area of TBP in standard solution		Background Area	
	14510	3464	
	14514	4003	
	14707	3260	
	14847	4022	
	15572	4851	
	15176	3914	
	15282	5119	
	15708	3645	
	16471	3997	
	15648	3997	Ratio
Average	15244	4027	4

The LOD for TBP is therefore 16.3ng/ml which equates to 32.6 ng per sample (assuming a desorption volume of 2ml)



6.2 Limit of Detection- DBPP

Concentration of DBPP in standard (assuming 70% DBPP in Skydrol) = 69.2 ng/ml

Table 3 Calculation of LOD for DBPP

Area of DBPP in standard solution		Background Area	
4862		959	
5353		1154	
4234		1228	
5224		1145	
5831		829	
6831		1327	
9366		1004	
6731		1210	
6912		1173	
8188		1395	**Ratio**
Average	6353	1142	6

The LOD for DBPP is therefore 69.2ng/ml which equates to 138.4 ng per sample (assuming a desorption volume of 2ml)

6.3 Limit of Detection- BDPP

Concentration of BDPP in standard (assuming 30% DBPP in Skydrol) = 29.7ng/ml

Table 4 Calculation of LOD for BDPP

Area of BDPP in standard solution		Background Area	
936		738	
926		958	
1024		347	
1031		196	
941		83	
1019		19	
1120		102	
1285		136	
959		289	
946		289	**Ratio**
Average	1019	316	3

The LOD for BDPP is therefore 29.7ng/ml which equates to 59.4 ng per sample (assuming a desorption volume of 2ml)

6.4 Limit of Detection- TCP

Concentration of TCP in standard (using TCP as a calibration standard) = 89.1ng/ml.

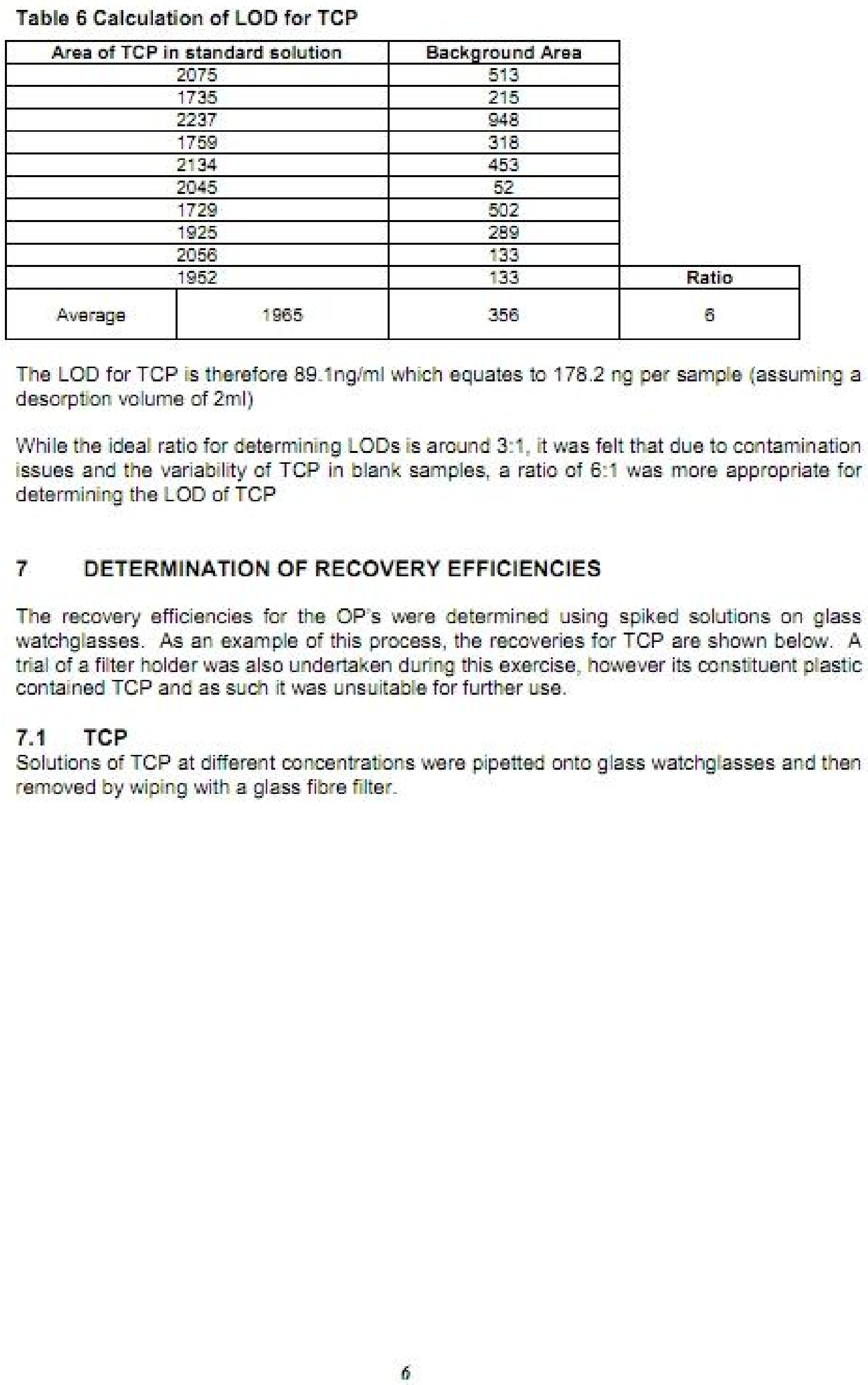


Table 6 Calculation of LOD for TCP

	Area of TCP in standard solution	Background Area	
	2075	513	
	1735	215	
	2237	948	
	1759	318	
	2134	453	
	2045	52	
	1729	502	
	1925	289	
	2056	133	
	1952	133	**Ratio**
Average	1965	356	6

The LOD for TCP is therefore 89.1ng/ml which equates to 178.2 ng per sample (assuming a desorption volume of 2ml)

While the ideal ratio for determining LODs is around 3:1, it was felt that due to contamination issues and the variability of TCP in blank samples, a ratio of 6:1 was more appropriate for determining the LOD of TCP

7 DETERMINATION OF RECOVERY EFFICIENCIES

The recovery efficiencies for the OP's were determined using spiked solutions on glass watchglasses. As an example of this process, the recoveries for TCP are shown below. A trial of a filter holder was also undertaken during this exercise, however its constituent plastic contained TCP and as such it was unsuitable for further use.

7.1 TCP

Solutions of TCP at different concentrations were pipetted onto glass watchglasses and then removed by wiping with a glass fibre filter.

Table 7 Recovery of TCP from glass

All of the recovery results shown in Table 7 were determined using TCP as a calibration standard

Spike Number	Description	TCP Recovery (%)
4VS	Vials + spike only	93.2
5VS		100.7
6VS		89.5
7VSF	Vials + spike + filters	98.8
8VSF		98.8
9VSF		90.9
1PH	wipe+hand+plate	82.0
2PH		104.4
3PH		92.8
4PFH	wipe+holder+plate	253.6*
5PFH		222.8*
6PFH		228.4*

* Contamination from holder

7.2 SAMPLE STORAGE STABILITY

To determine the potential stability of samples following collection and in subsequent transit, a number of tests of were carried out for the substances of interest on different substrates and for varying levels of containment. The results of these tests are shown below in tables 8-10 (for closed vials) and tables 11-19 (open watchglasses). The tests were carried out on Day 1 (day of preparation), then Day 15 and Day 24 following.

7.2.1 Closed Vials (Day 1)

All of the samples in Table 8 were stored in brown glass vials at room temperature for 15 days prior to analysis. Analyses of these samples were planned for the day following their preparation, however equipment malfunction necessitated the analyses being carried out on Day 15.

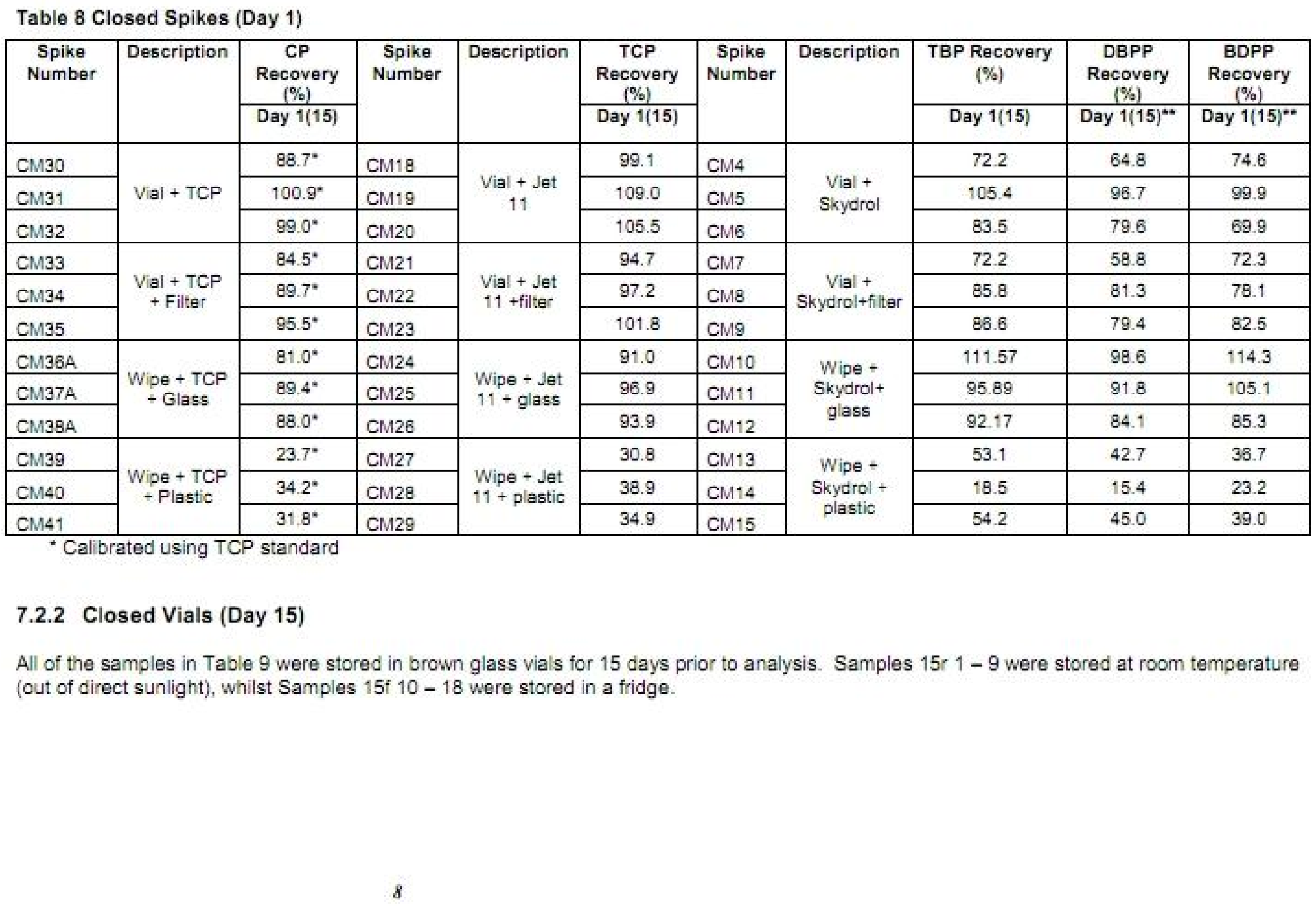


Table 8 Closed Spikes (Day 1)

