

## Analysis of Organophosphate Hydraulic Fluids in U.S. Air Force Base Soils

M. D. David, J. N. Seiber

Center for Environmental Sciences and Engineering and Department of Environmental and Resource Sciences, University of Nevada,  
Reno, Nevada 89557, USA

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**Abstract.** Tri-aryl and tri-alkyl organophosphates (TAPs) have been used extensively as flame-retardant hydraulic fluids and fluid additives in commercial and military aircraft. Up to 80% of the consumption of these fluids has been estimated to be lost to unrecovered leakage. Tri-aryl phosphate components of these fluids are resistant to volatilization and solubilization in water, thus, their primary environmental fate pathway is sorption to soils. Environmental audits of military air bases generally do not include quantification of these compounds in soils. We have determined the presence and extent of TAP contamination in soil samples from several U.S. Air Force bases. Soils were collected, extracted, and analyzed using GC/FPD and GC/MS. Tricresyl phosphate was the most frequently found TAP in soil, ranging from 0.02 to 130 ppm. Other TAPs in soils included triphenyl phosphate and isopropylated triphenyl phosphate. Observations are made regarding the distribution, typical concentrations, persistence, and need for further testing of TAPs in soils at military installations. Additionally, GC and mass spectral data for these TAPs are presented, along with methods for their extraction, sample clean-up, and quantification.

Tri-alkyl/aryl phosphate esters (TAPs) are widely used as flame-retardant plasticizers and functional fluids such as hydraulic fluids and additives to brake and transmission fluids (Federal Register 1983; Muir 1984; Boethling and Cooper 1985; Syracuse Research Corp. 1988; Carlsson *et al.* 1997; Seiber *et al.* 1998). Because of their flame retardancy, stability, and other physical properties, TAPs have been extensively used in aviation hydraulic fluids. Fluids in military aircraft use TAPs primarily as antiwear additives at 1–3% levels (S. Flannagan, personal communication 1997).

The total production volume of TAPs, including those used for hydraulic fluids, fluid additives, and plasticizers, exceeded 45 million kg during the peak production years of the late 1970s. In the early 1990s, total production was in the range of 30 million kg per year (Federal Register 1992). These figures and the relative lack of environmental data prompted the EPA, under the authority of the Interagency Testing Committee of the

Toxic Substances Control Act (TSCA), to request more data from the manufacturers in the early 1980s (Federal Register 1983). In 1992, rules were proposed by EPA requiring testing, reporting, and record keeping by manufacturers of aryl phosphate base stocks (Federal Register 1992).

Measurements of environmental residues of TAPs from hydraulic fluid release are sparse, although industrial TAPs have been reported in pine needles (Aston *et al.* 1996), surface waters (Ishikawa *et al.* 1985; Paxeus 1996), and in fish, sediment, and biota (Muir *et al.* 1981; LeBel *et al.* 1989). Some estimates have been made of the total amount of tri-aryl phosphates used for flame-retardant hydraulic fluids (including aviation and other applications) and the percentage of that use which is ultimately released and unrecovered. Up to 80% of the TAP hydraulic fluid consumption in the late 1970s (12 million kg in 1977) was for replacement of losses due to unrecovered leakage (Federal Register 1983; Muir 1984).

Localized fate of TAPs is dictated by their physical properties. Tri-aryl TAPs have water solubilities in the range of 0.36–2.2 mg/L, low vapor pressures ( $10^{-6}$ – $10^{-8}$  atm), very low Henry's Law constants ( $10^{-6}$ – $10^{-8}$  atm m<sup>3</sup>/mol) (Muir 1984; Boethling and Cooper 1985), and high calculated sorption coefficients (est.  $K_{oc}$  8,000–18,000) (Lyman *et al.* 1990). Water concentrations of TAPs due to releases are expected to be low, with accumulation occurring in the sediments. Bioaccumulation could also occur. Reported bioconcentration factors for the tri-aryl phosphate esters studied here are in the range of 570–1,420 in whole fish (Muir *et al.* 1983).

Triphenylphosphate (TPP) is acutely toxic to fish, up to 10–100 times more toxic than other tri-aryl phosphate esters found in hydraulic fluids such as isopropylphenyldiphenylphosphate (IPDP) (Mayer *et al.* 1981). The potential hazard posed by TAPs in soils at reported concentrations (100 ppm) (David and Seiber 1996) is difficult to assess with the current body of toxicity data.

