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Residues of Toxaphene in Insectivorous Birds (*Petrochelidon* spp.) From the Rio Grande, Texas

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Abstract. Although it has been documented that wildlife in the Rio Grande Valley (RGV) contain increased concentrations of organochlorine (OC) contaminants, particularly DDE, little has been published on residues of toxaphene throughout this major North American watershed. In this study, 28 liver composites from adult swallows (*Petrochelidon* spp.) collected along the Rio Grande from 1999 through 2000 were analyzed for toxaphene residues using congener-specific gas chromatography–electron-capture negative ionization–mass spectrometry. Estimated total toxaphene concentrations ranged from 12 to 260 ng/g wet wt and were highest in samples from the lower RGV near Llano Grande Lake in Hidalgo and Cameron counties (Texas). Toxaphene congener profiles were relatively invariant throughout the watershed and were dominated by 2,2,5-endo,6-exo,8,8,9,10-octachlorobornane (P-42a or B8-806) with lesser amounts of several other Cl_7-Cl_9 compounds, many of which remain unidentified. *Petrochelidon* spp. liver profiles appear to be intermediate in complexity between those in invertebrates and fish (more complex) and mammals (less complex) and differs somewhat from those reported for other avian species. In addition to other legacy OC contaminants, toxaphene residues were most concentrated in the lower RGV and accumulated at up to hundreds of parts per billion in these insect-eating birds, underscoring their utility as avian bioindicators of persistent organic pollutants.

Technical toxaphene, a several-hundred component mixture of highly chlorinated C-10 monoterpenes produced by exhaustive chlorination of α-pinene (Saleh 1991), was used heavily in the southern United States as an agricultural pesticide for cotton, soybean, and vegetable crops before it was banned in 1982. Because its production and use were not limited to North America, residues of technical toxaphene (or simply ''toxaphene'') are abundant and ubiquitous, thus its inclusion as a primary persistent organic pollutant of national (USEPA 2003) and international concern (Narbonne 2003). Individual components of technical toxaphene, however, are selectively transformed in and transported through the environment, resulting in differential residue congener patterns depending on the compartment of interest (Bidleman *et al*. 1993; Stern *et al*. 1996; Maruya *et al*. 2000; Hoekstra *et al*. 2002). A limited number (<12) of chlorobornane congeners that share common structural features, particularly those with alternating exo, endo chlorine substitution on the six-membered carbon skeleton, are thought to be particularly recalcitrant to biotransformation (Vetter and Scherer 1999) and thus long lived in the atmospheric, aquatic, and oceanic environments. Still others have yet to be fully resolved or identified (Maruya *et al*. 2001; Ruppe *et al*. 2003, 2004).

The Rio Grande is a major North American watershed that forms the border between Texas and Mexico. During the past several decades, agriculture has dominated the economy and thus land use in this watershed, particularly in the lower Rio Grande Valley (LRGV). As such, legacy organochlorine (OC) pollutants such as DDT, polychlorinated biphenyls, and toxaphene have been detected in various environmental compartments including sediment, fish, and mammals (White *et al*. 1983; Mora *et al*. 2000, 2001). Toxaphene concentrations in particular were highest in wading bird eggs in the LRGV (Wainwright *et al*. 2001). Little remains known about the environmental effects of toxaphene residues, particularly in birds and in conjunction with other legacy OCs, although recent studies have documented likely metabolic pathways (Van Hezik *et al*. 2001) and effects on growth and reproduction in fish and reptiles (Fåhræus-Van Ree and Payne 1997; Palmer *et al*. 1998).

Although toxaphene is often reported in studies of environmental OC residues, little has been published on congener concentrations and distributions in terrestrial wildlife, particularly in insectivorous birds. Moreover, even less is known about congener-specific toxicity of toxaphene residues regardless of species. In this study, livers from adult swallows (*Petrochelidon* spp.) collected throughout the Rio Grande were analyzed by gas chromatography–electron-capture negative ionization–mass spectrometry (GC-ECNI-MS) (1) to determine total and congener-specific toxaphene concentrations and (2) to compare residue congener profiles by species, sex, and sampling region.

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Materials and Methods

Target Species, Study Area, and Sampling Sites

During 1999 and 2000, approximately 200 adult cave and cliff swallows (*Petrochelidon fulva* and *P. pyrrhonota*, respectively) were collected from 8 locations along the Rio Grande from Brownsville to El Paso, TX (Fig. 1). Birds were captured with mist nets dropped over culverts and bridges where the colonies were established. On collection, blood samples were taken for biochemical analyses, and the birds were killed by cervical dislocation. Carcasses were wrapped in aluminum foil and stored in plastic bags under dry ice during transport to the laboratory. On arrival, the head, wings, feet, and stomach contents were removed, and a portion of the liver excised from approximately 80 specimens. Livers from 3 individual birds were pooled by species, sex (where possible), and location into 28 composite samples for toxaphene analyses (Table 1). A single composite sample of *P. fulva* spp. from area 8 consisted of livers from 2 individuals (1 female and 1 male).