Spike Number	Description	CP Recovery (%)	Spike Number	Description	TCP Recovery (%)	Spike Number	Description	TBP Recovery (%)	DBPP Recovery (%)	BDPP Recovery (%)
		Day 1(15)			Day 1(15)			Day 1(15)	Day 1(15)**	Day 1(15)**
CM30	Vial + TCP	88.7*	CM18	Vial + Jet 11	99.1	CM4	Vial + Skydrol	72.2	64.8	74.6
CM31		100.9*	CM19		109.0	CM5		105.4	96.7	99.9
CM32		99.0*	CM20		105.5	CM6		83.5	79.6	69.9
CM33	Vial + TCP + Filter	84.5*	CM21	Vial + Jet 11 +filter	94.7	CM7	Vial + Skydrol+filter	72.2	58.8	72.3
CM34		89.7*	CM22		97.2	CM8		85.8	81.3	78.1
CM35		95.5*	CM23		101.8	CM9		86.6	79.4	82.5
CM36A	Wipe + TCP + Glass	81.0*	CM24	Wipe + Jet 11 + glass	91.0	CM10	Wipe + Skydrol+ glass	111.57	98.6	114.3
CM37A		89.4*	CM25		96.9	CM11		95.89	91.8	105.1
CM38A		88.0*	CM26		93.9	CM12		92.17	84.1	85.3
CM39	Wipe + TCP + Plastic	23.7*	CM27	Wipe + Jet 11 + plastic	30.8	CM13	Wipe + Skydrol + plastic	53.1	42.7	36.7
CM40		34.2*	CM28		38.9	CM14		18.5	15.4	23.2
CM41		31.8*	CM29		34.9	CM15		54.2	45.0	39.0

* Calibrated using TCP standard

7.2.2 Closed Vials (Day 15)

All of the samples in Table 9 were stored in brown glass vials for 15 days prior to analysis. Samples 15r 1 – 9 were stored at room temperature (out of direct sunlight), whilst Samples 15f 10 – 18 were stored in a fridge.

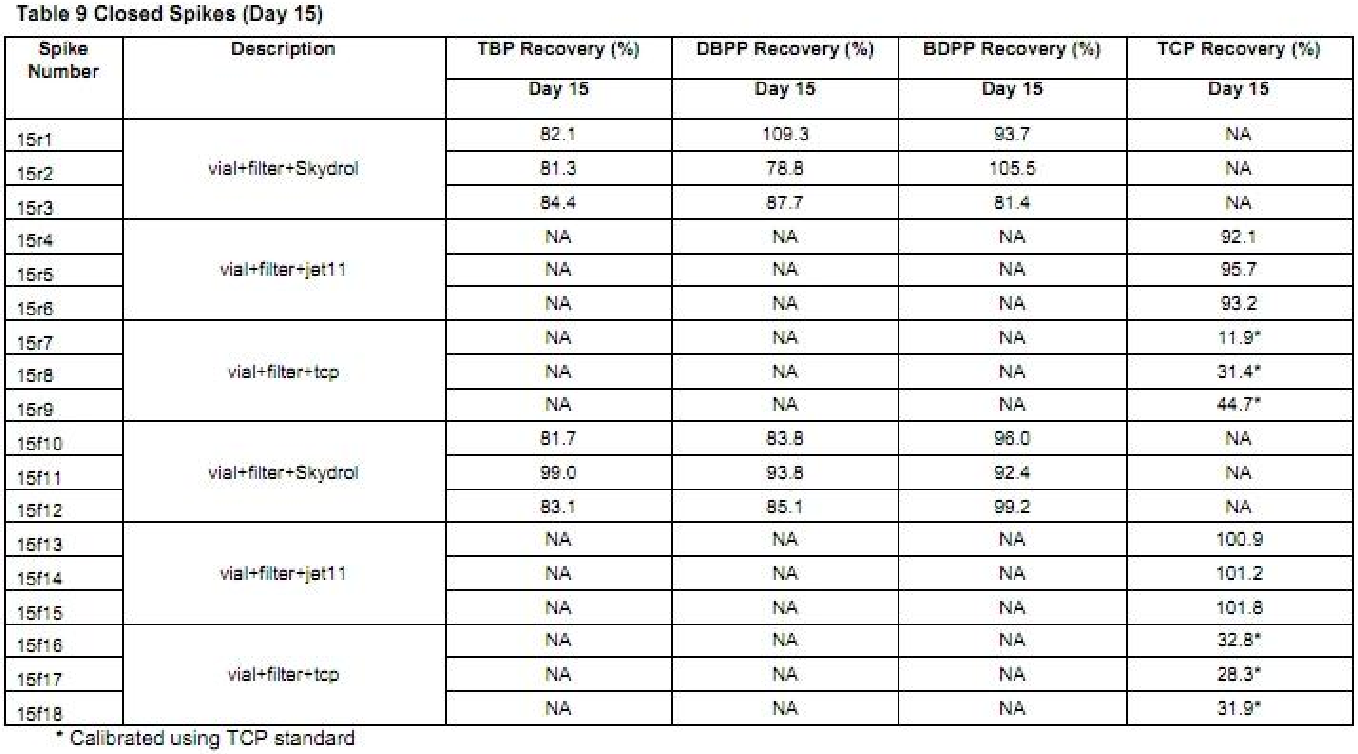


Table 9 Closed Spikes (Day 15)

Spike Number	Description	TBP Recovery (%)	DBPP Recovery (%)	BDPP Recovery (%)	TCP Recovery (%)
		Day 15	Day 15	Day 15	Day 15
15r1	vial+filter+Skydrol	82.1	109.3	93.7	NA
15r2		81.3	78.8	105.5	NA
15r3		84.4	87.7	81.4	NA
15r4	vial+filter+jet11	NA	NA	NA	92.1
15r5		NA	NA	NA	95.7
15r6		NA	NA	NA	93.2
15r7	vial+filter+tcp	NA	NA	NA	11.9*
15r8		NA	NA	NA	31.4*
15r9		NA	NA	NA	44.7*
15f10	vial+filter+Skydrol	81.7	83.8	96.0	NA
15f11		99.0	93.8	92.4	NA
15f12		83.1	85.1	99.2	NA
15f13	vial+filter+jet11	NA	NA	NA	100.9
15f14		NA	NA	NA	101.2
15f15		NA	NA	NA	101.8
15f16	vial+filter+tcp	NA	NA	NA	32.8*
15f17		NA	NA	NA	28.3*
15f18		NA	NA	NA	31.9*

* Calibrated using TCP standard

7.2.3 Closed Vials (Day 24)

All of the samples in Table 10 were stored in brown glass vials in a fridge for 24 days prior to analysis.

Table 10 Closed Spikes (Day 24)

Spike Number	Description	TBP Recovery (%)	DBPP Recovery (%)	BDPP Recovery (%)	TCP Recovery (%)
		Day 24	Day 24	Day 24	Day 24
CM237	TCP	NA	NA	NA	46.1*
CM238		NA	NA	NA	40.1*
CM239		NA	NA	NA	37.7*
CM240	Jet 11	NA	NA	NA	95.3
CM241		NA	NA	NA	84.3
CM242		NA	NA	NA	110.0
CM243	Skydrol	41.85	68.97	53.35	NA
CM244		62.53	89.96	78.59	NA
CM245		91.42	114.60	100.95	NA

* Calibrated using TCP standard

7.3 STABILITY OF ORGANOPHOSPHATES ON OPEN SURFACES

7.3.1 Sealed spikes for comparison with open samples

A number of sealed vials were prepared to allow a comparison of the theoretical maximum recoverable amount with those obtained from the samples on open watchglasses. A known amount of analyte in solution was injected directly into the vial which was then closed and stored for the relevant time period. Details of these samples are shown in Table 11.

Table 11 Sealed samples for comparison

Spike Number	Description	TBP Recovery (%)	DBPP Recovery (%)	BDPP Recovery (%)	TCP Recovery (%)
24/11/7	Mobil Jet 11 in vial	NA	NA	NA	116.1
24/11/8		NA	NA	NA	129.4
24/11/9		NA	NA	NA	196.1
24/11/10	Skydrol on in vial	102.0	127.0	96.2	NA
24/11/11		114.8	135.6	78.2	NA
24/11/12		122.8	157.6	122.6	NA
24/11/19	Mobil Jet 11 on filter in vial	NA	NA	NA	144.6
24/11/20		NA	NA	NA	173.9
24/11/21		NA	NA	NA	185.8
24/11/22	Skydrol on filter in vial	92.7	117.8	105.8	NA
24/11/23		123.4	160.1	124.3	NA
24/11/24		137.7	185.3	140.9	NA

7.3.2 Open samples (Day 1)

These samples were prepared by injecting a known amount of analyte in solution onto an open watchglass (recovered by wiping with a glass fibre filter) or onto a glassfibre filter on a watchglass. This approach allowed a comparison of the stability of the solution on an impermeable glass surface with that on a porous matrix surface (the glassfibre filter). The samples were then analysed on that day (Batch 1) or after 12 hours (Batch 2).

7.3.2.1 TBP Recovery

Table 12a Open samples – TBP Recovery (Batch 1)