Although environmental contamination of U.S. military bases is being actively studied, there is no protocol for the sampling and determination of TAPs. As decommissioned military bases are being transferred to civilian uses, environmental levels of these compounds need to be assessed in order to determine exposure and risks for humans and wildlife. We describe here the distribution and concentration of TAPs in soil resulting from their use in hydraulic fluids at U.S. Air Force bases. The types of TAPs present and their concentrations and

locations in the soil of the bases are presented. Additionally, analytical methods for the extraction, clean-up, identification, and quantification of these TAPs were developed appropriate for contaminated soils.

## Materials and Methods

### Chemicals

All solvents were HPLC-grade (Fisher Scientific). Pure TAP standards included triphenylphosphate (TPP, Aldrich, 99+%), tri-*m*-cresylphosphate (TmCP, Pfaltz and Bauer, 93%), tri-*p*-cresylphosphate (TpCP, Pfaltz and Bauer), tri-*o*-cresylphosphate (ToCP, ICN Biomedicals), and tributylphosphate (TBP, Aldrich, 99%). Synthesis of tri-*p*-isopropylphenylphosphate used the reagents *p*-isopropylphenol (Pfaltz and Bauer, 98%), phosphorus oxychloride (POCl<sub>3</sub>, Aldrich, 99%), and triethylamine (TEA, Acros, 99%).

Samples of three flame-retardant hydraulic fluids were obtained for spectral analysis. The first was FMC's (Princeton, NJ) Kronitex-100. The second was a sample of a military fluid, MIL-H-83282, obtained from the stock supplies of Beale Air Force Base, the only active military installation from which soil samples were taken. The third fluid was a sample of Hy-Jet from Chevron (Richmond, CA).

### TAP Hydraulic Fluids

The MIL-H-83282 fluid was primarily poly- $\alpha$ -olefin with only 1–2% TAP esters. A sample was prepared for analysis by the following florisil clean-up method, which was developed for clean-up of soil extracts: florisil (7–8 g activated at 110°C for at least 5 h) was transferred to a glass clean-up column of 1–2 cm ID topped with clean sand. The florisil was packed under vacuum and soaked with hexane. The sample in hexane was transferred onto the column and was immediately followed by the first elution of 100 ml 10% ethyl ether in hexane. The first 90–100 ml of this elution, containing most of the poly-olefin fluid, was collected and disposed. TAP analytes were then eluted with 100 ml of 17% methanol in ethyl ether, which was reduced to <2 ml and adjusted to 2.0 ml in methanol. The Hy-Jet and Kronitex-100 samples were diluted in ethyl acetate and analyzed by GC/FPD and GC/MS. Identification of TAP components was accomplished by comparison of GC retention times with known standards and GC-MS analysis.

### TAP Synthesis

Because standards were not readily available for isopropylated triphenylphosphate, one isomer was synthesized using a synthetic approach in general use for the production of TAP esters (Muir 1984). Phosphorus oxychloride (1.5 g) and 4-isopropylphenol (4.2 g) were combined in 50 ml toluene in the presence of excess TEA. The solution was refluxed for 5 h, then washed 3 times with 1.0 N aqueous NaOH, deionized water (3 $\times$ ) and dilute acid (3 $\times$  0.1 M HCl). The washed solution containing tri-*p*-isopropylphenylphosphate was filtered over sodium sulfate and diluted in toluene for analysis by GC-MS.

### Soil Samples

Three TAP-contaminated soil samples were obtained from the U.S. Air Force Armstrong Laboratory Occupational and Environmental Health Directorate, Brooks Air Force Base, TX. The three samples, originating

from different unidentified sites, were labeled AFB 1, 2, and 3. Field sampling was accomplished at three current or former USAF air fields as described below. All samples taken from these sites consisted of 500–1,000 g collected by combining triplicate subsamples of a 1 m<sup>2</sup> area at the described location. Zero background levels were established with blank samples taken during the sampling events.

Mather AFB in Rancho Cordova, Sacramento County, CA, was sampled on September 9, 1994. Mather AFB has subsequently been decommissioned and now supports multiple uses, including serving as a private airport. When active, Mather AFB was used by a variety of Air Force cargo and refueling aircraft. Soil samples were taken at two sites, defined by an environmental audit of the Mather base as sites 15 and 69. Site 15 included a ditch that received surface drainage from the entire base and the outflow from the hangar area, washpads, and service areas of the base through a concrete culvert. Site 69 was a munitions disposal site.

