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Hydraulic Oil Infiltration into Potable Water through Aircraft Pneumatic Systems: A Qualitative Assessment of Chemical Contamination

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Abstract: Potable water on aircraft is currently monitored for microbiological contaminants of water quality such as *E. coli*, but because the source water for aircraft is pre-treated water from municipalities, chemical contaminants are not assessed. This neglects the possibility of aircraft pneumatic systems, interconnected with other systems such as the engines and hydraulic oil reservoirs, from becoming fouled and contaminating the potable water onboard with organophosphate esters and other contaminants of concern. In this novel initial qualitative study potable water samples were taken on twenty domestic and international flights on various commercial aircraft. The samples were analyzed with high-resolution liquid chromatography mass spectrometry and compared against 18 Mohm ultrapure water and tap water blanks drawn from departing airports. Suspect compounds were identified using safety data sheets for commonly used aircraft oils and compounds previously identified in aircraft cabin contamination research. Tributyl phosphate, the primary component in aircraft hydraulic oil, was confirmed to be present in the potable water of the majority of flights sampled (11 of 20 flights). Other organophosphates were also identified in the water on a high percentage of flights (tris (chloropropyl) phosphate (TCPP): 20%; triphenyl phosphate (TPhP): 10%; tris (butoxyethyl) phosphate (TBEP): 10%). The qualification of the compounds is supported by mass accuracy, fragment, isotope abundance, and adduct data. This work suggests that as there is currently a potentially unaddressed occupational and public health risk. Detailed quantitative chemical monitoring of aircraft potable water is therefore recommended to fully establish the magnitude of this risk.

Keywords: aircraft; contamination; hydraulic oil; pneumatic system; potable water

1. Introduction

By its definition, for water to be considered potable, it must be safe for human consumption. The World Health Organization strengthens this definition, adding that the water must "not represent any significant risk to health over a lifetime of consumption" [1]. Drinking water guidelines/regulations/directives require that this water meet various microbiological, chemical, radiological, and aesthetic requirements to meet this definition [1–4]. Adulteration of the water by contaminants may make the water hazardous to consume/use for other purposes, such as bathing or cleaning surfaces [5,6]. Water treatment and monitoring take place to prevent or limit contaminated

water from reaching human receptors, but further complexity exists when water systems are utilized by the public but are operated outside of those managed and regulated by local authorities; an example is potable water systems found in various modes of transportation, such as ocean-going vessels, rail systems, and airplanes. The potable water systems on aircraft, to a greater extent than municipal water systems or those on other forms of mass transport, are vulnerable to chemical contamination [7]. The aircraft systems contain relatively small volumes of water, limiting the effects of dilution, and have no water treatment capabilities [7,8].

Water is loaded onto aircraft at the departing airport using locally available water supplied by the municipality [9]. The aircraft operators, the airport, and the relevant local health authorities are responsible for ensuring that the water is of sufficient quality for its transfer into an aircraft potable water system. However, once on board, the water's quality and safety become the airline's sole responsibility [8]. The onboard system services both employees and the public; therefore, the safety and enforcement guidance fall under the purview of the various occupational health and safety agencies and government entities responsible for public health [10,11]. The aircraft potable water system is composed of an external filling port, a pressurized tank (typically made of stainless steel), and a variety of plumbing and fixtures used to transport the potable water from the tank(s) to the onboard galleys and lavatories [8]. The water is then used for a variety of purposes: Directly consuming chilled water is now less common, as bottled water is often available on flights, but hot beverages (coffee, tea, baby formula, etc.) are prepared with the aircraft potable water; the water is also used for oral hygiene, cleaning hands, and cleaning surfaces [12].

Historically, concerns about the microbiological aspects of water quality have dominated both the research and regulatory guidance regarding aircraft potable water [8,12,13]. However, the pressurization of the potable water tank and other aircraft systems by engine bleed air, accompanied by the interconnectedness of the pneumatic system on most aircraft, may result in chemical contamination of the potable water with engine oil, hydraulic oil, or other potential contaminants such as deicing fluids, aircraft exhaust, oil or fuel additives, etc. [14,15]. That the water systems are rarely fully drained and are not cleaned with this type of contamination in mind, means that the pressurized water tanks of aircraft may act as a reservoir for these unwanted chemical contaminants [10,12,14–16]. While heating the water (i.e., for tea or coffee preparation) may remedy much of the microbiological concern, it will not prevent chemical exposure should the water be ingested or otherwise introduced to the body [13,17].