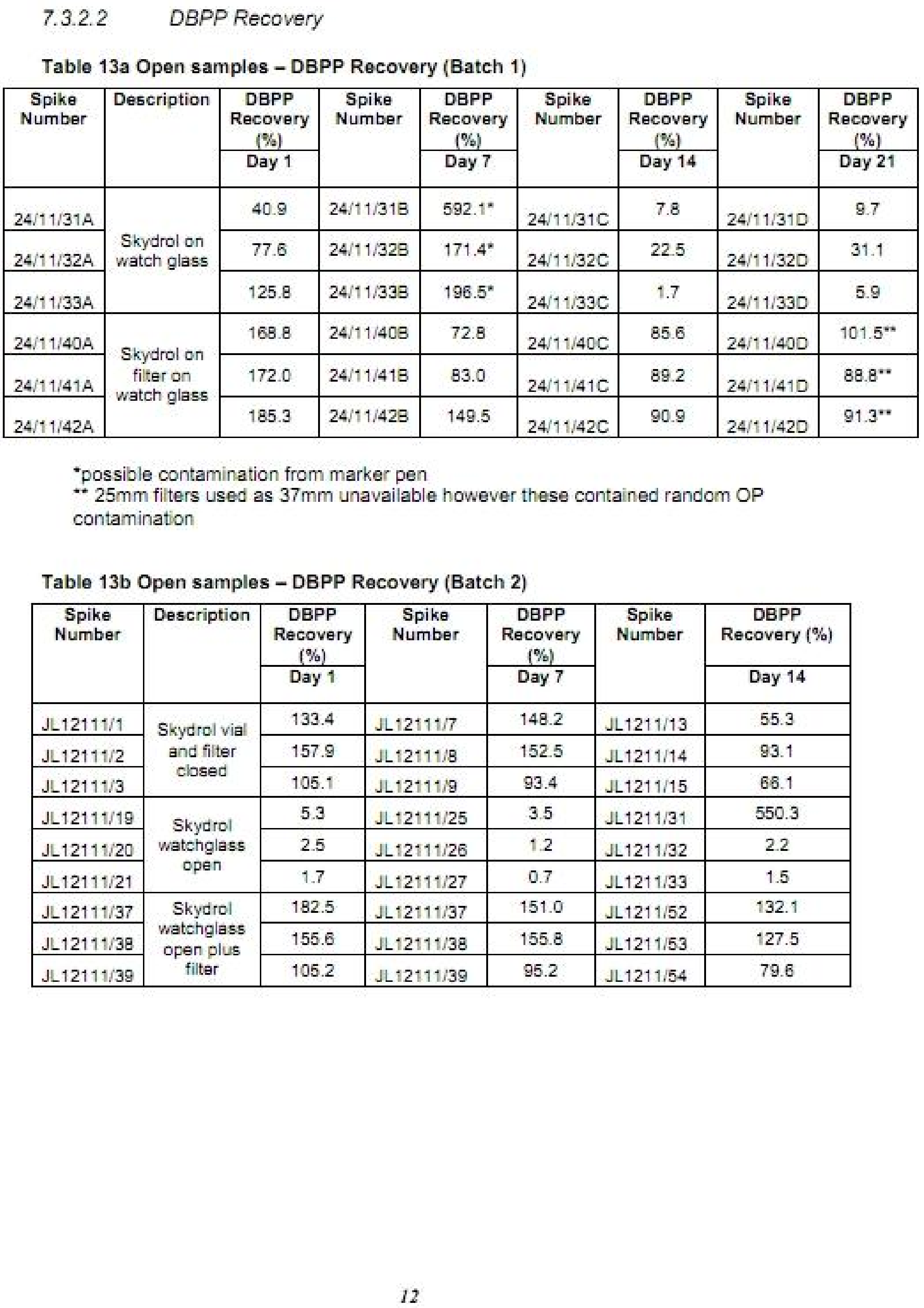
Spike Number	Description	TBP Recovery (%)	Spike Number	TBP Recovery (%)	Spike Number	TBP Recovery (%)	Spike Number	TBP Recovery (%)
		Day 1		Day 7		Day 14		Day 21
24/11/31A	Skydrol on watch glass	118.4	24/11/31B	689.4*	24/11/31C	28.3	24/11/31D	2.8
24/11/32A		108.5	24/11/32B	209.3*	24/11/32C	27.4	24/11/32D	1.5
24/11/33A		50.5	24/11/33B	253.7*	24/11/33C	2.9	24/11/33D	2.4
24/11/40A	Skydrol on filter on watch glass	144.3	24/11/40B	107.1	24/11/40C	131.1	24/11/40D	300.2**
24/11/41A		136.4	24/11/41B	106.2	24/11/41C	146.2	24/11/41D	196.9**
24/11/42A		137.7	24/11/42B	157.4	24/11/42C	94.1	24/11/42D	150.9**

*possible contamination from marker pen

** 25mm filters used as 37mm unavailable however these contained random OP contamination

Table 12b Open samples – TBP Recovery (Batch 2)

Spike Number	Description	TBP Recovery (%)	Spike Number	TBP Recovery (%)	Spike Number	TBP Recovery (%)
		Day 1		Day 7		Day 14
JL12111/1	Skydrol vial and filter closed	112.3	JL12111/7	125.4	JL1211/13	61.7
JL12111/2		122.8	JL12111/8	130.7	JL1211/14	91.4
JL12111/3		86.2	JL12111/9	86.4	JL1211/15	65.8
JL12111/19	Skydrol watchglass open	<1.0	JL12111/25	<1.0	JL1211/31	<1.0
JL12111/20		<1.0	JL12111/26	<1.0	JL1211/32	<1.0
JL12111/21		<1.0	JL12111/27	<1.0	JL1211/33	<1.0
JL12111/37	Skydrol watchglass open plus filter	162.3	JL12111/37	144.4	JL1211/52	152.6
JL12111/38		147.7	JL12111/38	151.5	JL1211/53	144.3
JL12111/39		98.2	JL12111/39	91.1	JL1211/54	90.5



7.3.2.2 DBPP Recovery

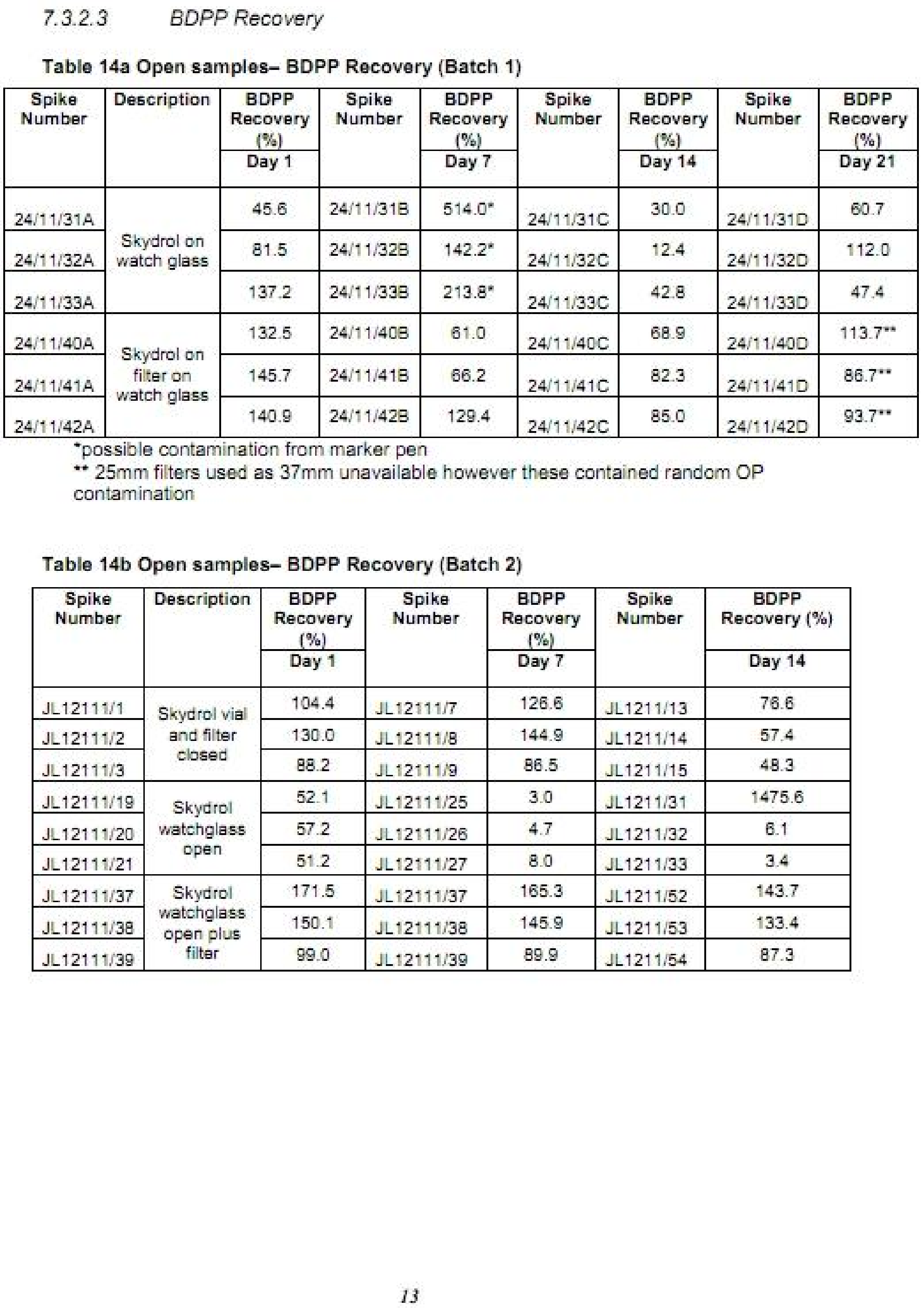
Table 13a Open samples – DBPP Recovery (Batch 1)

Spike Number	Description	DBPP Recovery (%)	Spike Number	DBPP Recovery (%)	Spike Number	DBPP Recovery (%)	Spike Number	DBPP Recovery (%)
		Day 1		Day 7		Day 14		Day 21
24/11/31A	Skydrol on watch glass	40.9	24/11/31B	592.1*	24/11/31C	7.8	24/11/31D	9.7
24/11/32A		77.6	24/11/32B	171.4*	24/11/32C	22.5	24/11/32D	31.1
24/11/33A		125.8	24/11/33B	196.5*	24/11/33C	1.7	24/11/33D	5.9
24/11/40A	Skydrol on filter on watch glass	168.8	24/11/40B	72.8	24/11/40C	85.6	24/11/40D	101.5**
24/11/41A		172.0	24/11/41B	83.0	24/11/41C	89.2	24/11/41D	88.8**
24/11/42A		185.3	24/11/42B	149.5	24/11/42C	90.9	24/11/42D	91.3**

*possible contamination from marker pen
** 25mm filters used as 37mm unavailable however these contained random OP contamination

Table 13b Open samples – DBPP Recovery (Batch 2)

Spike Number	Description	DBPP Recovery (%)	Spike Number	DBPP Recovery (%)	Spike Number	DBPP Recovery (%)
		Day 1		Day 7		Day 14
JL12111/1	Skydrol vial and filter closed	133.4	JL12111/7	148.2	JL1211/13	55.3
JL12111/2		157.9	JL12111/8	152.5	JL1211/14	93.1
JL12111/3		105.1	JL12111/9	93.4	JL1211/15	66.1
JL12111/19	Skydrol watchglass open	5.3	JL12111/25	3.5	JL1211/31	550.3
JL12111/20		2.5	JL12111/26	1.2	JL1211/32	2.2
JL12111/21		1.7	JL12111/27	0.7	JL1211/33	1.5
JL12111/37	Skydrol watchglass open plus filter	182.5	JL12111/37	151.0	JL1211/52	132.1
JL12111/38		155.6	JL12111/38	155.8	JL1211/53	127.5
JL12111/39		105.2	JL12111/39	95.2	JL1211/54	79.6



7.3.2.3 BDPP Recovery

Table 14a Open samples– BDPP Recovery (Batch 1)