Stead AFB, located in Stead, Washoe County, NV, was sampled on September 20, 1994. Although the Stead AFB was closed to military use in the 1950s, it is still active for some private use, including seasonally heavy traffic of private and vintage aircraft. A soil sample was taken from a drainage ditch just outside the hangar area.

Beale AFB near Grass Valley, Nevada County, CA, was sampled on April 24, 1996. Beale is an active base that, until 1989, housed SR-71 reconnaissance aircraft. At the time of sampling, the only military aircraft being flown from Beale was the U2 reconnaissance aircraft. Soil samples were taken from sites 1, 5, and 11, as defined by an internal Beale site survey. Site 1 is a drainage ditch approximately 225 m west of the runway that drains runoff from the flightline areas and runway surfaces. Samples were taken in the drainage ditch from the sandy lining of the culvert just below the outflow (soil 1A), from the soil lining the ditch about 20 m downstream from the outflow (soil 1B), and from sediment near the bank, which was displaced from the ditch during dredging of the channel in 1991 (soil 1C). Site 5 is the drainage area between the old SR-71 hangars and the runways. Four soil samples were taken and labeled soils 5A, B, C, and D. Site 11 is the soil-lined drainage near the aircraft ground equipment (AGE) maintenance area. Two soil samples were taken of the sediment just at the water surface level of this grass covered drainage, and labeled soils 11A and 11B.

### Sample Preparation

Samples were stored under ambient conditions during transport and processed within 48 h of their collection. Soil samples were air-dried over a period of 12–18 h and sieved through a USGS standard sieve (#18). Extractions of 10–60 g were accomplished using Soxhlet extractors for 5–7 h (approximate cycle time = one every 10 min) with 175 ml ethyl acetate. The extraction solvent was exchanged for hexane and adjusted using nitrogen evaporation to 2 ml. The florisil clean-up method described previously for industrial fluid samples was then applied to the soil extracts.

### Analysis

Quantification of TAPs in soil extracts was accomplished by GC/FPD peak heights. TAPs for which standards were obtained (*i.e.*, TPP and TCP isomers) were quantified based on standard curves for the individual compounds. Quantification of isopropylated triphenylphosphate (IPTPP) in soils was based on standard curves developed with the Hy-Jet fluid.

All hydraulic fluids and soil extracts were analyzed using a Hewlett-Packard model 5890 series II gas chromatograph equipped with a flame photometric (FPD, P mode) detector. GC temperature was programmed from an initial temperature of 165°C for 1 min, ramped to 245°C at 10°C/min, with a final time of 9–15 min. Two columns were