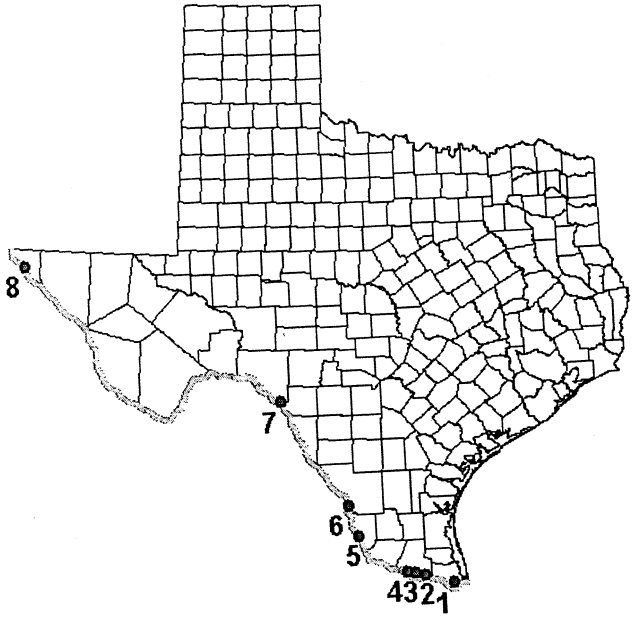

Fig. 1. Sampling areas for swallows (*Petrochelidon* spp.) along the Rio Grande, TX. The study area encompasses El Paso (area 8) in the upper watershed, the agriculturally dominated lower river valley (areas 2 through 4), and its confluence with the Gulf of Mexico (area 1). 1 = Brownsville, 2 = Llano Grande, 3 = Pharr-San Juan, 4 = Mission, 5 = Falcon Lake, 6 = Laredo, 7 = Del Rio, 8 = El Paso

Sample Processing

Thawed composite samples were homogenized with approximately 5 g pre-extracted Hydromatrix (Varian, Palo Alto, CA) using a ceramic mortar and pestle; packed into a 33-ml stainless steel extraction cell with pre-extracted Ottawa sand; and spiked with dibromooctafluorobiphenyl (DBOFB) as a recovery surrogate. Samples were extracted with three sequential 10-ml aliquots of CH_2Cl_2 at 100°C and 2000 psi using an accelerated solvent extraction system (model no. 200; Dionex, Salt Lake City, UT). Extracts were then exchanged to hexane using a TurboVap II (Zymark, Hopkington, MA) operating at 50°C and with high purity (>99.99%) N_2 delivery pressure of 8 psi; transferred to pre-tared 25-ml glass scintillation vials; and allowed to evaporate to dryness in a fume hood. Extractable lipid on a wet-tissue basis was determined gravimetrically to the nearest 0.001 g using a microbalance.

After redissolving in hexane, the sample extract was applied to a glass column (500 mm L x 11 mm i.d.) dry packed with 18 g 1.0% deactivated Florisil (Fisher Scientific, Fair Lawn, NJ; 60 to 100 mesh). Before deactivation, the Florisil was activated at 550°C for >10 hours. Two fractions were collected at an elution rate of 1 drop/s –fraction 1 (F1) with 100 ml hexane followed by fraction 2 (F2) consisting of 150 ml 20% CH_2Cl_2 in hexane (v/v). Both fractions were reduced and the F2s exchanged to hexane using a Turbo Vap II; transferred to 2-ml amber GC vials; and adjusted to a final volume of 1.0 ml.

Table 1. Sample size, species, and sex for swallow (*Petrochelidon* spp.) liver composite samples

Area[a]	No. of composites	Species[b]	Sex	% Lipid[c]
1	3	Cave/cliff	2F; 1F/M	6.28 ± 1.36
2	5	Cave	2F; 3M	4.26 ± 0.34
3	4	Cave	2F; 2M	5.71 ± 1.56
4	3	Cave	2F; 1M	5.52 ± 1.02
5	3	Cliff	1F; 2M	5.10 ± 0.57
6	3	Cave	1F; 2M	5.27 ± 0.37
7	2	Cave	1F; 1M	3.92 ± 0.18
8	5	Cave/cliff	1F; 2M; 2F/M	4.17 ± 0.57
Total	28		12F; 13M; 3F/M	4.98 ± 1.17

[a] See Figure 1 for sampling areas.
[b] Cave swallow (*P. fulva*) and cliff swallow (*P. pyrrhonota*).
[c] Mean ± SD; wet-weight basis.
F = Female.
F/M = Mixture of female and male.
M = Male.