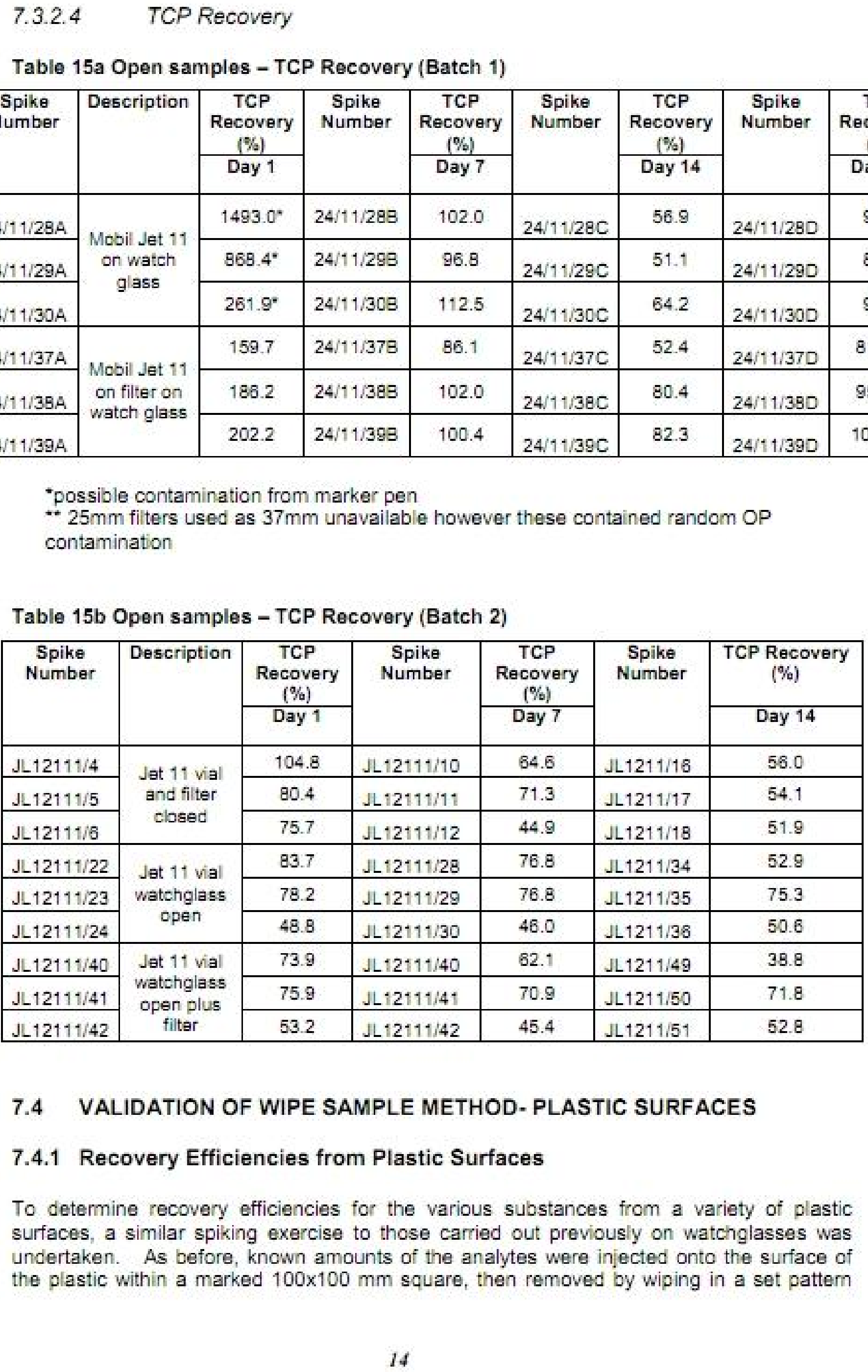
Spike Number	Description	BDPP Recovery (%)	Spike Number	BDPP Recovery (%)	Spike Number	BDPP Recovery (%)	Spike Number	BDPP Recovery (%)
		Day 1		Day 7		Day 14		Day 21
24/11/31A	Skydrol on watch glass	45.6	24/11/31B	514.0*	24/11/31C	30.0	24/11/31D	60.7
24/11/32A		81.5	24/11/32B	142.2*	24/11/32C	12.4	24/11/32D	112.0
24/11/33A		137.2	24/11/33B	213.8*	24/11/33C	42.8	24/11/33D	47.4
24/11/40A	Skydrol on filter on watch glass	132.5	24/11/40B	61.0	24/11/40C	68.9	24/11/40D	113.7**
24/11/41A		145.7	24/11/41B	66.2	24/11/41C	82.3	24/11/41D	86.7**
24/11/42A		140.9	24/11/42B	129.4	24/11/42C	85.0	24/11/42D	93.7**

*possible contamination from marker pen

** 25mm filters used as 37mm unavailable however these contained random OP contamination

Table 14b Open samples– BDPP Recovery (Batch 2)

Spike Number	Description	BDPP Recovery (%)	Spike Number	BDPP Recovery (%)	Spike Number	BDPP Recovery (%)
		Day 1		Day 7		Day 14
JL12111/1	Skydrol vial and filter closed	104.4	JL12111/7	126.6	JL1211/13	76.6
JL12111/2		130.0	JL12111/8	144.9	JL1211/14	57.4
JL12111/3		88.2	JL12111/9	86.5	JL1211/15	48.3
JL12111/19	Skydrol watchglass open	52.1	JL12111/25	3.0	JL1211/31	1475.6
JL12111/20		57.2	JL12111/26	4.7	JL1211/32	6.1
JL12111/21		51.2	JL12111/27	8.0	JL1211/33	3.4
JL12111/37	Skydrol watchglass open plus filter	171.5	JL12111/37	165.3	JL1211/52	143.7
JL12111/38		150.1	JL12111/38	145.9	JL1211/53	133.4
JL12111/39		99.0	JL12111/39	89.9	JL1211/54	87.3



7.3.2.4 *TCP Recovery*

Table 15a Open samples – TCP Recovery (Batch 1)

Spike Number	Description	TCP Recovery (%)	Spike Number	TCP Recovery (%)	Spike Number	TCP Recovery (%)	Spike Number	TCP Recovery (%)
		Day 1		Day 7		Day 14		Day 21
24/11/28A	Mobil Jet 11 on watch glass	1493.0*	24/11/28B	102.0	24/11/28C	56.9	24/11/28D	90.8
24/11/29A		868.4*	24/11/29B	96.8	24/11/29C	51.1	24/11/29D	83.4
24/11/30A		261.9*	24/11/30B	112.5	24/11/30C	64.2	24/11/30D	90.0
24/11/37A	Mobil Jet 11 on filter on watch glass	159.7	24/11/37B	86.1	24/11/37C	52.4	24/11/37D	81.9**
24/11/38A		186.2	24/11/38B	102.0	24/11/38C	80.4	24/11/38D	95.9**
24/11/39A		202.2	24/11/39B	100.4	24/11/39C	82.3	24/11/39D	105.4**

*possible contamination from marker pen
** 25mm filters used as 37mm unavailable however these contained random OP contamination

Table 15b Open samples – TCP Recovery (Batch 2)

Spike Number	Description	TCP Recovery (%)	Spike Number	TCP Recovery (%)	Spike Number	TCP Recovery (%)
		Day 1		Day 7		Day 14
JL12111/4	Jet 11 vial and filter closed	104.8	JL12111/10	64.6	JL1211/16	56.0
JL12111/5		80.4	JL12111/11	71.3	JL1211/17	54.1
JL12111/6		75.7	JL12111/12	44.9	JL1211/18	51.9
JL12111/22	Jet 11 vial watchglass open	83.7	JL12111/28	76.8	JL1211/34	52.9
JL12111/23		78.2	JL12111/29	76.8	JL1211/35	75.3
JL12111/24		48.8	JL12111/30	46.0	JL1211/36	50.6
JL12111/40	Jet 11 vial watchglass open plus filter	73.9	JL12111/40	62.1	JL1211/49	38.8
JL12111/41		75.9	JL12111/41	70.9	JL1211/50	71.8
JL12111/42		53.2	JL12111/42	45.4	JL1211/51	52.8

7.4 VALIDATION OF WIPE SAMPLE METHOD- PLASTIC SURFACES

7.4.1 Recovery Efficiencies from Plastic Surfaces

To determine recovery efficiencies for the various substances from a variety of plastic surfaces, a similar spiking exercise to those carried out previously on watchglasses was undertaken. As before, known amounts of the analytes were injected onto the surface of the plastic within a marked 100x100 mm square, then removed by wiping in a set pattern

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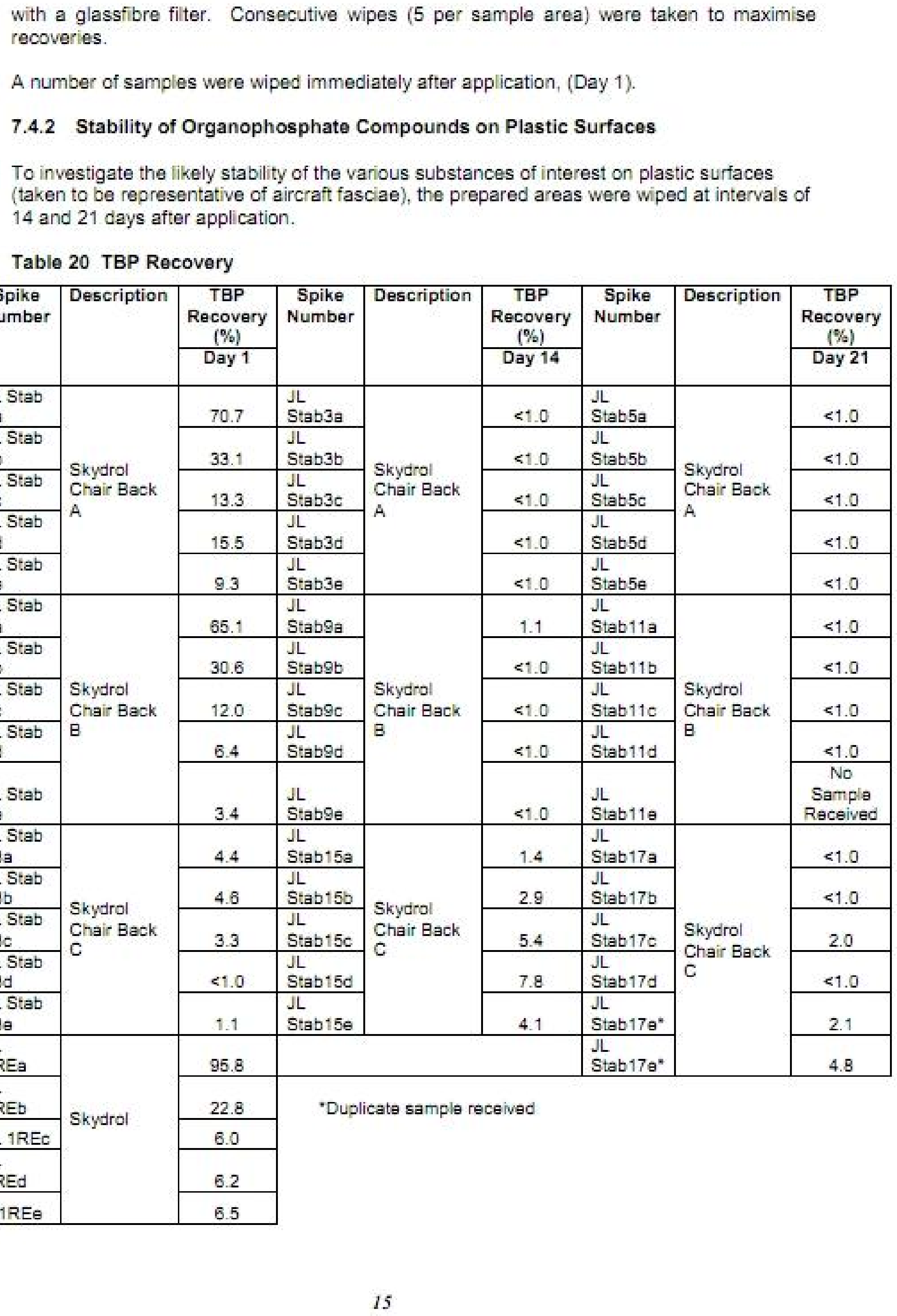

with a glassfibre filter. Consecutive wipes (5 per sample area) were taken to maximise recoveries.

A number of samples were wiped immediately after application, (Day 1).