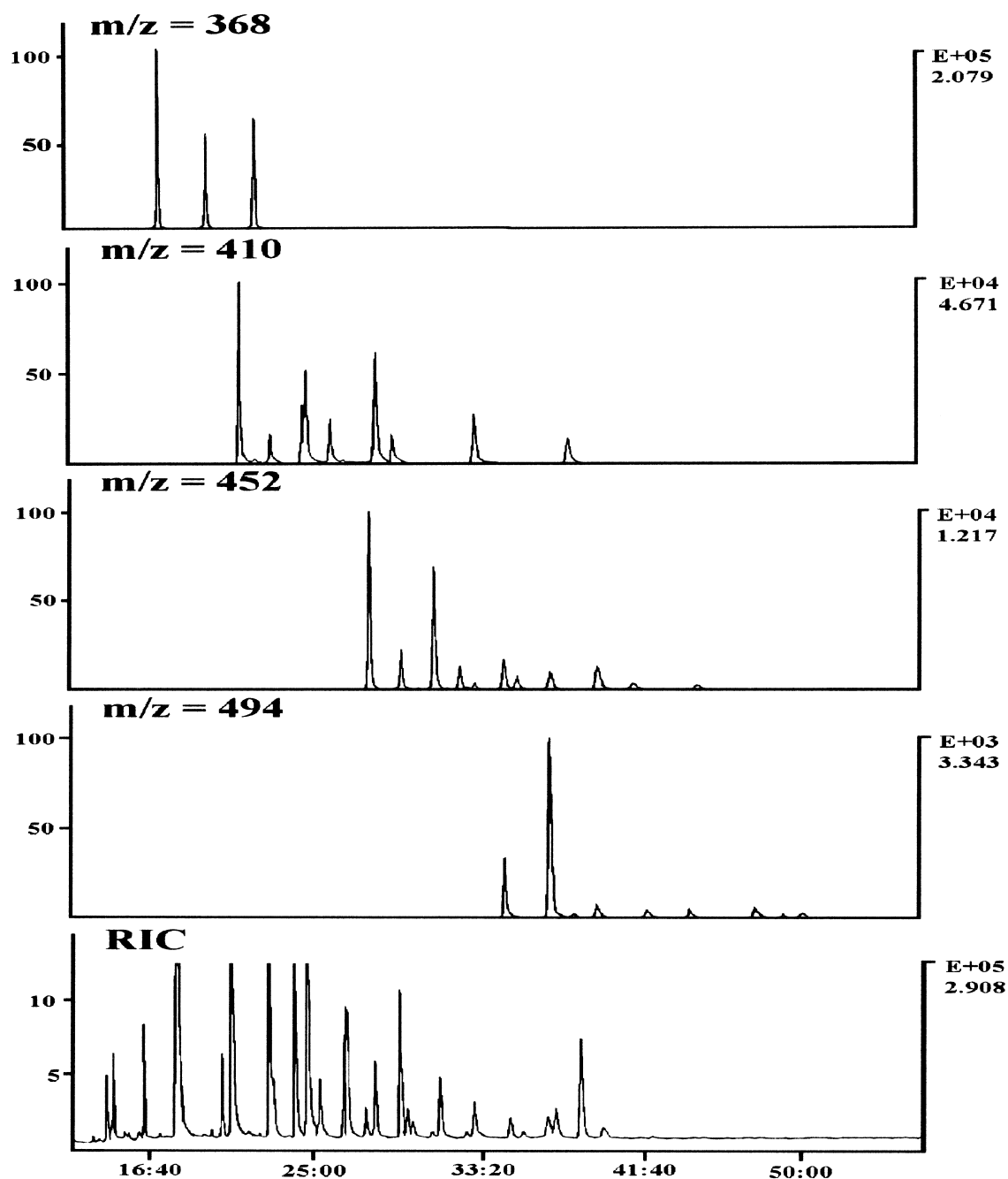


Fig. 1. GC/MS SIM chromatogram of Hy-Jet fluid containing IPTPP: RIC and 368, 410, 452, and 494 ions displayed

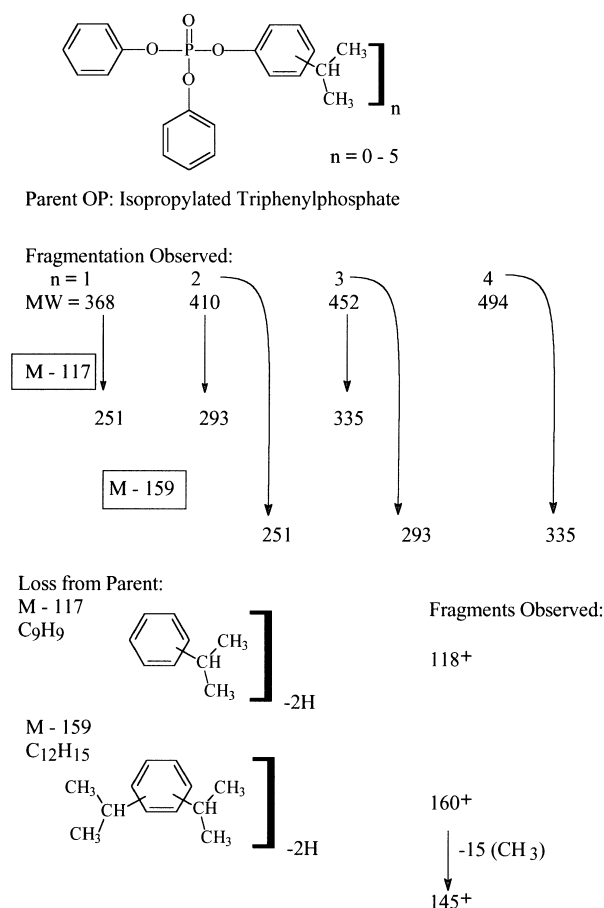
used: a 30-m 0.32 mm ID DB-5 of 1.0  $\mu\text{m}$  film thickness and a 30-m 0.53 mm ID RTX-1 of 0.25  $\mu\text{m}$  film thickness. Both columns were used with a carrier gas of helium at 3 ml/min.