GC-MS

F1 and F2 extracts (1 µl injection volume) were analyzed on a Hewlett Packard 6890 gas chromatograph coupled to a 5973 mass-selective detector (GC-MSD) operating in the electron-capture negative-ionization (ECNI) mode. A 60 m L x 0.25 mm i.d. fused silica capillary column coated with 0.25 µm DB-XLB (Agilent/J&W Scientific, Folsom, CA) was used to separate toxaphene congeners. After a 1-minute hold at 60°C, the GC oven was ramped to 200°C at 20°C/min followed by a second ramp to 300°C at 2°C/min. Total GC run time was 70 minutes. The injector was programmed to track the column oven temperature. Methane at a pressure of approximately 1 torr (1.8×10^{-4} torr cavity pressure) was used as the moderating gas; the ion source and quadrupole temperatures were maintained at 106°C and 150°C, respectively. The MSD was operated in the selected ion-monitoring (SIM) mode using the following ions (homologs) in five overlapping time windows: 273, 275 (Cl_5); 309, 307 (Cl_6); 343, 345 (Cl_7); 377, 379 (Cl_8); 413, 411 (Cl_9); and 445, 447 (Cl_{10}).

Serial dilutions (2.0 to 100 pg) of a 22-component mixture containing 17 chlorobornane (CB) and 5 chlorocamphene congeners representing Cl_6-Cl_{10} homologs (TM2; Dr. Ehrenstorfer, Augsburg, Germany) were used to generate a six-point calibration curve for congener-specific analysis. Three additional residue congeners—2-exo,3-endo,6-exo,8,9,10-hexaCB (B6-923 or Hx-Sed); 2-endo,3-exo,5-endo,6-exo,8,9,10-heptaCB (B7-1001 or Hp-Sed); and 2-endo,3-exo,5-endo,6-exo,8,8,10-heptaCB (B7-1000)—were identified

by retention time in solutions provided by Drs. G. Fingerling (Technical University, Munich, Germany) and W. Vetter (University of Hohenheim, Stuttgart, Germany) and quantified using the mean response factor for all 22 TM2 components. A toxaphene congener was considered confirmed if the retention time (± 0.1 second) and ion abundance matched that of the corresponding peak in standard solutions. For congeners confirmed in both F1 and F2 extracts of the same sample, concentrations were reported as the sum of both fractions. An 8-point calibration for estimating total toxaphene residue concentrations ($\sum$TOX) was generated from serial dilutions in hexane (0.011 to 55.4 µg/ml) of a technical toxaphene product standard (TTX) provided by J. Hoffman of Hercules, Inc. (Wilmington, DE). A mean TTX response factor was generated by summing the peak areas for Cl_7-Cl_9 bornane fragment ions (m/z 343/345, 377/379, and 411/413) and dividing by the known calibration mass. $\sum$TOX was estimated by summing ion peak areas in sample F1s and F2s, i.e., $\sum$TOX = $\sum$TOX (F1) + $\sum$TOX (F2).

Quality Assurance and Quality Control

Congener-specific concentrations and $\sum$TOX were validated against a set of performance based quality-assurance and quality-control criteria. Solvents and reagents of high purity (e.g., Optima grade; Fisher Scientific, Fair Lawn, NJ) were used throughout. Sample (glass) containers were thoroughly hand washed, kiln fired, and solvent rinsed before use. Initial GC-ECNI-MS calibration curves were highly linear (r^2 >0.999). Midlevel calibration standards were injected every 10 samples to monitor instrument stability, which deviated <20% from the initial calibration level throughout the analytic run. No toxaphene congeners were detected in procedural blanks (n = 4) consisting of approximately 5 g kiln-fired Na_2SO_4. The mean recoveries for TM2 components and TTX spiked into a reference fish liver were 84 ± 10% and 104%, respectively. The mean recovery for three toxaphene congeners—2-endo,3-exo,5-endo,6-exo,8,8,10,10-octaCB (P-26 or B8-1413), 2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-nonaCB (P-50 or B9-1679), and 2,2,5,5,8,9,9,10,10-nonaCB (P-62 or B9-1025)—and $\sum$TOX in SRM1588 (organics in cod liver oil; NIST, Gaithersburg, MD) was 91% ± 13%. Sample concentrations were corrected for DBOFB recovery (65% ± 6.2%).

Data and Statistical Analysis

All concentrations and instrument calibration parameters were computed using Excel 2002 spreadsheet software (Microsoft, Redmond, WA). Analysis of variance (ANOVA) was performed on untransformed congener-specific concentration and $\sum$TOX data using SAS version 8.02 (Cary, NC). When differences among mean concentrations (by sex, species, and/or sampling area) were significant by ANOVA (p <0.05), pair-wise comparisons were performed using Tukey's multiple comparison test.