Certain organophosphate esters (OPEs), which constitute or are additives present in aircraft hydraulic and engine oil, have the potential to contaminate potable water on aircraft. Tricresyl phosphate (TCP), an engine oil anti-wear additive, is suspected of contributing to increased neurological illness and injury experienced by pilots and flight attendants [14,18–22]. Tributyl phosphate (TBP), another organophosphate ester, is used as a plasticizer, solvent, and metal ion extractant and is also the primary component of aircraft hydraulic oil (55–100% *w*/*w*) [23–26]. It is commonly found within the aircraft cabin [27–30]. The hydraulic oil reservoirs on commercial jet aircraft are pressurized via the bleed air/pneumatic system, and a known problem on certain aircraft is the contamination of the pneumatic system with hydraulic oil and fumes from this source [31–33]. Once in the pneumatic system, there are no barriers to the hydraulic oil/ fumes from being transported to the potable water tanks. TBP is listed as a chemical contaminant on the US EPA Contaminant Candidate List 5; it is currently unregulated but has been identified as a potential risk to drinking water [34,35]. Ingestion is a known prevalent pathway for exposure to organophosphate esters [36]. For the public who fly regularly, the estimated daily intakes for the OPEs present in aircraft potable water, may need to be adjusted substantially [36].

It has already been established that engine and hydraulic oil fumes and additives can enter the cabin via bleed air transport through the pneumatic system [27,30,37]. What has yet to be definitively established is if the same is true of the potable water systems on board aircraft. This study is the first of its kind and aims to determine if the water systems are becoming contaminated by engine oil, engine oil additives, or hydraulic oils. The confirmed presence of suspect compounds could warrant an examination of the chemical safety and the potability of the water used by passengers and crew.

2. Materials

2.1. Sample Collection and Preparation

Potable water samples were collected from domestic and international flights within North America, the United Kingdom, and Europe. Water samples were collected from aircraft lavatory sinks (n = 25) and hot water via the rear galley (n = 1). Collection occurred on 20 unique flights, including nine aircraft types and/or airframe configurations, with duplicate samples collected from 7 flights (Table 1). Nitrile gloves were worn, and the water was dispensed into certified clean 250 mL wide-mouth amber glass bottles (VWR, Radnor, Pennsylvania, USA), rinsed completely with the sampled water, and filled and capped. The collection occurred during the cruise phase of each flight. Blanks of airport tap water (potable water from source reservoirs that had not been on a plane) were

collected from water fountains prior to two individual flight departures (samples 10 and 10b and 21 and 21b); each blank was collected in duplicate. Sample collection was opportunistic. The collection procedures, along with the overall project, were submitted and reviewed by the Manchester Metropolitan University Science and Engineering Research Ethics and Governance Committee and given a favorable ethical opinion (Reference Number: 16308). Samples were collected from December 2019 until March 2022 and stored at 4 °C upon arrival at the final destination (maximum storage duration = 2.25 years). Samples remained in the sealed amber glass storage vessels in an effort to minimize photodegradation until analysis.

In preparation for instrumental analysis, aliquots were drawn from just below the water's surface, with care taken not to displace potential sediment at the bottom of the sample vessel nor draw in any film that may have formed at the sample's surface. A new, solvent cleaned (18 Megaohm milli-Q water/MeOH) glass Pasteur pipette was used to transfer the water from each amber sample vial to 1.5 mL amber LC vials. The uncapped LC Vial was zeroed on an analytical balance (Accuris Instruments Analytical Series W3100A-120). Following this, 0.9500 g (Mean: 0.9517 g; min–max: 0.9368 g–0.9676 g; Standard Deviation: 0.0076 g) of aircraft water was pipetted into the vial on the scale. The transfer was completed unfiltered, as the glass fiber/nylon filters were determined to be a source of coeluting contamination (679.5129 & 396.8020 *m*/*z*). The scale was then zeroed, and 50 µL/0.0500 g of 1 ng·µL^{-1} ^{13}C pentaerythritol was dosed to each sample via a 50 µL Hamilton pipette (Mean: 0.0495 g; min–max: 0.0481 g–0.0507 g; Standard Deviation: 0.0006 g; mean RT = 3.02; RSD% of RT = 1.02%; mean peak area = 179116; RSD% peak area = 11.22)). This method was completed for all analytical samples and airport tap water and Milli-Q water blanks. Milli-Q water blanks consisting of 18 Mohm deionized water (Milli-Q) and 13C pentaerythritol at the same concentrations as the analytical samples were run in duplicate before and following each 10 sample injections (maximum) to monitor for carry-over.

Table 1. Sampled aircraft and location. Samples taken in duplicate from the same aircraft are indicated by the letter b. Samples 3 and 4 are from the same flight but differing sample locations resulting in unique sample numbering. Note that sample number 1 was collected but is not included in subsequent analysis due to instrument error.