7.4.2 Stability of Organophosphate Compounds on Plastic Surfaces

To investigate the likely stability of the various substances of interest on plastic surfaces (taken to be representative of aircraft fasciae), the prepared areas were wiped at intervals of 14 and 21 days after application.

Table 20 TBP Recovery

Spike Number	Description	TBP Recovery (%)	Spike Number	Description	TBP Recovery (%)	Spike Number	Description	TBP Recovery (%)
		Day 1			Day 14			Day 21
JL Stab 1a	Skydrol Chair Back A	70.7	JL Stab3a	Skydrol Chair Back A	<1.0	JL Stab5a	Skydrol Chair Back A	<1.0
JL Stab 1b		33.1	JL Stab3b		<1.0	JL Stab5b		<1.0
JL Stab 1c		13.3	JL Stab3c		<1.0	JL Stab5c		<1.0
JL Stab 1d		15.5	JL Stab3d		<1.0	JL Stab5d		<1.0
JL Stab 1e		9.3	JL Stab3e		<1.0	JL Stab5e		<1.0
JL Stab 7a	Skydrol Chair Back B	65.1	JL Stab9a	Skydrol Chair Back B	1.1	JL Stab11a	Skydrol Chair Back B	<1.0
JL Stab 7b		30.6	JL Stab9b		<1.0	JL Stab11b		<1.0
JL Stab 7c		12.0	JL Stab9c		<1.0	JL Stab11c		<1.0
JL Stab 7d		6.4	JL Stab9d		<1.0	JL Stab11d		<1.0
JL Stab 7e		3.4	JL Stab9e		<1.0	JL Stab11e		No Sample Received
JL Stab 13a	Skydrol Chair Back C	4.4	JL Stab15a	Skydrol Chair Back C	1.4	JL Stab17a	Skydrol Chair Back C	<1.0
JL Stab 13b		4.6	JL Stab15b		2.9	JL Stab17b		<1.0
JL Stab 13c		3.3	JL Stab15c		5.4	JL Stab17c		2.0
JL Stab 13d		<1.0	JL Stab15d		7.8	JL Stab17d		<1.0
JL Stab 13e		1.1	JL Stab15e		4.1	JL Stab17e*		2.1
JL 1REa	Skydrol	95.8				JL Stab17e*		4.8
JL 1REb		22.8						
JL 1REc		6.0						
JL 1REd		6.2						
L 1REe		6.5						

*Duplicate sample received

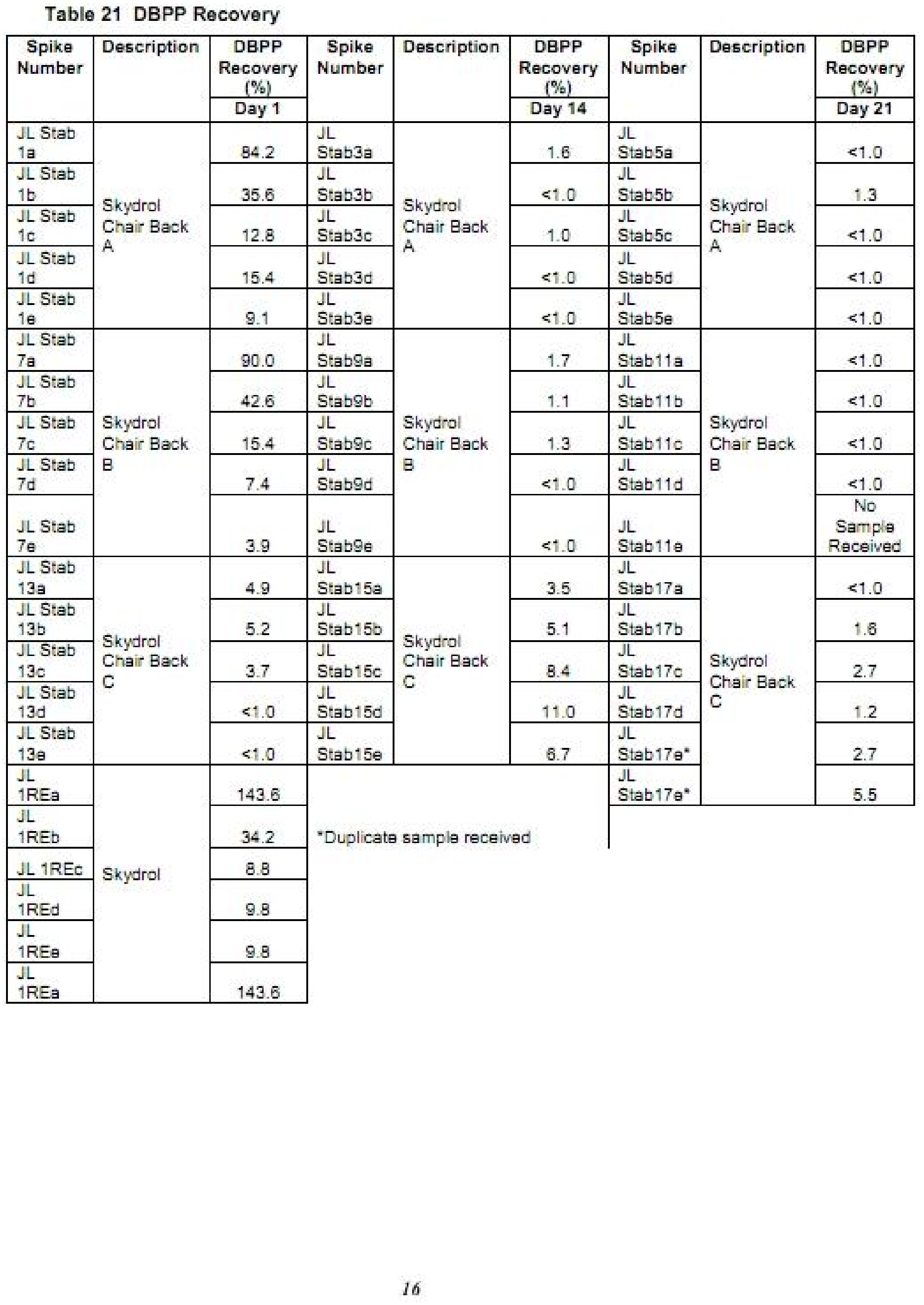

Table 21 DBPP Recovery

Spike Number	Description	DBPP Recovery (%)	Spike Number	Description	DBPP Recovery (%)	Spike Number	Description	DBPP Recovery (%)
		Day 1			Day 14			Day 21
JL Stab 1a	Skydrol Chair Back A	84.2	JL Stab3a	Skydrol Chair Back A	1.6	JL Stab5a	Skydrol Chair Back A	<1.0
JL Stab 1b		35.6	JL Stab3b		<1.0	JL Stab5b		1.3
JL Stab 1c		12.8	JL Stab3c		1.0	JL Stab5c		<1.0
JL Stab 1d		15.4	JL Stab3d		<1.0	JL Stab5d		<1.0
JL Stab 1e		9.1	JL Stab3e		<1.0	JL Stab5e		<1.0
JL Stab 7a	Skydrol Chair Back B	90.0	JL Stab9a	Skydrol Chair Back B	1.7	JL Stab11a	Skydrol Chair Back B	<1.0
JL Stab 7b		42.6	JL Stab9b		1.1	JL Stab11b		<1.0
JL Stab 7c		15.4	JL Stab9c		1.3	JL Stab11c		<1.0
JL Stab 7d		7.4	JL Stab9d		<1.0	JL Stab11d		<1.0
JL Stab 7e		3.9	JL Stab9e		<1.0	JL Stab11e		No Sample Received
JL Stab 13a	Skydrol Chair Back C	4.9	JL Stab15a	Skydrol Chair Back C	3.5	JL Stab17a	Skydrol Chair Back C	<1.0
JL Stab 13b		5.2	JL Stab15b		5.1	JL Stab17b		1.6
JL Stab 13c		3.7	JL Stab15c		8.4	JL Stab17c		2.7
JL Stab 13d		<1.0	JL Stab15d		11.0	JL Stab17d		1.2
JL Stab 13e		<1.0	JL Stab15e		6.7	JL Stab17e*		2.7
JL 1REa	Skydrol	143.6				JL Stab17e*		5.5
JL 1REb		34.2						
JL 1REc		8.8						
JL 1REd		9.8						
JL 1REe		9.8						
JL 1REa		143.6						