Results and Discussion

Congener-Specific and Total Toxaphene Concentrations

Toxaphene residues were detected in all 28 *Petrochelidon* spp. liver composite samples, with as many as 10 individual congeners (B6-923, B7-1000, B7-1001, B8-1413, B8-1414, B8-1945, B8-806, B8-2229, B9-1679, and B9-2206) confirmed by GC-ECNI-MS SIM (Table 2). $\sum$TOX by sampling area ranged from 12 ± 0.96 (area 7) to 260 ± 27 (area 3) ng/g wet weight. On a lipid basis, the range for $\sum$TOX was 240 ± 38 (area 6) to 5900 ± 1600 (area 2) ng/g (Table 3). Extractable lipid content was much less variable than $\sum$TOX and ranged from 3.19 (*P. fulva*, area 8) to 7.37% (*P. pyrrhonota*, area 1) in individual composites with a grand mean of 4.98% ± 1.17% (Table 1). There was no relationship between $\sum TOX_{wet}$ and percent extractable lipid using simple linear regression. Lipid-normalized toxaphene concentrations were used in subsequent statistical analyses.

Table 2. Toxaphene residue (chlorobornane) congeners confirmed by GC-ECNI-MS in swallow (*Petrochelidon* spp.) livers

Structure[a]	Homolog	AV code[b]	Parlar no.[c]	Other
2-exo, 3-endo, 6-exo, 8, 9, 10	6	B6-923	–	Hx-sed, M1
2-endo, 3-exo, 5-endo, 6-exo, 8, 8, 10	7	B7-1000	–	–
2-endo, 3-exo, 5-endo, 6-exo, 8, 9, 10	7	B7-1001	–	Hp-Sed
2-endo, 3-exo, 5-endo, 6-exo, 8, 8, 10, 10	8	B8-1413	26	T2
2-endo, 3-exo, 5-endo, 6-exo, 8, 9, 10, 10	8	B8-1414	40	–
2-exo, 3-endo, 5-exo, 8, 9, 9, 10, 10	8	B8-1945	41	–
2, 2, 5-endo, 6-exo, 8, 8, 9, 10	8	B8-806	42a	–
2-exo, 5, 5, 8, 9, 9, 10, 10	8	B8-2229	44	–
2-endo, 3-exo, 5-endo, 6-exo, 8, 8, 9, 10, 10	9	B9-1679	50	T12, Tox Ac
2-exo, 3-endo, 5-exo, 6-exo, 8, 8, 9, 10, 10	9	B9-2206	63	–

[a] One enantiomer only.
[b] Andrews and Vetter (1995).
[c] Parlar *et al*. (1995).

Two-way ANOVA revealed no differences in $\sum$TOX based on sex or sampling year (1999 vs. 2000) for areas 2 and 3. A direct comparison of $\sum$TOX in *P. fulva* versus *P. pyrrhonota* was only possible for area 8 (Table 1). $\sum$TOX was significantly greater (p = 0.025) in 2000 *P. fulva* liver composites compared with 1999 *P. pyrrhonota* samples; however, it is possible that this difference was influenced by sampling year. Because of the limited sample sizes associated with each factor (i.e., sex, species, and sampling year) and the fact that significant differences (p <0.05) among these factors for a given area were in general not observed, samples were pooled by area for subsequent statistical comparisons.

Mean congener-specific concentrations ranged from nondetect (<1.3 ng/g) to 2700 ± 640 ng/g lipid for 2,2,5-endo,6-exo,8,8,9,10-octachlorobornane (B8-806 or P-42a) in area 2 *P. fulva* livers. In addition to B8-806, only 2-endo,3-exo,5-endo,6-exo,8,9,10,10-octaCB (B8-1414 or P-40), 2-exo, 3-endo,5-exo,8,9,9,10,10-octaCB (B8-1945 or P-41), and 2-exo,3-endo,5-exo,6-endo,8,8,9,10,10-nonaCB (B9-2206 or P-63) were detected in all samples (Table 3).