Sample Number	Aircraft	Sample Location
1	Boeing 737-700	Lavatory Sink
1b	Boeing 737-700	Lavatory Sink
2	Boeing 737-700	Lavatory Sink
2b	Boeing 737-700	Lavatory Sink
3	Boeing 737 Max	Hot water from galley
4	Boeing 737 Max	Lavatory Sink
5	Boeing 737 Max	Lavatory Sink
6	Airbus A330-300	Lavatory Sink
7	Boeing 737 Max	Lavatory Sink
8	Boeing 737-800	Lavatory Sink
9	Airbus A330-300	Lavatory Sink
9b	Airbus A330-300	Lavatory Sink
10	Airbus A320-211	Lavatory Sink
10b	Airbus A320-211	Lavatory Sink
11	Boeing 737-800	Lavatory Sink
11b	Boeing 737-800	Lavatory Sink
12	Boeing 787-900	Lavatory Sink
12b	Boeing 787-900	Lavatory Sink
13	Boeing 737-800	Lavatory Sink
14	Avro RJ100	Lavatory Sink
15	Embraer E190	Lavatory Sink
16	Airbus A330-300	Lavatory Sink
17	Boeing 737-800	Lavatory Sink
18	Boeing 737-700	Lavatory Sink
19	Boeing 737 Max	Lavatory Sink
20	Boeing 737 Max	Lavatory Sink
21	Boeing 787-900	Lavatory Sink
21b	Boeing 787-900	Lavatory Sink
BLK1	Airport Water Fountain	Toronto, ON
BLK1b	Airport Water Fountain	Toronto, ON
BLK2	Airport Water Fountain	Calgary, AB
BLK2b	Airport Water Fountain	Calgary, AB

2.2. Instrumental Analysis

An Agilent 1260 Infinity II high-performance liquid chromatography (HPLC) system was coupled to an Agilent 6546 quantitative time-of-flight mass spectrometer (QToF-MS) (Santa Clara, California, USA) and used for all instrumental analysis. The column used was an Agilent InfinityLab Poroshell 120 EC-C18 (3.0 × 100 mm, 2.7 μm), and ionization was performed using a Dual Agilent Jet Stream (AJS) ESI ion source.

The separation method was previously presented in Fries and Sühring (2023) [38], with minor modifications (Supplementary Materials Table S1). Briefly, an initial composition of 90% water (with 0.1% formic acid) and 10% acetonitrile (ACN) was used at a constant flow rate of 0.2 $mL \cdot min^{-1}$. This was increased to 40% ACN over five minutes, then to 100% ACN over seven minutes, and held for an additional eight minutes. Finally, the mobile phase composition was returned to starting conditions over 0.1 min, with a seven-minute post-run used to equilibrate the column.

The auto-MS/MS feature of the QToF-MS was used to ionize and automatically fragment possible contaminant ions measured in the potable water samples. Two collision energies, 15 eV and 30 eV, were used to fragment ions of different labilities. Detailed parameters and thresholds used in the auto-MS/MS method are presented in Supplementary Materials Table S2.

2.3. Statistical Methods and Identification Confidence

Initial screening of compounds within samples was completed using MassHunter Qualitative Analysis software 10.0 (Agilent Technologies, Santa Clara, CA, USA), utilizing a Water Contaminants spectral library (Personal Compound Database and Library-PCDL) (Agilent Technologies, Santa Clara, CA, USA). Compounds pre-identified as potential suspects were sought in the list of spectral library matches. A minimum match score of 90.00 was selected to qualify a compound for further analysis. Each suspect compound that met this criterion was then subject to further screening: Detection (LOD) and quantitation (LOQ) limits were established as the average of all Milli-Q water blanks plus three and ten times the standard deviation of the blank measurements of that compound, respectively. Airport tap water was found to contain a slightly greater concentration of analytes of interest (e.g., TBP) and as such additional LOD and LOQ thresholds were established with airport tap water blanks. The blank type (Milli-Q or Airport tap water) with the higher and therefore more stringent LOD and LOQ was used to determine the detection of each compound assessed. Mass accuracy, fragment, adduct, and isotope abundance testing were then employed to improve confidence in identifying the various compounds. Summary statistics and data handling were completed using Microsoft Excel and Access.

Confidence in compound identification utilizes the scale developed for non-targeted assessments in [39]. The highest confidence level (1) is reserved for compounds that have been matched with reference standards. This confidence level indicates that the chemical structure present in the sample is certain and defined. Level 2 is the next most robust, indicating a confidence level of probable structure. This requires previous knowledge of the compound's presence in related samples (suspect screening) along with structural information, or if completing non-targeted analysis, the exact mass, isotope, adduct, and fragment information to match the compound identification. Level three indicates a tentative candidate, in which all evidence to promote the compound to a probable structure is not present, but fragment data is consistent with the compound in question. Level 4 lacks sufficient structural evidence (i.e., the sample is run in only MS mode), but has an exact mass match and/or some other form of complementary information (adduct, isotope, etc.). Finally, level 5, or mass of interest, describes a compound for which the only information is that it is detected multiple times in samples and has an exact mass match. This scale is established for use when completing non-targeted analysis when utilizing high resolution mass spectrometry [39].