*Duplicate sample received

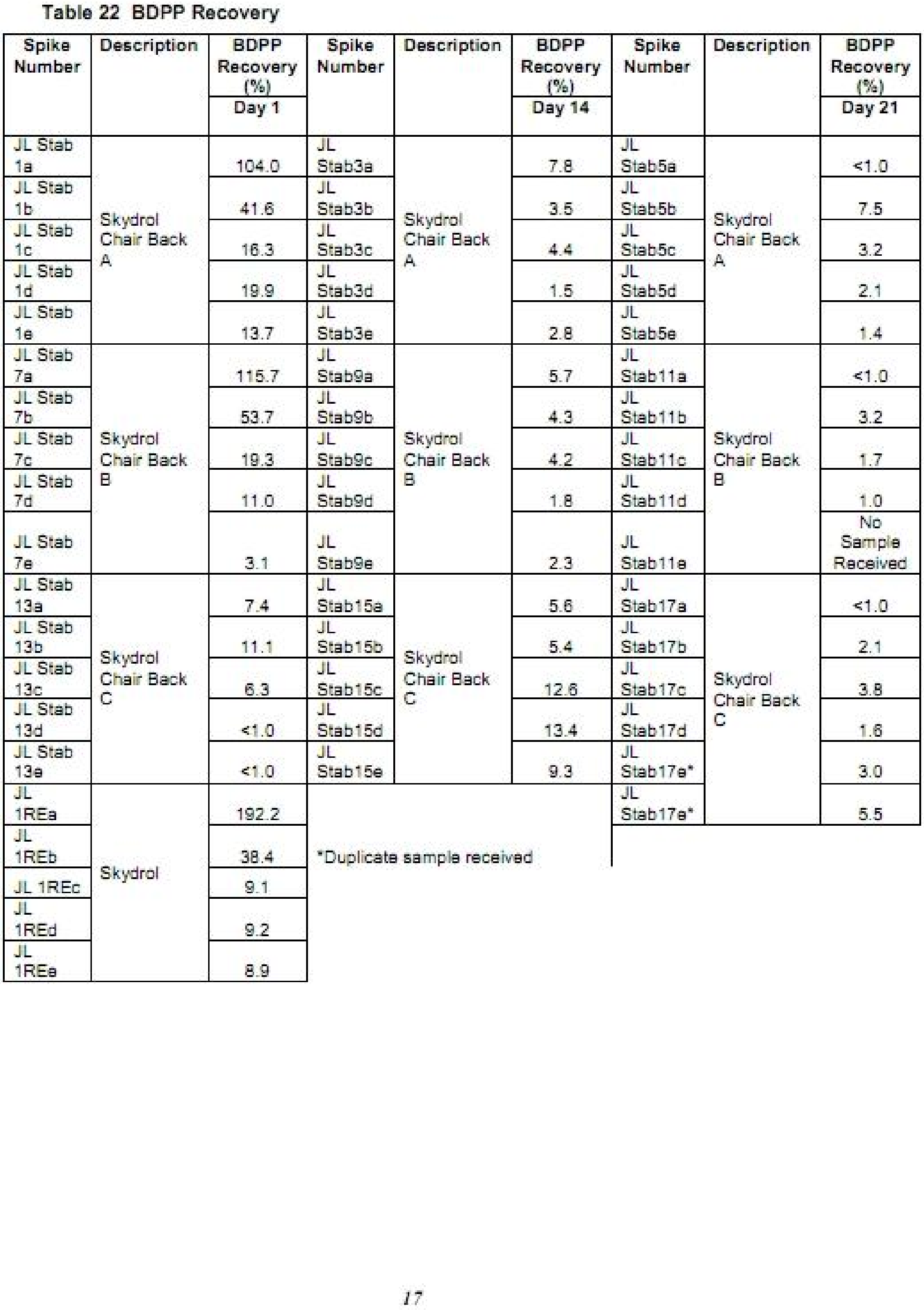

Table 22 BDPP Recovery

Spike Number	Description	BDPP Recovery (%) Day 1	Spike Number	Description	BDPP Recovery (%) Day 14	Spike Number	Description	BDPP Recovery (%) Day 21
JL Stab 1a	Skydrol Chair Back A	104.0	JL Stab3a	Skydrol Chair Back A	7.8	JL Stab5a	Skydrol Chair Back A	<1.0
JL Stab 1b		41.6	JL Stab3b		3.5	JL Stab5b		7.5
JL Stab 1c		16.3	JL Stab3c		4.4	JL Stab5c		3.2
JL Stab 1d		19.9	JL Stab3d		1.5	JL Stab5d		2.1
JL Stab 1e		13.7	JL Stab3e		2.8	JL Stab5e		1.4
JL Stab 7a	Skydrol Chair Back B	115.7	JL Stab9a	Skydrol Chair Back B	5.7	JL Stab11a	Skydrol Chair Back B	<1.0
JL Stab 7b		53.7	JL Stab9b		4.3	JL Stab11b		3.2
JL Stab 7c		19.3	JL Stab9c		4.2	JL Stab11c		1.7
JL Stab 7d		11.0	JL Stab9d		1.8	JL Stab11d		1.0
JL Stab 7e		3.1	JL Stab9e		2.3	JL Stab11e		No Sample Received
JL Stab 13a	Skydrol Chair Back C	7.4	JL Stab15a	Skydrol Chair Back C	5.6	JL Stab17a	Skydrol Chair Back C	<1.0
JL Stab 13b		11.1	JL Stab15b		5.4	JL Stab17b		2.1
JL Stab 13c		6.3	JL Stab15c		12.6	JL Stab17c		3.8
JL Stab 13d		<1.0	JL Stab15d		13.4	JL Stab17d		1.6
JL Stab 13e		<1.0	JL Stab15e		9.3	JL Stab17e*		3.0
JL 1REa	Skydrol	192.2				JL Stab17e*		5.5
JL 1REb		38.4						
JL 1REc		9.1						
JL 1REd		9.2						
JL 1REe		8.9						

*Duplicate sample received

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Table 23 TCP Recovery

Spike Number	Description	TCP Recovery (%) Day 1	Spike Number	Description	TCP Recovery (%) Day 14	Spike Number	Description	TCP Recovery (%) Day 21
JL Stab 2a	Jet11 Chair Back A	60.1	JL Stab4a	Jet11 Chair Back A	10.0	JL Stab6a	Jet11 Chair Back A	<1.0
JL Stab 2b		14.9	JL Stab4b		3.3	JL Stab6b		6.7
JL Stab 2c		6.4	JL Stab4c		6.7	JL Stab6c		<1.0
JL Stab 2d		3.6	JL Stab4d		<1.0	JL Stab6d		<1.0
JL Stab 2e		13.5	JL Stab4e		1.7	JL Stab6e		<1.0
JL Stab 8a	Jet 11 Chair Back B	80.9	JL Stab10a	Jet 11 Chair Back B	8.0	JL Stab12a	Jet 11 Chair Back B	<1.0
JL Stab 8b		19.0	JL Stab10b		1.0	JL Stab12b		2.6
JL Stab 8c		9.8	JL Stab10c		<1.0	JL Stab12c		1.5
JL Stab 8d		2.9	JL Stab10d		<1.0	JL Stab12d		<1.0
JL Stab 8e		1.0	JL Stab10e		<1.0	JL Stab12e		<1.0
JL Stab 14a	Jet 11 Chair Back C	1.3	JL Stab16a	Jet 11 Chair Back C	2.7	JL Stab18a	Jet 11 Chair Back C	<1.0
JL Stab 14b		<1.0	JL Stab16b		1.7	JL Stab18b		<1.0
JL Stab 14c		<1.0	JL Stab16c		<1.0	JL Stab18c		<1.0
JL Stab 14d		17.9	JL Stab16d		<1.0	JL Stab18d		<1.0
JL Stab 14f		<1.0	JL Stab16e		<1.0	JL Stab18e		<1.0
JL 4REa	Jet 11	65.1						
JL 4REb		25.5						
JL 4REc		17.5						
JL 4REd		10.0						
JL 4REe		<1.0						

Reported by:

Carolyn McGonagle
Senior Chemist

Authorised by:

Alison Searl
Director Analytical Services

APPENDIX 3 – INTER-LABORATORY COMPARISON - ANALYTICAL METHOD AND RESULTS

Please note: In the interests of transparency, **t**he certificate of analysis and analytical methods below have been reproduced as received from BRE without alteration, with the exception of using the terminology “Total TCP (all isomers)” instead of “TCP 1+2+3+4” in the tables of results for clarity of comparison**.**

Sampling

Type of sampler:	Supplied by IOM
Sampled by:	Client
Sampling method:	N/A

Analysis

Date samples analysed:	12/08/2011
Analysis by:	VOC Analytical Laboratory, BRE
Analysis method:	Extraction with ethyl acetate spiked onto thermal desorption tubes and analysed by TD/GC/MS
Identification:	Agilent (mass spectrometer) coupled with Mass Selective Detector and Flame Photometric Detector(FPD)
Quantification:	Relative to triethyl phosphate Internal standards
Calibration identity:	Calibration compounds supplied by IOM

Results

Results are given in Tables 1-7.

Analysed by:		Date:	26/09/2011
Name	Mr Pawan Kumar	Position:	Scientist, Environmental Consultancy
Final approval by:		Date:	
Name	Mr J Rowley	Position:	Principal scientist, Environmental Consultancy

Table 1: Concentrations of IOM samples ID 01-05
Results in ug/ml in 2mls of extraction solution

Compound	Sample 01 JL225411	Sample 02 JL235411	Sample 03 JL276411	Sample 04 JL296411	Sample 05 JL316411
TBP	0.29	0.67	0.47	0.59	0.53
Skydrol (diBPhP)	0.19	0.41	0.25	3.84	0.45
Skydrol (BdiPhP)	0.38	0.63	0.27	3.4	0.35
Total TCP (all isomers)	0.29	0.25	0.15	0.14	0.13

Table 2: Concentrations of IOM samples ID 06-10
Results in ug/ml in 2mls of extraction solution

Compound	Sample 06 JL105411	Sample 07 JL55411	Sample 08 JL75411	Sample 09 JL95411	Sample 10 JL316511
TBP	1.2	0.31	0.34	0.54	0.29
Skydrol (diBPhP)	0.86	0.43	0.24	0.41	3.58
Skydrol (BdiPhP)	0.59	0.5	0.23	0.35	4.87
Total TCP (all isomers)	0.16	0.09	0.11	0.15	0.26

Table 3: Concentrations of IOM samples ID 11-15
Results in ug/ml in 2mls of extraction solution

Compound	Sample 11 JL1116511	Sample 12 JL516511	Sample 13 JL1016511	Sample 14 JL4285	Sample 15 JL5285
TBP	0.33	0.38	0.32	1.79	0.47
Skydrol (diBPhP)	0.2	0.44	0.27	1.1	0.26
Skydrol (BdiPhP)	0.35	2.08	0.21	0.67	0.5
Total TCP (all isomers)	0.14	3.25	0.14	1.98	0.22

Table 4: Concentrations of IOM samples ID 16-20
Results in ug/ml in 2mls of extraction solution

Compound	Sample 16 JL5205	Sample 17 JL10205	Sample 18 JL3205	Sample 19 JL11205	Sample 20 JL41
TBP	0.48	0.6	2.19	0.31	1.09
Skydrol (diBPhP)	0.39	0.48	2.9	3.5	0.66
Skydrol (BdiPhP)	0.73	0.26	1.73	2.72	0.37
Total TCP (all isomers)	0.16	0.06	0.19	0.25	0.1

Table 5: Concentrations of IOM samples ID 21-25
Results in ug/ml in 2mls of extraction solution

Compound	Sample 21 JL13	Sample 22 JL 48	Sample 23 JL 31	Sample 24 JL 30	Sample 25 JL 47
TBP	0.19	2.73	1.98	1.96	0.45
Skydrol (diBPhP)	0.51	1.55	2	1.74	0.42
Skydrol (BdiPhP)	0.67	0.61	1.22	0.65	0.39
Total TCP (all isomers)	0.09	0.11	0.16	0.21	0.1

Table 6: Concentrations of IOM samples ID 26-27/IS solvent/IOM blank 1
Results in ug/ml in 2mls of extraction solution

Compound	Sample 26 JLS	Sample 27 13 pc	1 ul IOM IS solvent	1 ul IOM IS solvent	1 ul IOM blank 1
TBP	0.54	0.64	0.75	0.33	0.37
Skydrol (diBPhP)	0.71	0.6	0.67	0.17	0.33
Skydrol (BdiPhP)	0.97	0.5	0.35	0.26	0.62
Total TCP (all isomers)	0.13	0.1	0.07	0.08	0.74

Table 7: Concentrations of IOM blanks and IS I ul spike
Results in ug/ml in 2mls of extraction solution

Compound	1 ul IOM blank 2	1 ul IOM blank 3	1 ul IOM blank 4	1 ul IOM blank 5	1 ul IOM blank 6	1 ul IOM IS spike
TBP	0.36	1.45	1.62	1.23	1.03	1.76
Skydrol (diBPhP)	0.31	0.79	1.28	0.86	0.74	1.26
Skydrol (BdiPhP)	0.63	0.41	0.33	0.44	0.43	0.27
Total TCP (all isomers)	0.16	0.37	1.62	0.47	0.76	0.05

BRE protocol for TD/GC/MS analysis of Q/Tenax tubes used to analyze extraction solutions

Internal standard solution.

A solution containing 5 µl triethyl phosphate in 250 mls ethylacetate was prepared this was used to make the calibration solutions and extractions.

Calibration

Calibration solutions were prepared for target analytes supplied by IOM. The relative response of each target analyte was determined relative to triethyl phosphate internal standard. Four point calibrations were used. Four point calibrations were used with quantification using Agilent Chemstation. A detection limit was not calculated as all samples gave a satisfactory peak for quantification.

Analysis

The samples were extracted using 2 ml of ethyl acetate solution containing triethylphosphate internal standard. As per the method supplied by IOM. 1 µl of extraction solution from a calibrated 1 µl syringe was spiked onto adsorbent tubes containing quartz wool and Tenax TA using a flow of nitrogen and analysed by thermal desoprtion and gas chromatography/mass spectrometry.