Mass spectral analyses of selected soil extracts, TAP standards, and hydraulic fluids were obtained using a Finnigan MAT ssQ-710 quadrupole mass spectrometer interfaced with a Varian 3400 GC. MS of the synthetic tri-*p*-isopropylphenylphosphate was obtained on a Hewlett-Packard 5989A with a 5890 II GC. Both instruments were operated in electron impact mode at 70 eV with a molecular scan range of 50–600 AMU and a 5-min solvent delay. Both GCs were equipped with similar 30-m DB-5 columns of 0.25  $\mu\text{m}$  film thickness and 0.25 mm ID GC temperature profiles were similar to the program described previously, with the temperature ramp slowed to 5°C/min and the final

time extended by 5 min. The carrier gas was helium with flow rate of 1 ml/min.

## Results and Discussion

Comparison of retention times of peaks present in the initial chromatograms of the hydraulic fluids with TAP standards was used to identify the main TAP components of FMC's Kronitex-100 and the MIL-H-83282. Kronitex-100 is primarily TCP fluid, containing a mixture of four TCP isomers: tri-*m*-cresylphosphate, bis-*m,p*-cresylphosphate, bis-*p,m*-cresylphos-



**Fig. 2.** Mass spectral fragmentation patterns of isopropylated triphenylphosphate

**Table 1.** Spectral and chromatographic data of hydraulic fluids

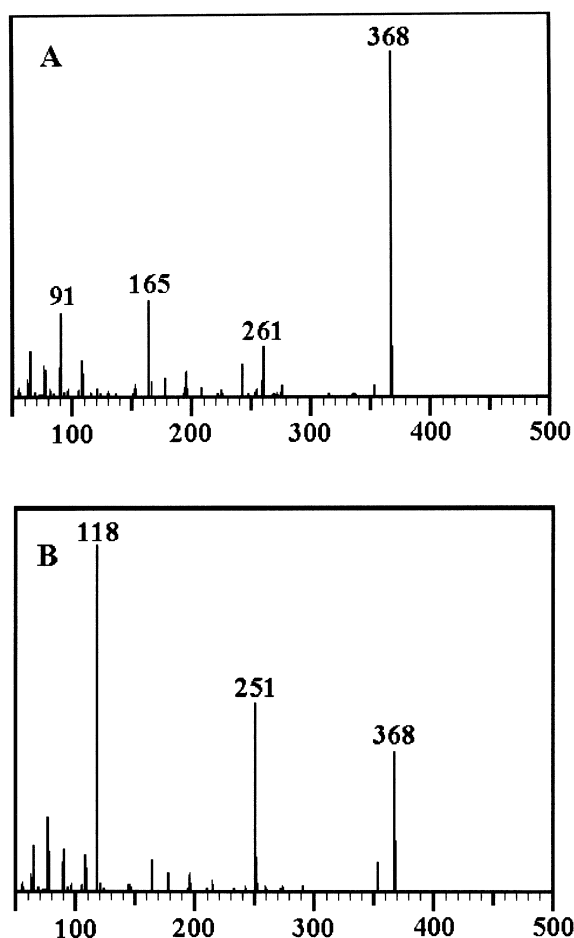
Hydraulic Fluid	Mass. Spec. Ions (m/z)		GC RT (min) <sup>a</sup>	Number of Isomers
	Parent	Fragments		
Hy-Jet (IPTPP)	368	118, 251, 353	23–25	3
	410	118, 251, 293, or 145, 160	24.5–37	11
	452	118, 251, 335, 437, and/or 145, 160	28–44	11+
	494	118, 251, 335, and 145, 160	35–50	9+
Kronitex (TCP)	368	165, 261	24–27	4
Tri- <i>p</i> -isopropyl phenylphosphate <sup>b</sup>	452	437, 251, 335	38	1

<sup>a</sup> GC retention time, in minutes, from total ion chromatograph

<sup>b</sup> Synthesized product

phate, and tri-*p*-cresylphosphate. The same isomers of TCP were present at a level of about 2% in the MIL-H-83282 fluid. The neurotoxic ortho isomer of TCP was absent in both of these fluids.