3. Results and Discussion

3.1. Suspect Screening: Hydraulic Oil in the Potable Water

Tributyl phosphate is the primary chemical constituent of aircraft hydraulic fluid (55–100% *w*/*w*) [23–26]. TBP exceeded the match score for all samples (mean score: 99.03; Standard Deviation: 0.51) and blanks (mean score: 99.28; Standard Deviation: 0.52). The peak area counts for TBP present in Milli-Q and airport water blanks were more substantial than expected. As such, 3σ and 10σ method LOD and LOQ values were applied to ensure that declarations of detection were made with greater than 99% confidence. When applying the LOD and LOQ values to the samples collected on the aircraft, 11 of the 20 unique flights demonstrated peak areas above the detection limit established with Milli-Q water blanks. On ten flights, TBP was detectable above airport tap water blanks (Figure 1). One flight (Sample 13) demonstrated a peak area that greatly exceeded LOQ (2.90 times 18-Mohm LOQ; 2.87 times airport tap water LOQ) (Figure 1).

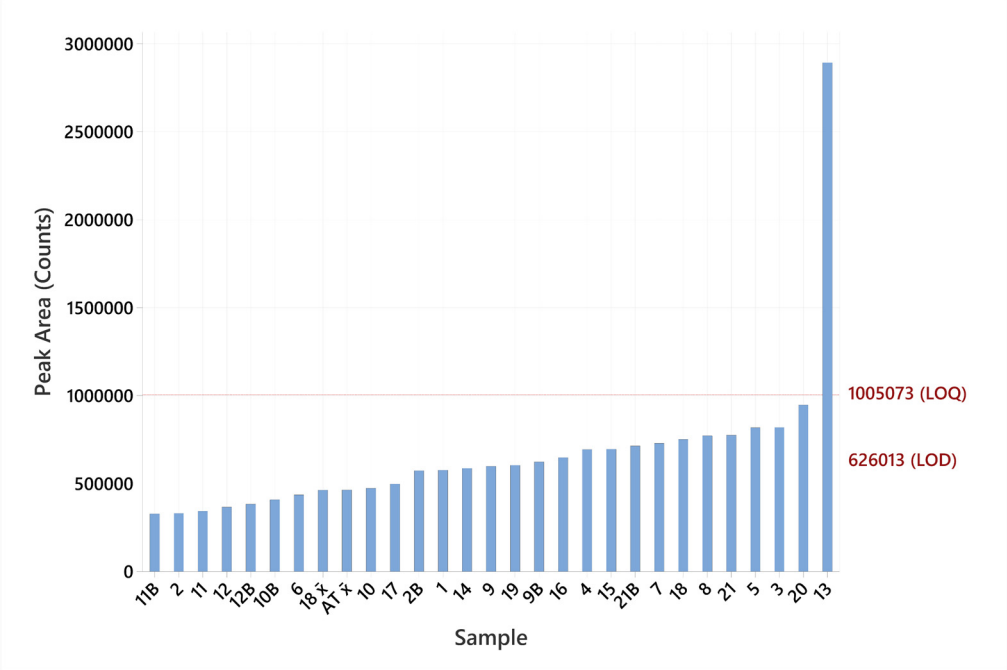

Figure 1. Relative peak areas of TBP in aircraft potable water as compared to airport tap water blanks (AT x̄). Samples are ordered by increasing peak area counts. LOD (3 times the standard deviation of airport tap water blank measurements added to the mean of blank measurements) and LOQ (10 times the standard deviation of aircraft tap water blank measurements added to the mean of blank measurements) of TBP are displayed in the figure as dashed lines. (18 x̄) refers to the average peak area of TBP within Milli-Q water blanks. Sample 1 as represented in this figure is sample 1B.

The presence of TBP in the samples was supported with an exact mass match with the predicted (M+H)+ mass associated with the compound (*m*/*z* 267.1719) with sub-ppm mass accuracy in all samples ($\bar{x}$ = −0.26) and blanks ($\bar{x}$ = −0.17) (Table 2). However, potential isobaric compounds, with differing molecular formulas but masses that fell within instrumental accuracy tolerances, were found: Atenolol and the sodium adduct of ADBI/Celestolide (1-(6-tert-butyl-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethanone). These compounds were assigned the same retention time and mass-to-charge ratio as TBP. Atenolol was identified by the software alongside TBP in 16 of the analytical samples; the Na+ adduct of ADBI was identified in 26 samples, and TBP was found in all samples (n = 27) (Supplementary Materials, Table S1).

The HPLC QTof-MS was operated in (MSMS) mode in an effort to generate identifiable fragments which could further support or assist in rejecting the suspected presence of TBP in the potable water. In all aircraft water samples, with the exception of sample 11B, a prominent fragment (*m*/*z* 98.984~; Max *m*/*z* 98.9847, Min *m*/*z* 98.9837) was detected (Table 2). This mass appears to represent the fully protonated phosphate fragment from TBP ([H4 O4 P]+: Predicted *m*/*z*: 98.9847). In contrast, the Atenolol molecule could not explain this fragment; and while the sodium adduct of ADBI could make a fragment of similar mass [C5 Na O]+, it is unlikely to be prominent given the molecular structure of the compound and the requirement for the sodium adduct to be included with the fragment.