Table 3. Mean (± SD) congener-specific and ∑TOX residue concentrations[a] (ng/g lipid) by sampling area

Area	B7-1000	B6-923	B7−1001	B8-1413	B8-1945	B8-1414	B8-806	B8-2229	B9-1679	B9-2206	∑TOX
1	<1.3	<1.3	<1.3	51 ± 23	9.7 ± 0.64	22 ± 1.4	330 ± 24	24 ± 2.9	22 ± 11	4.6 ± 2.0	610 ± 39
2	25 ± 6.5	20 ± 5.0	85 ± 22	480 ± 170	110 ± 41	340 ± 110	2700 ± 640	280 ± 62	220 ± 64	33 ± 13	5900 ± 1600
3	14 ± 0.052	20 ± 3.9	120 ± 50	580 ± 260	87 ± 30	250 ± 69	2200 ± 820	220 ± 97	180 ± 42	36 ± 17	5000 ± 1600
4	18 ± 5.0	12 ± 2.1	52 ± 1.8	280 ± 34	46 ± 9.3	140 ± 25	1200 ± 250	100 ± 11	47 ± 9.1	12 ± 2.2	2700 ± 610
5	<1.3	<1.3	<1.3	<1.3	5.5 ± 1.5	19 ± 5.6	150 ± 87	<1.3	<1.3	13 ± 0.34	260 ± 130
6	<1.3	<1.3	<1.3	<1.3	4.5 ± 0.080	17 ± 0.85	150 ± 26	<1.3	<1.3	1.7 ± 0.94	240 ± 38
7	<1.3	<1.3	<1.3	<1.3	3.2 ± 0.002	16 ± 4.8	99 ± 1.6	<1.3	<1.3	4.1 ± 1.5	300 ± 11
8	22 ± 7.5	<1.3	30 ± 12	90 ± 13	13 ± 2.4	37 ± 6.9	270 ± 98	35 ± 0.052	21 ± 8.3	1.7 ± 0.55	490 ± 100

[a] Reported if all composites for a given area contained detectable (>1.3 ng/g) concentrations.
∑TOX = Total toxaphene residue concentrations.

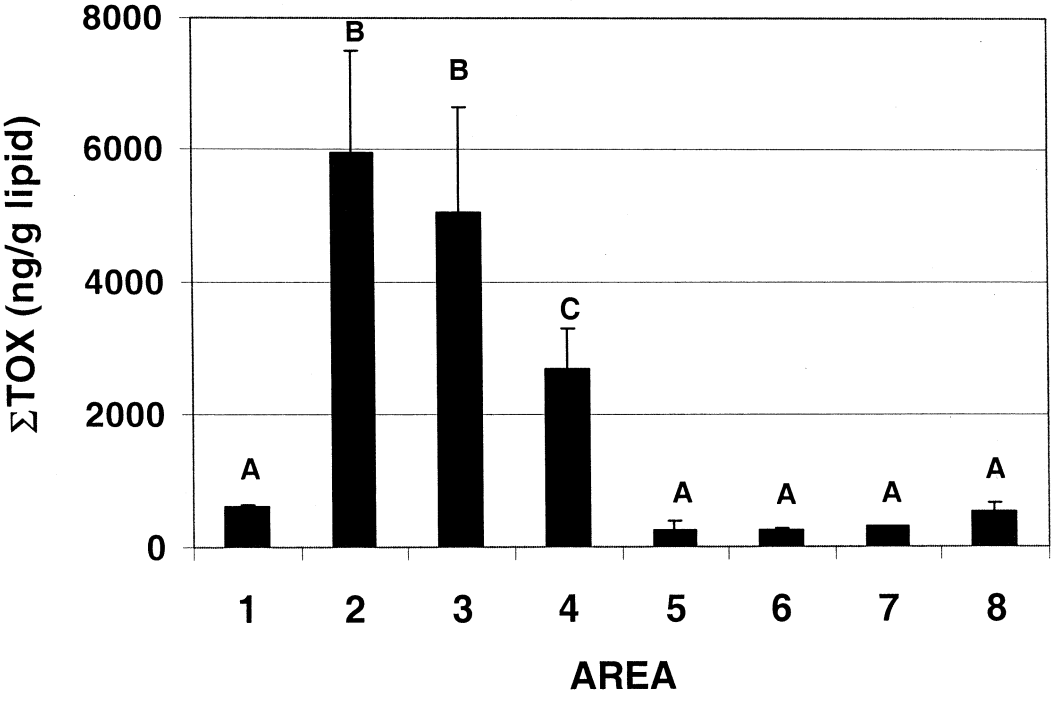

Fig. 2. Total ∑TOX in *Petrochelidon* spp. livers (ng/g lipid) were significantly higher in the LRGV (areas 2 through 4). Error bars represent 1 SD. Means with the same letter (A through C) were not significantly different ($p < 0.05$). ∑TOX = estimated total toxaphene concentrations; LRGV = lower Rio Grande valley