Sample input being achieved using a Markes Unity Thermal Desorber (TD) and Markes Ultra Autosampler and analysis using an Agilent 5975 Mass Selective Detector (MSD) coupled to an Agilent 6890N Gas Chromatograph (GC). The column used was a 30m DB-5MS 0.25mm film thickness 0.25µm temperature programmed to 300°C. The method has been shown to be suitable for analysis of SVOCs.

Quantification was by single ion monitoring as in the following table

Compound	Mass
Triethyl phosphate	155.0
Tributyl phosphate	99.0
Dibutylphenyl phosphate	175.1
Butyldiphenyl phosphate	251.05
total tricresyl phosphates	368.1

We experienced problems in getting a good calibration for tributylphosphate due to high and inconsistent background levels.

There was little butyldiphenylphosphate in the hydraulic fluid supplied and therefore not a particularly good calibration.

Sample 14 (high TCPs) there was a peak in the region expected for oil esters, but it did not correspond to the retention times seen for esters in Jet2 or Aeroshell.

APPENDIX 4 – TABLES OF RESULTS- FOLLOW-UP/AFTER SAMPLES

Tables A1- A9 below describe the results obtained from the second (follow-up/after) samples taken on the second site visit of the sampling exercise. These samples were taken to determine if there had been any deposition of surface residues in the interim period between visits.

Table A1 : Average levels of TBP/(ng m^{-2}) by site and plane/control type

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	6.9x10^{4}	-	-
B	<LOD	4.3 x10^{3}	5.8 x10^{3}	6.5x10^{3}	-	<LOD	-
C	-	7.9x10^{4}	<LOD	-	-	6.1 x10^{4}	-
D	-	1.3x10^{4}	-	6.2x10^{4}	-	3.0 x10^{4}	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection = 3.3 x10^{3} ngm^{-2})

Table A2 : Average levels of DBPP/(ng m^{-2}) (70%) by site and plane/control type

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	5.4x10^{5}	-	-
B	<LOD	<LOD	<LOD	2.4x10^{4}	-	<LOD	-
C	-	1.7x10^{4}	<LOD	-	-	1.7x10^{4}	-
D	-	1.4 x10^{4}	-	1.2x10^{5}	-	1.7x10^{4}	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection= 1.4 x10^{4} ngm^{-2})

Table A3 : Average levels of BDPP/(ng m^{-2}) (30%) by site and plane/control type

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	8.5x10^{4}	-	-
B	9.8x10^{3}	<LOD	<LOD	1.2x10^{4}	-	<LOD	-
C	-	5.9x10^{3}	<LOD	-	-	2.3x10^{4}	-
D	-	1.7x10^{4}	-	7.0x10^{4}	-	6.3x10^{3}	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection= 5.9 x10^{3} ngm^{-2})

Table A4 : Average levels of TCP/(ng m^{-2}) by site and plane/control type

			Plane			Vehicle	Building
Site	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**		
A	-	-	-	-	<LOD	-	-
B	<LOD	<LOD	<LOD	<LOD	-	<LOD	-
C	-	<LOD	<LOD	-	-	<LOD	-
D	-	25000	-	<LOD	-	<LOD	-
E	-	-	-	-	-	-	<LOD
F	-	-	-	-	-	-	<LOD

(Limit of detection= 1.8 x10^{4} ngm^{-2})

Table A5: Average levels of TBP/(ng m^{-2}) by location within plane

	Plane				
Location	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	$3.5x10^4$	$5.8x10^3$	$6.5x10^4$	$1.1x10^4$
Rear	<LOD	$5.0x10^3$	<LOD	<LOD	$1.1x10^5$

(Limit of detection = 3.3 x10^3 ngm^{-2})

Table A6: Average levels of DBPP/(ng m^{-2}) (70%) by location within plane

	Plane				
Location	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	$2.0x10^4$	<LOD	$1.4x10^5$	$8.8x10^4$
Rear	<LOD	<LOD	<LOD	<LOD	$8.5x10^5$

(Limit of detection= 1.4 x10^4 ngm^{-2})

Table A7: Average levels of BDPP/(ng m^{-2}) (30%) by location within plane

	Plane				
Location	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	$2.0x10^4$	<LOD	$7.7x10^4$	$2.9x10^4$
Rear	$1.7x10^4$	<LOD	<LOD	<LOD	$1.2x10^5$

(Limit of detection= 5.9 x10^3 ngm^{-2})

Table A8: Average levels of TCP/(ng m^{-2}) by location within plane

	Plane				
Location	**B 737**	**B 757**	**B 767**	**Airbus**	**BAe 146**
Cockpit	<LOD	$2.6x10^4$	<LOD	<LOD	<LOD
Rear	<LOD	<LOD	<LOD	<LOD	<LOD

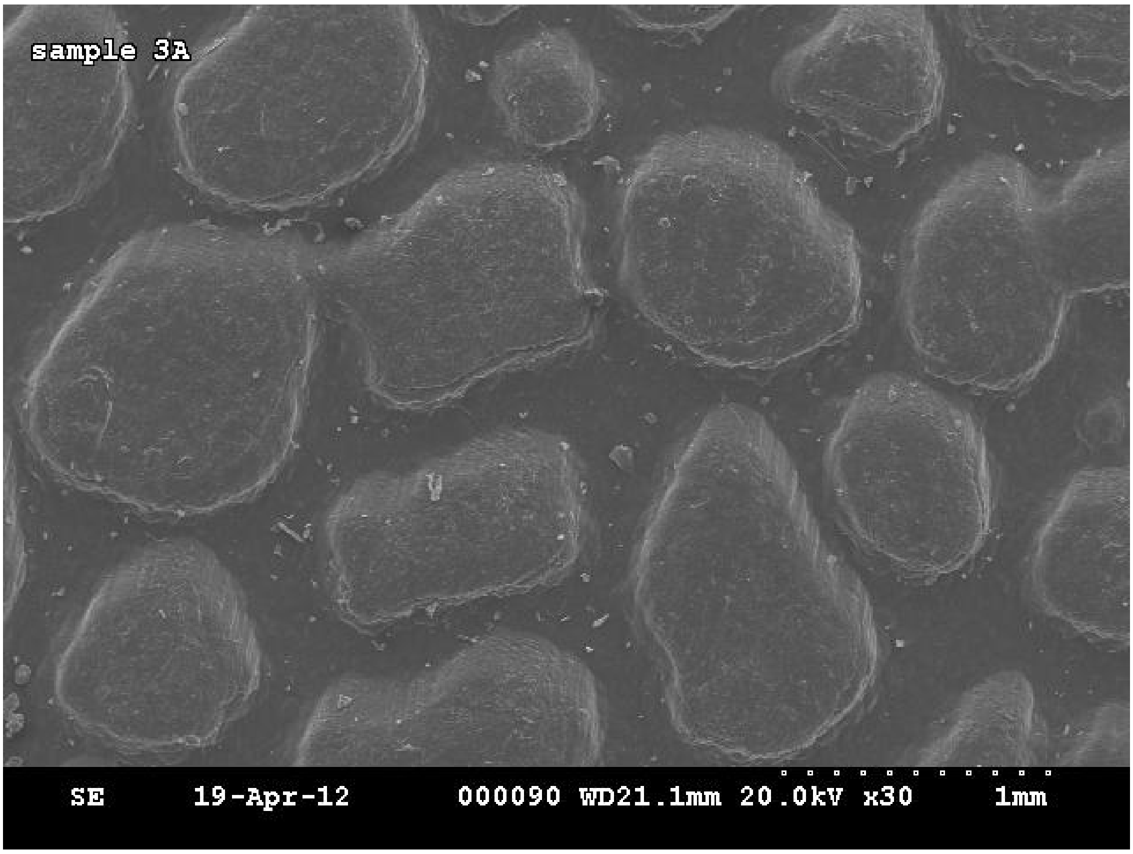
(Limit of detection= 1.8 x10^4 ngm^{-2})

Table A9: Average levels of TCP/(ng m^{-2}) by location within plane
(reliable samples only)

	Plane			
Location	**B 737**	**B 757**	**B 767**	**Airbus**
Cockpit	<LOD	$2.9x10^4$	<LOD	<LOD
Rear	<LOD	<LOD	<LOD	<LOD

(Limit of detection= 1.8 x10^4 ngm^{-2})

APPENDIX 5- SCANNING ELECTRON MICROSCOPE IMAGES OF TRIAL SURFACES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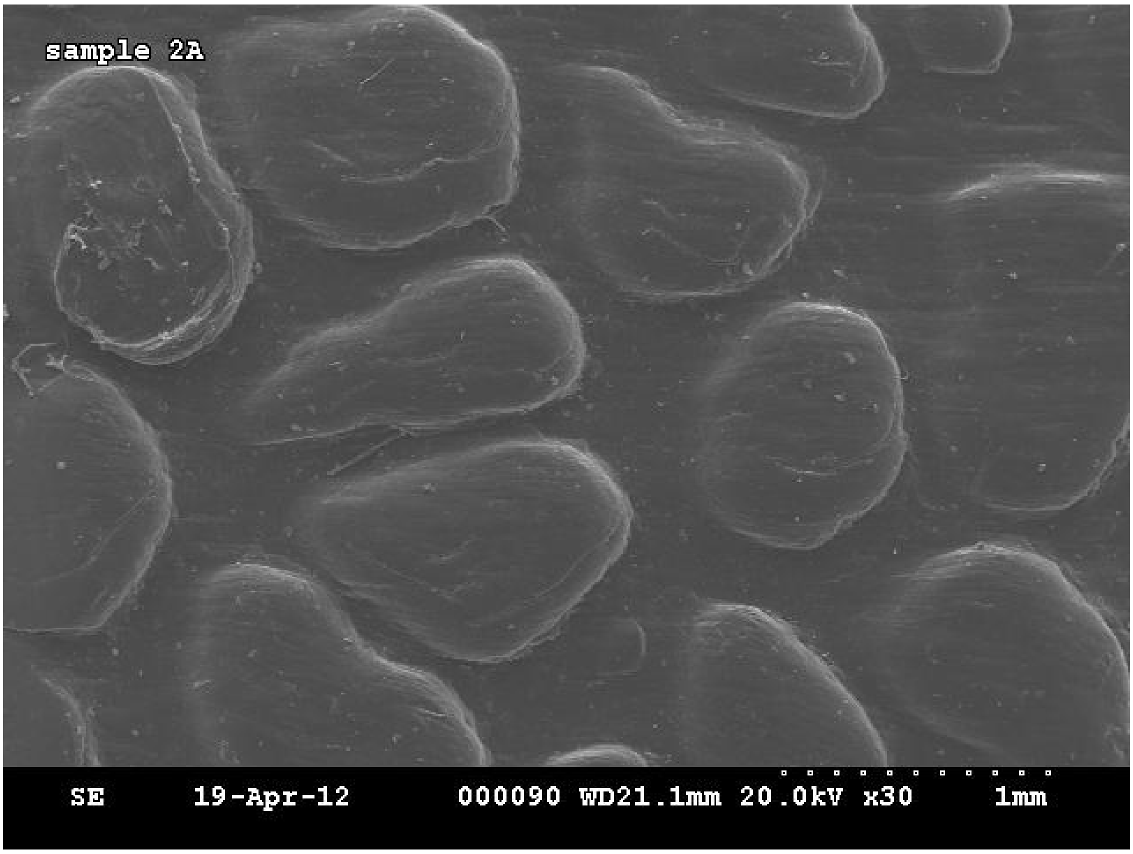
SE 19-Apr-12 000090 WD21.1mm 20.0kV x30 1mm