The abundance of 13C in the samples was used to estimate the carbon number to further distinguish between the mass-matched compounds (Table 3). The [M+]+1 abundance most closely resembles TBP with an average 13C: 12C ratio of 15.28% (Table 3). Isotopes of other elements present in the suspect compound were considered to be negligible in the calculation as their natural abundances are much lower than that of 13C or they are monoisotopic; however, their omission, accompanied by mass accuracy discrepancies may account for the difference between predicted and measured isotope ratio values (Table 3). Sodium adducts of TBP (*m*/*z* = 289.154~) were found within all aircraft water samples with concentrations above the LOD except for sample 18 (Tables 2 and 3). Sample 18 also demonstrated a lower 13C:12C percentage than predicted and cannot be tentatively qualified.

Based on these findings, it was considered probable that TBP was the compound found in aircraft water in excess of 18 Mohm and airport tap water blanks. The retention time, exact mass, and isotope data were compared against a TBP standard (Wellington Laboratories) and its presence in the aircraft water was confirmed. The existence of this compound as the primary component of hydraulic oil on commercial jet aircraft and the co-pressurization of hydraulic oil reservoirs and the potable water system by the pneumatic system of the aircraft provides a tenable contamination source and pathway.

Table 2. Detection and mass spectral data indicative of compound qualification. Percentage detected refers to suspect compound detection on a flight basis. Mass accuracy represents the mass accuracy of all suspect compounds with >90.00 match factor (MassHunter Qualitative Analysis; Common Water Contaminants PCDL). Confidence level is derived from "Matrix of Identification V. Identification Confidence" [39].

	Percentage Detected	Known on Aircraft	Molecular Ion (+H) *m*/*z*	Mass Accuracy (ppm)	Diagnostic Fragments *m*/*z*	^{37}Cl Isotope Match	Sodium Adduct	Confidence Level
TBP	55	Yes	267.1719	Mean −0.26 Min −0.63 Max 0.07	Present 98.984~, 155.047~	NA	Yes: <1 ppm mass accuracy	1
TPhP	15	Yes	327.0781	Mean 0.20 Min −0.88 Max 0.43	Absent NA	NA	Yes: >1 ppm mass accuracy	3
TEP	10	No	183.0781	Mean −0.21 Min −0.53 Max 0.14	Present 98.984~	NA	Yes: >1 ppm mass accuracy	3
TBEP	10	Yes	399.2505	Mean −0.36 Min −1.05 Max 0.24	Present 98.984~, 199.073~, 299.165~	NA	Yes: <1 ppm mass accuracy	3
TCIPP	20	Yes	327.0079	Mean −0.52 Min −0.83 Max −0.30	Absent NA	Yes	Yes: >1 ppm mass accuracy	3
TCP	0	Yes	369.12~	Mean NA Min NA Max NA	Absent NA	NA	NA	5

Table 3. Predicted and measured isotopic abundances of suspect compounds. Predicted values calculated with a ^{13}C abundance of 1.1%. Isotopic abundance is calculated only for samples that exceeded the LOD for the respective compound.

Compound	Carbon Number	Predicted 13C:12C
TBP	12	15.2
ADBI	17	23.0
Atenolol	14	18.2

Sample	M+ Abundance	M + 1 Abundance	M + 2 Abundance	M + Na Abundance	%M + 1	%M + 2	%M + Na
3	60,307.0	9280.7	1184.2	950.1	15.4	2.0	1.6
4	53,456.6	8242.0	1099.9	407.4	15.4	2.1	0.8
5	68,063.1	10,652.7	1496.6	844.9	15.7	2.2	1.2
7	50,865.9	7750.2	1132.9	610.3	15.2	2.2	1.2
8	56,329.1	9083.0	1058.6	699.5	16.1	1.9	1.2
13	284,690.1	43,417.5	5311.2	3686.6	15.3	1.9	1.3
15	54,049.8	8455.8	634.5	800.7	15.6	1.2	1.5
16	45,101.0	6888.2	818.0	573.0	15.3	1.8	1.3
18	60,769.6	8125.8	1225.2	Absent	13.4	2.0	Absent
20	69,527.8	10,387.5	952.2	1142.0	14.9	1.4	1.6
21	62,549.3	9614.8	1131.5	743.0	15.4	1.8	1.2
21B	61,207.8	9577.1	1459.4	392.3	15.6	2.4	0.6

Compound	Carbon Number	Predicted 13C:12C
TEP	6	7.1
TCPP	9	11.0
TBEP	18	24.7
TPPA	18	24.7