Geographic Differences in ∑TOX

Single-factor ANOVA revealed a significant difference in $\sum TOX_{lip}$ according to sample area. Subsequent Tukey's multiple-comparison tests indicated that mean $\sum TOX_{lip}$ in the LRGV (areas 2 and 3) were significantly greater than in the middle (areas 5 through 7), upper (area 8), and extreme lower (area 1) reaches of the Rio Grande (Fig. 2, Table 3). Moreover, the mean $\sum TOX_{lip}$ for area 4 was also greater than those for areas 1 and 5 through 8. The greatest $\sum TOX_{lip}$ occurred in areas 2 and 3, which is consistent with reported concentrations of toxaphene and other OCs (e.g., DDTs) in wading bird eggs and carp (*Cyprinus carpio*) in this region (Wainwright *et al*. 2001). The highest reported toxaphene concentrations were observed in green heron (*Butorides virescens*) eggs from bancos (settling basins) and in carp from resacas (oxbow lakes) in Cameron County, which lies geographically just a few kilometers east of areas 2 and 3 of this study. DDE, the major persistent metabolite of the agricultural pesticide DDT, was detected at concentrations up to 10 μg/g wet wt in carp and other fish species from two other resacas in Cameron and Hildago counties (Mora *et al*. 2001). DDE concentrations in *Petrochelidon* spp. carcasses (Mora *et al*. in press; Mora et al. 2002) were also higher than toxaphene in liver (this study). During the past several decades, the LRGV has become a largely irrigated agricultural land, and the bancos and resacas of this area store runoff and irrigation return water from these fields. Lack of flushing in and periodic maintenance of these water bodies has resulted in increased OC contamination (Wainwright *et al*. 2001). The relatively low toxaphene residue concentrations found in swallow livers from the middle Rio Grande (areas 5 through 7) reflect perhaps lower agricultural use of toxaphene in such areas. No corroborating information could be found for environmental concentrations of OC pesticides for the upper Rio Grande near El Paso (area 8).