Chromatograms of the Hy-Jet commercial product revealed its primary composition (65%) as TBP. Preliminary analysis of spectra from the GC/MS of Hy-Jet revealed that the most significant later eluting peaks of the total ion chromatograph,

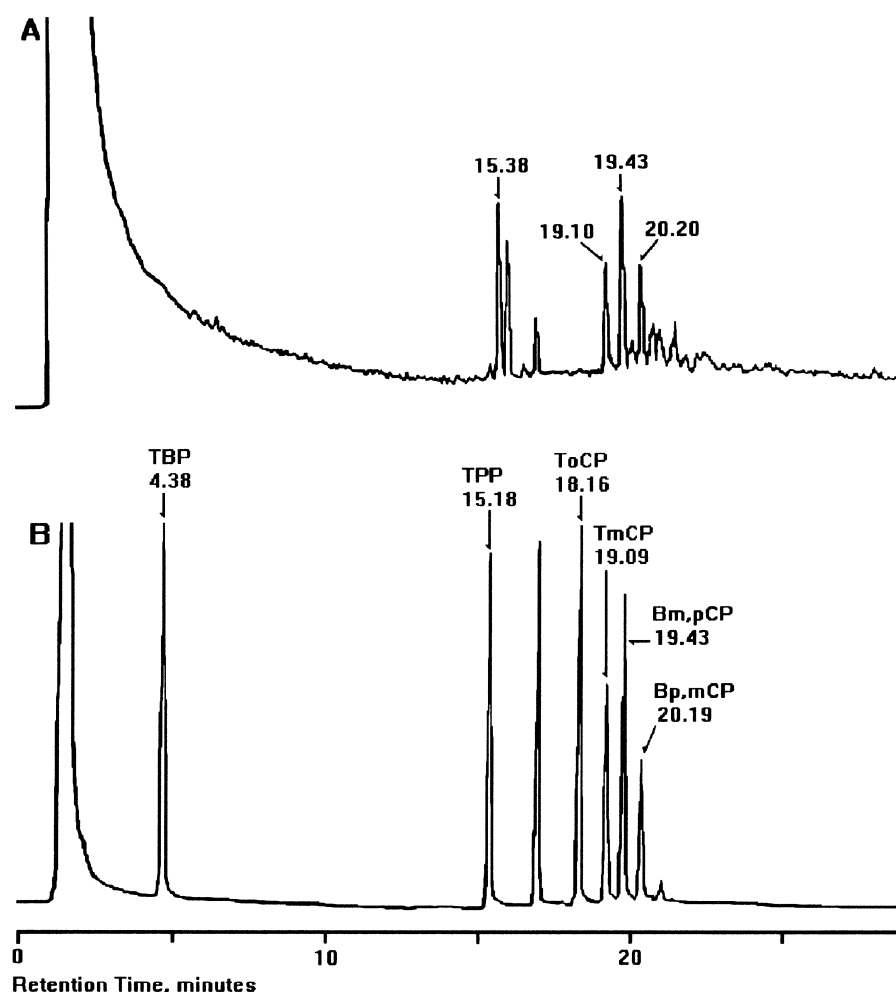


**Fig. 3.** Comparison of mass spectra of tricresylphosphate (A) and isopropylphenyldiphenylphosphate (B)

which corresponded to P-containing compounds in the GC/FPD analysis, had parent ion peaks of m/z 368, 410, 452, and 494. The consistent difference of 42 mass units between the peaks suggested C<sub>3</sub>H<sub>7</sub>, or propyl substituents. In the literature, an industrial mixture of isopropylated triphenyl phosphate (IPTPP) is described, with isopropyl substituents of TPP present in zero to five units (Syracuse Research Corp. 1988).

In SIM (single ion monitoring) mode set for the formula weights of 0–5 isopropyl substituents of TPP, the elution of at least 34 components of this mixture was observed. Figure 1 shows the SIM chromatograms for the ions m/z 368, 410, 452, and 494 (n = 1–4 isopropyl substituents, respectively), along with the reconstructed total ion chromatogram (RIC). As expected, the higher molecular weight components elute later. Compounds with 1–2 isopropyl groups are the more prevalent peaks in the mixture. Fragmentation patterns of the components of this mixture correspond to losses from the parent compound of mono- or diisopropyl phenyl groups. Figure 2 shows proposed structures of significant fragments.