sample 3B
SE 19-Apr-12 000090 WD21.2mm 20.0kV x250 200um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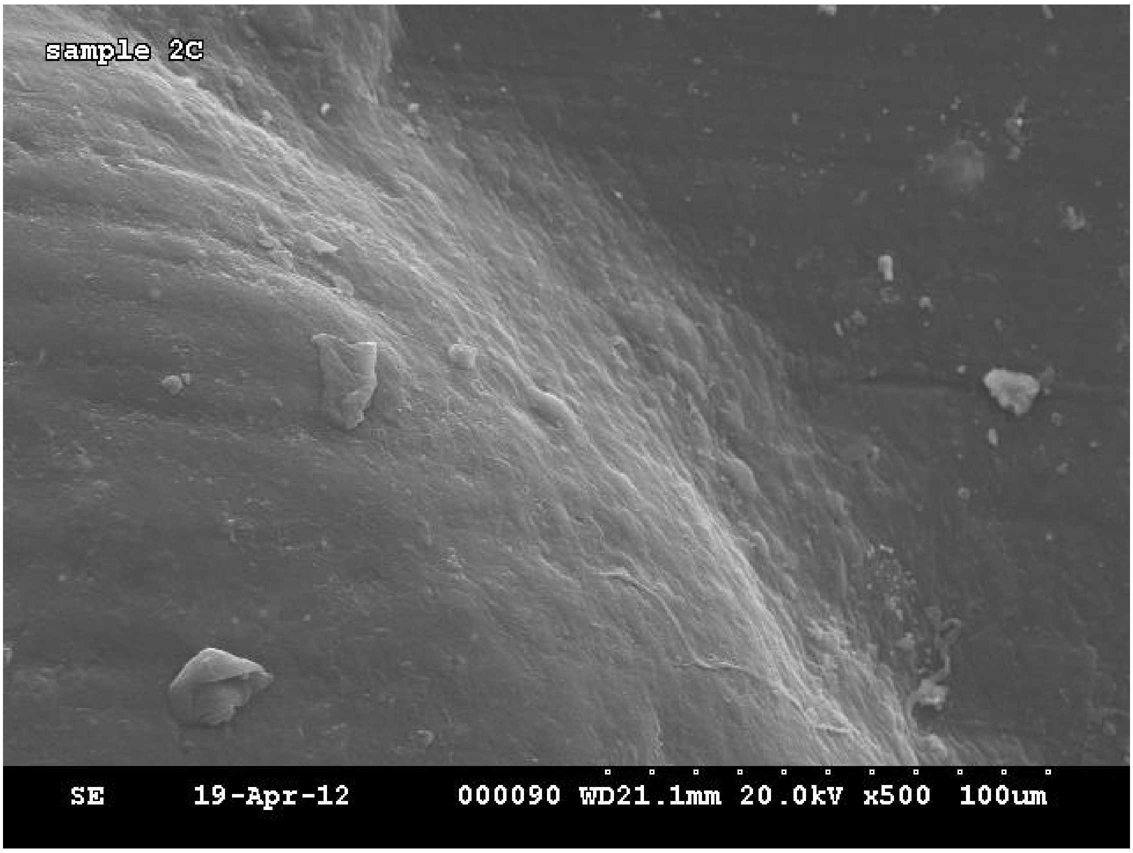
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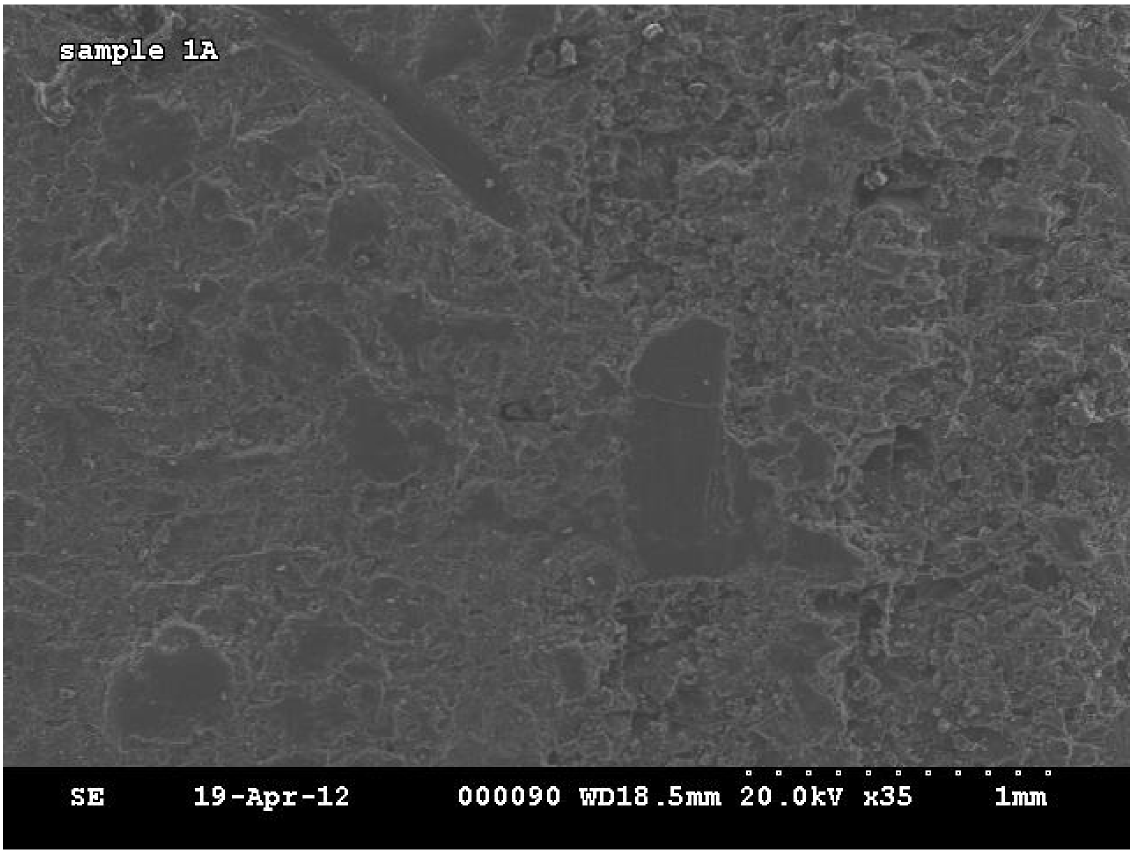
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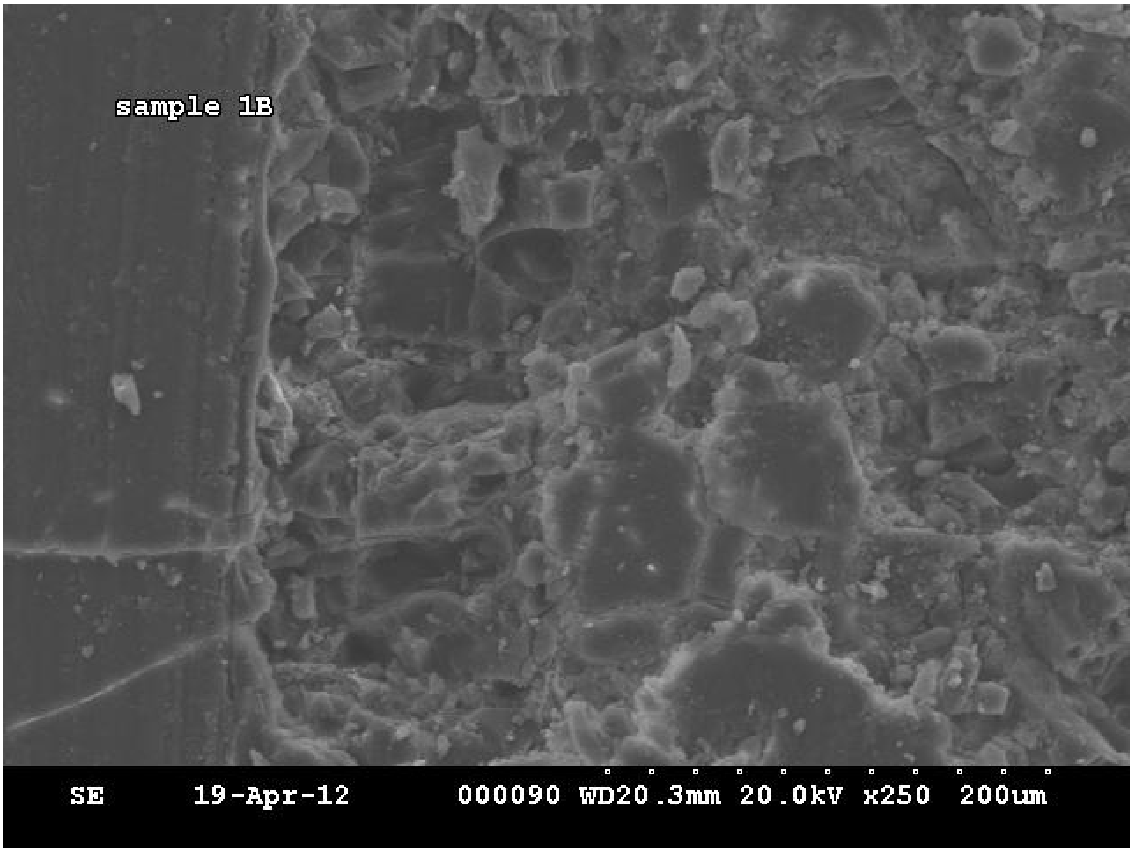
SE 19-Apr-12 000090 WD18.5mm 20.0kV x35 1mm


sample 1B
SE 19-Apr-12 000090 WD20.3mm 20.0kV x250 200um

APPENDIX 6 – GLOSSARY OF MEASUREMENT UNITS

Unit	Abbreviation	Scientific notation	Decimal	Description
MASS				
1 nanogram	ng	1 x 10^{-9} g	0.000000001 grams	One billionth of a gram
1 microgram	µg	1 x 10^{-6} g	0.000001 grams	One millionth of a gram
1 milligram	mg	1x 10^{-3} g	0.001 grams	One thousandth of a gram
1 kilogram	kg	1x 10^{3} g	1000 grams	One thousand grams
VOLUME				
1 centimetre squared	cm^2			Area of 1cm by 1cm
1 cubic centimetre	cm^3			Volume of 1cm by 1cm x1cm
1 metre squared	m^2			Area of 1m by 1m
1 metre cubed	m^3			Volume of 1m x 1m x 1m
CONCENTRATIONS				
nanograms per centimetre squared	ng cm^{-2}			nanograms of substance per square centimetre of surface area
nanograms per metre cubed	ng m^{-3}			nanograms of substance per cubic metre of air
micrograms per metre squared	µg m^{-2}			micrograms of substance per square metre of surface area
micrograms per metre cubed	µg m^{-3}			micrograms of substance per cubic metre of air
milligrams per metre squared	mg m^{-2}			milligrams of substance per square metre of surface area
milligrams per metre cubed	mg m^{-3}			milligrams of substance per cubic metre of air
milligrams per kilogram	mg kg^{-1}			milligrams of substance per total mass of sample in kilograms (e.g. for dust sample)
FLOW RATE				
litres per second	l s^{-1}			e.g. litres of air supplied per second

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