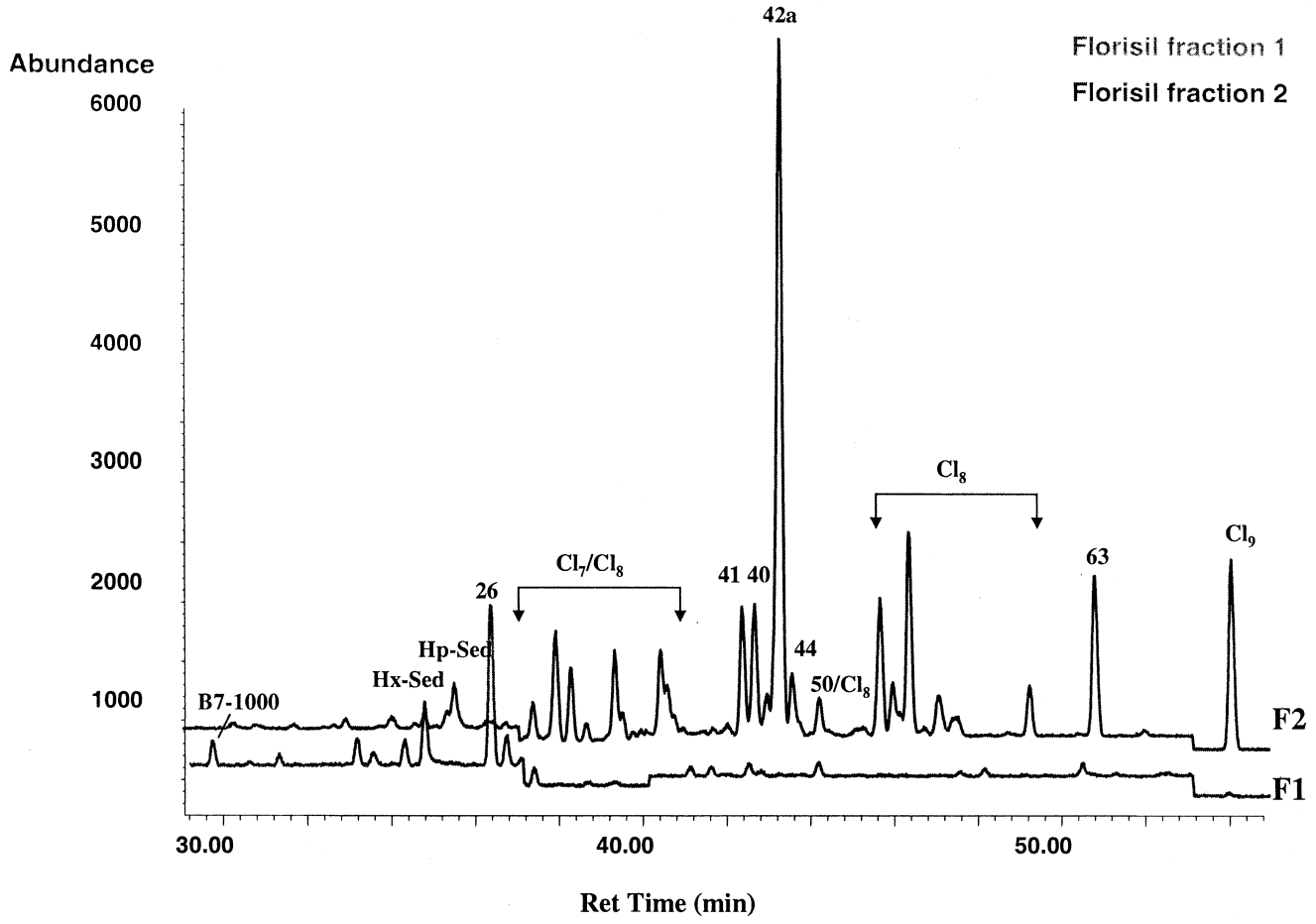

Fig. 3. GC-ECNI-MS-SIM profile of toxaphene residues in cave swallow (*P. fulva*) livers from the lower Rio Grande (area 2) includes several Cl_6-Cl_9 congeners and is dominated by 2,2,5-endo,6-exo,8,8,9,10-octachlorobornane (B8-806 or P-42a). B7-1000 and B8-1413 (P-26) elute in the (nonpolar) first fraction from Florisil. Peaks with homolog labels only are unidentified

Residue Congener Patterns

Of the ten congeners confirmed in these samples, the dominant congener in each case was B8-806 (P-42a) (Fig. 3), a major component of technical toxaphene (Fingerling *et al.* 1996) (Fig. 4). Other TTX components detected (in order of decreasing abundance) were B8-1413 (P-26), B8-1414 (P-40), B9-2229 (P-44), B9-1679 (P-50), B8-1945 (P-41), and B9-2206 (P-63). In addition, several minor TTX components—including B6-923 (Hx-Sed), B7-1001 (Hp-Sed), and B7-1000—were present in selected extracts, mostly those from LRGV areas 2 through 4. Last, several unidentified Cl_6-Cl_9 congeners were also present (Fig. 3), some of which may have been detected in samples from other parts of the world (Maruya *et al.* 2001; Ruppe *et al.* 2003 2004).

The distribution of toxaphene residue congeners observed was similar across sample areas (Fig. 5), which represented a >1000-km stretch of the Rio Grande. This characteristic profile differs, however, from those documented in both lower trophic– and higher trophic–level species in other ecosystems including marine crustaceans, fishes, terrestrial, and marine mammals. B6-923 (Hx-Sed) and B7-1001 (Hp-Sed), known reductive dechlorination metabolites of higher chlorinated toxaphene components (Fingerling *et al.* 1996; Stern *et al.* 1996), dominated congener profiles in sediment, fish, and crustaceans from a toxaphene-contaminated tidal creek in coastal Georgia (Maruya *et al.* 2000, 2001). B8-1413, B8-1414/1945, B8-806/809, B8-2229, and B9-1679 were also present as minor constituents in these tidal creek samples as were several unknown octaCBs eluting after B9-1679 (P-50) (Fig. 3). 2-endo,3-exo,5-endo,6-exo,8,8,9,10-octaCB (B8-1412), a persistent residue congener found in higher trophic–level biota, may prove to be one of these unknown Cl_8 bornane contaminants (Vetter *et al.* 1997a). More recently, however, B8-806 (P-42a) was found to be a major residue congener in estuarine fish from the Georgia coast using a 60-m DB-XLB column (K. Maruya, unpublished data, 2004).

In contrast, the toxaphene residue congener pattern in higher trophic–level biota tends to be much simpler. For example, B8-1413, B9-1679, and B9-1025 (P-26, -50, and -62) account for the majority (65% to 80%) of the total toxaphene load in mysticete (Hoekstra *et al.* 2002) and odontocete cetaceans (Tuerk 2003), pinnipeds (Vetter *et al.* 1997b), and other marine mammals (Vetter *et al.* 2001). In lower trophic–level species, such as fish, this trio of "indicator" congeners accounts for a somewhat lower proportion (25% to 50%) of total