The number of isomers for each molecular weight can be determined from the SIM data. The three isomers of MW = 368 represent isopropylphenyldiphenylphosphate, with a single isopropyl group in either the ortho, meta, or para position on one of the three phenyl groups. The 11 isomers of MW = 410 represent either two singly substituted isopropyl phenyls, which



**Fig. 4.** Comparison of GC/FPD chromatograms of (A) Mather AFB soil extract (soil 15C) and (B) TCP-containing hydraulic fluid (Kronitex) and TBP, TPP, and ToCP standards

can each be either *o*, *m*, or *p* (six possible isomers), or a single disubstituted phenyl, which could be five possible different isomers (*o,o*, *m,m*, *m,p*, *o,p*, or *o,m*) for a total of 11.

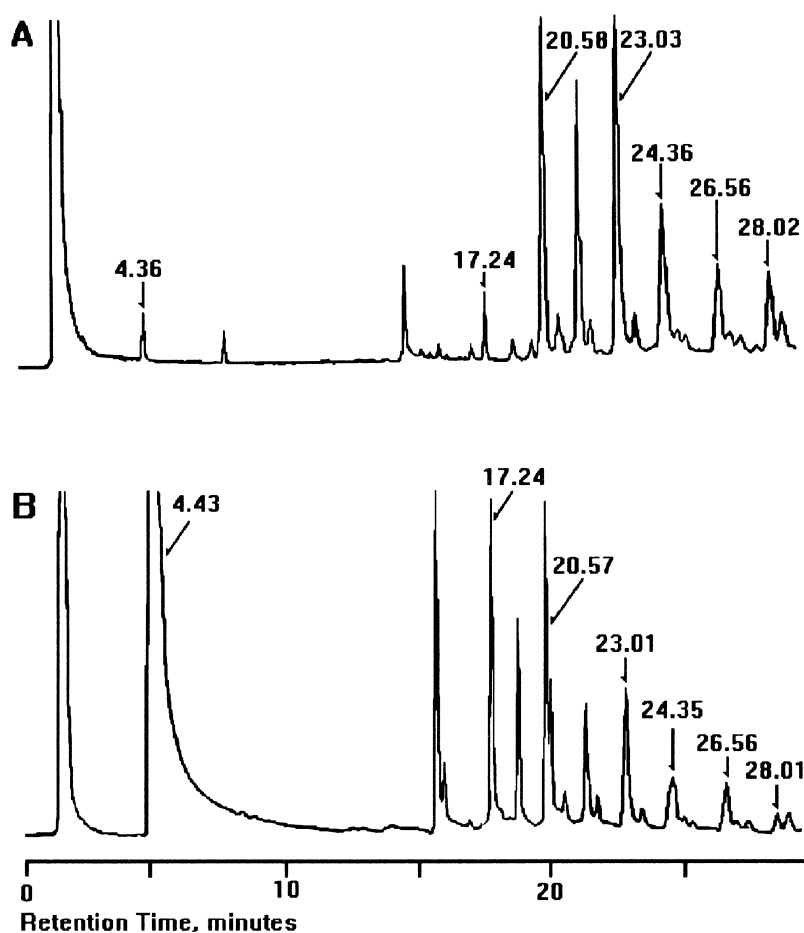
From the numbers of isomers present in the industrial Hy-Jet fluid, it is apparent that the ortho-isopropylated component is included in the mixture (*i.e.*, if it were not, there would be only five possible isomers of IPTPP with MW = 410, while 11 isomers are observed). Although certain *o*-alkylated derivatives of triphenyl phosphate, including tri-*o*-cresyl phosphate, are potent delayed neurotoxins (Eto 1974), the ortho-isopropyl isomer is apparently not of sufficient toxicological concern to be eliminated from the mixture.

A similar mass spectral analysis was accomplished with the TCP-based Kronitex fluid. Identifications of the four significant isomers present in the fluid were made by matching of GC retention times with individual isomer standards. Table 1 summarizes the important mass spectral data from the analysis of both the Hy-Jet and the Kronitex TAP based hydraulic fluids, including approximate GC retention time, the parent ions, and the significant EI/MS fragments. GC retention times listed are from GC/MS analyses under the conditions previously described. Mass spectral analysis of the synthesized tri-*p*-isopropylphenylphosphate demonstrated fragmentation patterns consistent with those observed for the components of the Hy-Jet fluid.