Compound	Sample	M+ Abundance	M + 1 Abundance	M + 2 Abundance	M + Na Abundance	%M + 1	%M +2	%M + Na
TEP	1B	38,476.3	2814.3	339.9	100.7	7.3	0.9	0.3
TEP	9	57,530.3	4713.6	439.5	61.8	8.2	0.8	0.1
TCPP	3	18,689.9	2223.2	18,071.1	275.8	11.9	96.7	1.5
TCPP	6	12,844.8	1654.1	13,683.1	223.0	12.9	106.5	1.7
TCPP	9	16,919.9	2008.9	16,692.4	158.0	11.9	98.7	0.9
TCPP	9B	13,482.5	1822.2	13,147.0	181.7	13.5	97.5	1.3
TCPP	10	13,497.1	1392.4	12,449.6	143.7	10.3	92.2	1.1
TBEP	9	42,664.4	9630.9	2224.3	1401.7	22.6	5.2	3.3
TBEP	9B	31,192.9	6713.6	1398.3	885.4	21.5	4.5	2.8
TBEP	19	24,305.3	5471.6	873.2	1043.7	22.5	3.6	4.3
TPPA	3	3424.7	862.6	108.6	98.2	25.2	3.2	2.9
TPPA	4	5045.6	761.5	193.1	95.2	15.1	3.8	1.9
TPPA	5	5494.5	1258.8	160.4	53.3	22.9	2.9	1.0
TPPA	9	19,139.7	4210.9	809.0	593.5	22.0	4.2	3.1
TPPA	9B	12,102.1	3054.9	315.2	315.7	25.2	2.6	2.6

3.2. SDS Suspect Screening: Engine and Hydraulic Oil

A suspect screening for organophosphate compounds was completed, searching for compounds known to exist in aircraft engine oil and hydraulic oil, as well as those OPEs commonly found in the aircraft cabin in previous research [14,28–30]. Suspect compounds were selected for analysis by their listed presence at percent levels within Material Safety Data Sheets of oils approved for, and commonly used on commercial turbojet aircraft [23–26].

Of the other compounds listed as contributing to the composition of aircraft engine and hydraulic oil on the SDS sheets, only triphenyl phosphate (TPhP) and tricresyl phosphate (TCP) were identified with sufficient match factors to warrant further analysis in aircraft potable water (Table 2). In previous studies, TPhP has been found in the aircraft cabin via air and wipe sampling [28–30]. Of the samples tested in this study, TPhP was identified in four of the 18 Mohm blanks, three of the airport tap water blanks, and fifteen of the aircraft water samples. TPhP is listed as contributing 1–5% of a commonly used hydraulic fluid 24 and is also found in the same concentration range within new fluid formulations [40]. TPhP is suspected to have been found above LOD in five samples representing three flights (Table 4). Three samples: 3, 9, and 9B, exceeded LOQ for the compound (Table 4).

Table 4. Identification, detection, and quantification key for suspected compounds. ND indicates that the compound was not found above 90.00 in a spectral library match. ID indicates that the suspect compound was identified via spectral library match with a score above 90.00. >LOD indicates that the level of detection threshold was reached. >LOQ indicates that the level of quantification over 18 Mohm and airport tap water blanks was reached.

Sample	Aircraft	TBP	TCPP	TEP	TBEP	TPP	TCP
1b	Boeing 737-700	ID	ID	>LOD	ID	ID	ND
2	Boeing 737-700	ID	ID	ID	ID	ND	ND
2b	Boeing 737-700	ID	ID	ID	ID	ND	ND
3	Boeing 737 Max	>LOD	>LOQ	ID	ID	>LOD	ID
4	Boeing 737 Max	>LOD	ID	ID	ID	>LOQ	ND
5	Boeing 737 Max	>LOD	ID	ID	ID	>LOD	ND
6	Airbus A330-300	ID	>LOD	ID	ID	ND	ND
7	Boeing 737 Max	>LOD	ID	ID	ID	ID	ND
8	Boeing 737-800	>LOD	ID	ID	ND	ND	ND
9	Airbus A330-300	ID	>LOQ	>LOD	>LOD	>LOQ	ND
9b	Airbus A330-300	ID	>LOD	ID	>LOD	>LOQ	ND
10	Airbus A320-211	ID	>LOD	ID	ID	ND	ND
10b	Airbus A320-211	ID	ID	ID	ID	ND	ND
11	Boeing 737-800	ID	ID	ID	ID	ID	ND
11b	Boeing 737-800	ID	ID	ID	ID	ID	ND
12	Boeing 787-900	ID	ID	ID	ID	ID	ND
12b	Boeing 787-900	ID	ID	ID	ID	ID	ND
13	Boeing 737-800	>LOQ	ID	ID	ID	ID	ND
14	Avro RJ100	ID	ID	ID	ID	ID	ND
15	Embraer E190	>LOD	ID	ID	ID	ID	ND
16	Airbus A330-300	>LOD	ID	ID	ID	ID	ND
17	Boeing 737-800	ID	ID	ID	ID	ID	ND
18	Boeing 737-700	>LOD	ID	ID	ID	ND	ND
19	Boeing 737 Max	ID	ID	ID	>LOD	ID	ND
20	Boeing 737 Max	>LOD	ID	ID	ID	ID	ND
21	Boeing 787-900	>LOD	ID	ID	ID	ID	ND
21b	Boeing 787-900	>LOD	ID	ID	ID	ND	ND