One of the most prevalent compounds in the IPTPP mixture, the mono-substituted isopropylphenyldiphenylphosphate, has the same molecular weight as TCP (368) and similar GC retention patterns. Distinguishing between the two can be accomplished by observation of MS fragmentation patterns (Figure 3). While both show a strong parent ion peak at  $m/z = 368$ , the fragmentation patterns are distinctive, thus allowing ready differentiation in unknown environmental samples.

#### OPs in AFB Soils

Identification and quantification of the TAPs present in soil extracts was accomplished, when possible, by matching retention times with TAP peaks present in the flame-retardant hydraulic fluids. Figure 4 shows a comparison of a GC/FPD chromatogram of an extract of Mather AFB site 15 soil to the TCP-based fluid Kronitex. Figure 5 compares a GC/FPD chromatogram of an extraction of the Stead soil sample to that of Hy-Jet. Because of the matching retention times and the similarities of pattern of elution of these TAP-containing peaks, identification of the type of fluid responsible for the contamination was relatively straightforward. GC/MS analysis of the Stead soil extract confirmed the presence of the mixed IPTPP components of Hy-Jet in the soil. Low levels of TCP and



**Fig. 5.** Comparison of GC/FPD chromatograms of (A) Stead AFB soil extract and (B) TBP and IPTPP-containing hydraulic fluid (Hy-Jet)

**Table 2.** Spectral and chromatographic data of selected AFB soil extracts

AFB Soil Extract	Mass. Spec. Ions (m/z)		GC RT (min) <sup>a</sup>	Number of Isomers	OP Identified
	Parent	Fragments			
Stead	368	118, 251	21	1	IPTPP
	410	118, 251, 293	24–27	3	
	452	118, 251, 335	28–33	3	
	494	145, 160	36	1	
Beale 11A	368	251	21–25	3	IPTPP
	410	251	23–35	11	
Beale 1B	368	165	24–27	4	TCP

<sup>a</sup> GC Retention Time from Total Ion Chromatograph

**Table 3.** Concentrations of OPs in Air Force base soil samples, in ppm (μg/g)

Soil Sample	Site Description	TPP	Total TCP	Total IPTPP
AFB 1	Unknown	2	103	—
AFB 2	Received from	6	130	—
AFB 3	USAF	5	28	—
Stead #1	Hangar drainage	—	—	5.8
Mather 15C	Flightline, hangar drainage	2	9	—
Beale 1B	Flightline, hangar drainage	—	0.10	—
Beale 5D	SR-71 hangar drainage	—	0.03	—
Beale 11A	AGE drainage <sup>a</sup>	—	—	0.90
Beale 11B	AGE drainage <sup>a</sup>	—	—	2.0

<sup>a</sup> AGE = aircraft ground equipment maintenance area

IPTPPs in Beale AFB soils were identified using GC/MS in single ion monitoring mode, selecting for m/z 368, 251, and 165.

The GC/MS analyses of selected AFB soil extracts is in Table 2. Differentiation between TCP and IPTPP was accomplished by comparing the fragmentation patterns of the compounds with MW = 368. The presence of IPTPP was also supported by the presence of larger isomers, those with molecular weights of 410, 452, and 494. Although not all isomers of IPTPP present in the industrial isomer were present in detectable levels in the soil extracts, the GC retention time patterns and fragmentation data provide further evidence of the

presence of IPTPP in soils. Quantification of the TAPs present in soil samples are in Table 3.

The location and types of TAP residues found in AFB soils leads to some general conclusions. The TAP compound found in the soil that is most directly related to use of military aircraft is TCP. TCP contamination was found in soil at Mather, which was inactive at the time of sampling, and at Beale in soil 1C, which was from soil displaced from the drainage and exposed for 4 to 5 years. These residues suggest that TCP is particularly recalcitrant. Because TCP is in military hydraulic fluids at 1–2% levels, its presence in the soil may be a marker of additional non-TAP hydrocarbon contamination. IPTPP soil

contamination is more likely the result of fluid leakage from commercial and private aircraft rather than from military jets. Civilian airports and aircraft facilities may also be contaminated with IPTPP. More extensive sampling of military and municipal airports is needed in order to reveal the extent of contamination and persistence of these compounds in soil.

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