It should be noted that TPhP was found in other flights with peak areas above the LOD and, in one case, above LOQ but were not included due to the match score threshold (example: Flight 13 met LOQ for TPhP; Score 89.07; as such it was omitted from further analysis). Sub-ppm mass accuracy for the compound was determined for all samples (Table 2). No isobaric compounds were identified in the suspect screening. When analyzing the MSMS data, no identifiable fragments were generated for the compound. However, for most samples in which TPhP was detected, the 13C:12C ratio closely resembled the predicted value for samples that met LOQ (Table 3).

An exception was sample 4, which met LOQ for TPhP but had an isotope ratio that suggested a much lower carbon number (Table 3). Sodium adducts of TPhP were found in each of the detected samples, but the mass accuracy in four of the five samples for the adduct exceeded one ppm ($|\bar{x}| = 2.45$ ppm). TCP had a sufficient match factor in only one aircraft water sample (3), and this sample did not meet LOD or LOQ requirements.

3.3. Other Organophosphates

Several other organophosphates have been identified in previous research in the aircraft cabin [14]. Included amongst these compounds are tris(chloroethyl) phosphate (TCEP), tris(chloropropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(butoxy ethyl) phosphate (TEBP), 2-ethylhexyl diphenyl phosphate (DPEHP), dibutyl phenyl phosphate (DBPP), tris(ethylhexyl) phosphate (TEHP), and trixylenyl phosphate (TXP).

When inspecting aircraft potable water for the compounds listed, TBEP and TCPP were identified (Tables 2 and 4). Additionally, Triethyl phosphate (TEP), while not previously described on aircraft, was also identified. TEP and TCPP met the 90.00 match score for all samples and blanks; TBEP met the match score for all samples and blanks, excluding Airport Water Blank 1 and Aircraft Water Sample 8. The compounds were found and met LOD or LOQ thresholds on multiple flights, albeit less frequently than TBP (Tables 2 and 4)

TEP displayed the same confirmatory phosphate fragment as TBP (m/z = 98.984~) and a mass accuracy below 1ppm. Of the two TBEP detects, one (sample 9b) had the same fragment (m/z = 98.984~), as well as fragments present at m/z 299.165~ and 199.073~ describing the molecular ion less one and two butoxyethyl groups respectively (Table 2). No confirmatory fragments were determined for TCPP, but mass accuracy for the molecular ion remained below one ppm for the samples that met LOD ($|\bar{x}|$ = 0.45 ppm). The ^{13}C:^{12}C percentages for each compound suggest that the carbon number matches the suspected molecule (Table 3). Additionally, the M^{+2} isotope percentages of TCPP detections suggest the presence of three chlorine atoms in the molecule (Tables 2 and 3). Sodium adducts of TEP, TCPP, and TBEP were found in all samples in which they were detected. The mass accuracy of the sodium adducts was below one ppm for TBEP but above one for TEP and TCPP (Table 2).

3.4. Confidence of Qualification

The presence of TBP on aircraft, coupled with the exact mass match, fragment, isotope, and adduct data, and a standard match, confirms that TBP is in the potable water of a large percentage of the jet aircraft included in this study. Reference standards for the remaining compounds identified in this study were not available and this precludes them from the application of the same confidence level under the identification confidence scale outlined by Schymanski et al. [39]. Of the other organophosphates screened for, TPhP can be considered a tentative candidate (Level 3) (Table 2). This is supported by its known presence in aircraft fluids and an identical pathway to the potable water system of aircraft. TEP, TBEP, and TCPP can also be considered tentative candidates as aircraft water contaminants, as each was identified with a high degree of mass accuracy. TBEP and TCPP are known to exist on aircraft, but a contaminant pathway for the compounds to enter the potable water system onboard the aircraft is not established (Table 2). TBEP is supported by fragment and sodium adduct data, strengthening the confidence in its identification. TCPP lacks conclusive fragment data but has a robust isotopic match and was detected in 20% of all flights. TEP is not previously known to exist on aircraft, and the mechanism by which it could be concentrated in or otherwise enter aircraft potable water systems is not established; the identification is supported by fragment, adduct, and isotopic data (Table 2).

^{13}C pentaerythritol, a potential polymeric fragment of the C5 to C10 fatty acid esters of pentaerythritol and dipentaerythritol, was selected as an internal standard. The intact esters were identified as the primary component in Mobil Jet oil II 19. The selection of the internal standard proved to be a misstep, as fragments of the intact esters of the aircraft oil were not identified in any sample. Additionally, the selection does not allow for comparison or quantification with compounds of concern that were identified, (namely organophosphates) because of molecular and retention time dissimilarity. Increased peak area of the IS in the 18 Mohm blanks (First 18 Mohm blank preparation: Mean peak area = 721574, RSD% peak area = 1.13) suggests that the analytical sample matrix may be interacting with or suppressing the instrumental response for the IS compound. While not useful for analyte identification or quantification, the internal standard, prepared as described above, demonstrates instrument operational parameters for the analytical samples. Future quantitative work will require the selection of more appropriate internal standards, however, as the primary purpose of this research is the qualitative suspect screening for compounds of concern, this does not impact our findings.

3.5. Discussion of Significance and Aircraft Implications

The suspect organophosphates were detected across aircraft manufacturers and airframes (Table 4). Contaminant accumulation in potable water seemed commonplace regardless of aircraft type (Table 4). Of importance was the detection of TBP in the potable water of samples 21 and 21b: This aircraft type, unlike all other commercial jet aircraft, does not use bleed air to pressurize the cabin; but, like other commercial jet aircraft, does utilize the pneumatic system and bleed air for a variety of other functions on the aircraft, including, pressurizing the hydraulic system reservoirs and the potable water storage tank in flight [41,42]. The detection of TBP in these samples indicates that an alternative route of exposure to organophosphates of concern is present for this aircraft type, regardless of removing bleed air from use in cabin pressurization. Additionally, the comparatively high concentration of TBP found in sample 13 may be indicative of a leak of hydraulic fluid into the pneumatic system on that aircraft. This study, largely due to the challenges of opportunistic sampling on aircraft, has a relatively small sample size. To determine the scale of aircraft water contamination, further samples

are required and quantitative methods should be employed. Notwithstanding these caveats, this manuscript demonstrates the proof of the contaminant pathway and the necessity for further research.

4. Conclusions

This study provides evidence that TBP, the primary aircraft hydraulic oil constituent, is present in aircraft potable water, detected regularly when compared against relative peak areas of the compound in municipal tap water and 18 Mohm blanks. Similarly, there is a high likelihood that other organophosphate esters, both previously known and unknown to exist within the aircraft cabin, are present in the potable water of a large percentage of aircraft. These findings are not exclusive to an individual aircraft, airframe, or manufacturer, and appear to impact both bleed-air cabin pressurized and non-bleed air cabin pressurization aircraft. With this conclusion, the contaminant pathway from the pneumatic system to the potable water system is validated and implies that any contaminant from the engines, hydraulic system, or other aircraft systems connected to the pneumatic system may contribute to water fouling.

Airport tap water was not collected from all municipalities, and as such, the municipal source water for each flight cannot be directly compared with each flight. This limits direct comparison to two flights (samples 10, 21 and respective duplicates) and slightly more broadly to other flights departing from Calgary or Toronto with the assumption that the municipal water chemical composition remains relatively consistent over time. This is further limited by the fact that aircraft do not drain to empty and fill their potable water tanks as a practice at each departing airport. This means that there is a high likelihood that the potable water found in every aircraft is not solely from one airport municipality and may be an assemblage of water from many municipalities. Aircraft receiving water from multiple municipal sources, both domestic and international, may seem to add variability; however, this study has multiple samples taken from aircraft with potable water topped up in the same municipal water districts. This repeat sampling limits the likelihood of contamination being solely attributed to water sources and strengthens the argument that the contamination is originating on the aircraft; namely, that because water was taken from multiple aircraft, that were topped up at the same municipal source, and then demonstrated different chemical compositions, that the aircraft themselves were likely substantial contributors of the observed chemical loadings. The OPEs (TEP, TCPP, and TBEP) suspected to be present in the water but not yet attributed to a source linked to the potable water system on aircraft, should be further investigated to establish the contamination pathway. Additionally, further research should seek to establish thresholds that may establish oil leak conditions on aircraft, examine additional chemical classes, confirm the tentative and probable contaminants with standards, and quantify the contaminants' concentrations.

The results of this study indicate that aircraft potable water systems should be monitored for a variety of chemical contaminants. The currently monitored and regulated microbiological water quality standards on aircraft are insufficient, as they do not accurately describe the potential chemical risk of consumption or use of the product. Quantification of this exposure risk to those flying and flying on aircraft should be completed and steps taken to mitigate the contaminants identified from entering the potable water system.

Supplementary Materials

The additional data and information can be downloaded at: https://media.sciltp.com/articles/others/25050 91110587297/ECCS-738-Supplementary-final.pdf. Table S1: Analytical separation method used for potable water analysis; Table S2: ESI ion source and auto-MS/MS parameters used for potable water analysis.

Author Contributions

Conceptualization: K.H. Methodology: K.H., G.O'., E.F., R.S. Investigation: K.H., Trained citizen scientists. Formal analysis: K.H., E.F. Data curation: K.H., G.R. Writing—original draft: K.H., E.F. Writing—review & editing: K.H., D.M., E.F., R.S., G.R., A.D., G.O'. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Raw and processed data is available by request to the corresponding author.

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Conflicts of Interest

There is no conflict of interest to declare.

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