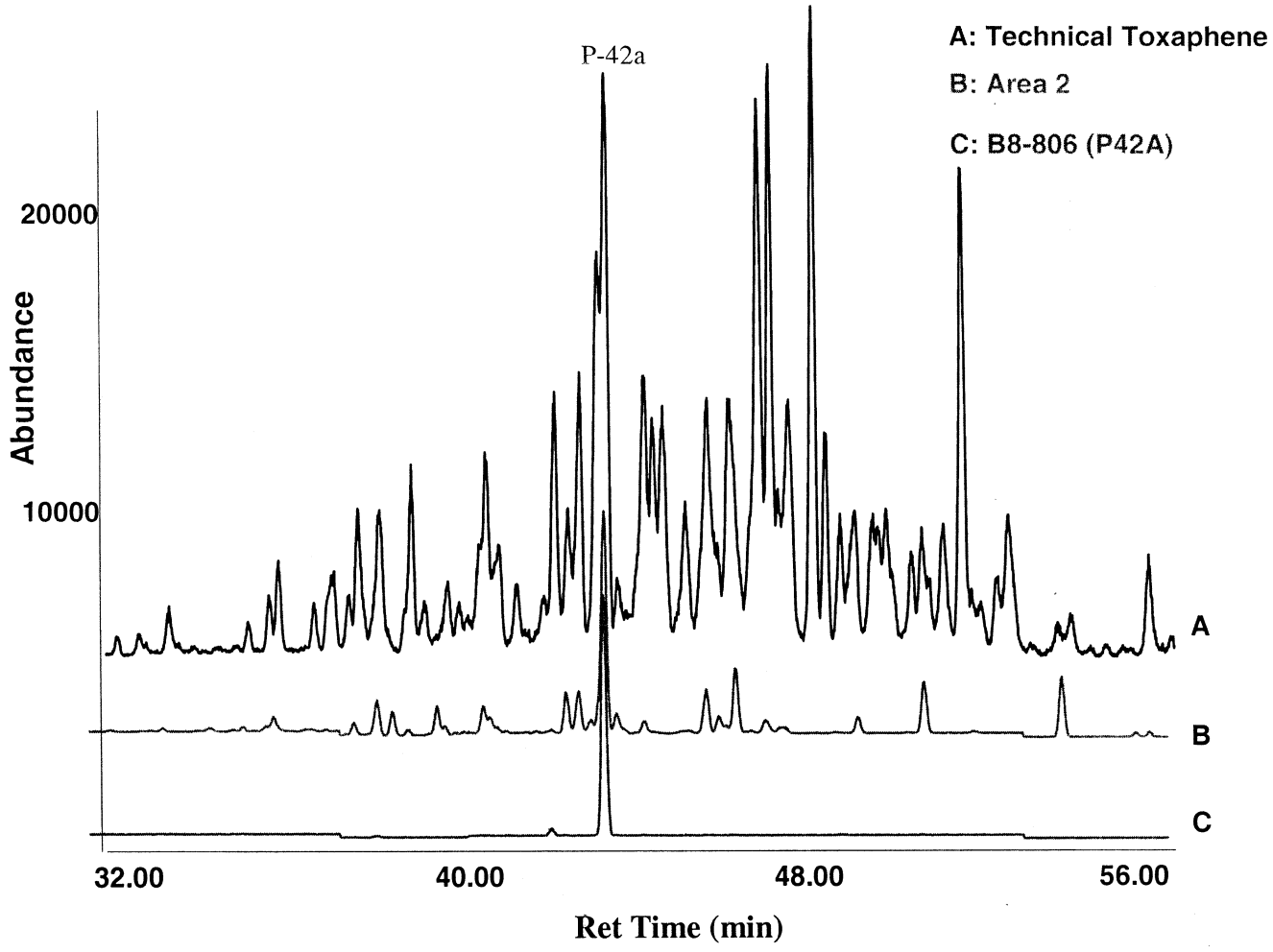

Fig. 4. GC-ECNI-MS SIM profile of (**A**) technical toxaphene, (**B**) liver extract of cave swallows (*P. fulva*) from the lower Rio Grande (area 2), and (**C**) 2,2,5-endo,6-exo,8,8,9,10-octachlorobornane (B8-806 or P-42a). Note that B8-806 (P-42a) is a major component of unmodified technical toxaphene. GC-ECNI-MS = gas chromatography–electron-capture negative ionization–mass spectrometry; SIM = selected ion-monitoring

toxaphene concentrations (Alder and Vieth 1996). Minor residue congeners in various marine mammal species—including B8-1414, B8-1945, B8-2229, and B9-1025 (P-40, 41, 44 and 62) as well as 2-exo,3-endo,5-exo,9,9,10,10-heptaCB (B7-1453) and B8-1412 (Vetter *et al.* 2001)—are much the same as those reported here.

Two other studies previously reported congener-specific toxaphene residue concentrations for birds. Vetter *et al.* (2001) found that although B8-1413 and B9-1679 (P-26 and -50) dominated in various tissues of skuas (*Catharacta* spp.) collected in the Antarctic, the relative abundances of B9-1679 and B8-1414 (P-40) varied widely, with relatively higher proportions of the latter congener in liver. Conversely, B8-1414 was less than, at, or near the detection limit (<0.1 ng/g) in blubber and liver of Adelie penguins (*Pygoscelis adeliae*). In the second study, Witte *et al.* (2000) examined spatial and temporal trends in common tern (*Steno hirundo*) eggs from the German North Sea coast using an HT-8 GC column. Total toxaphene concentrations were on average 1 order of magnitude lower than those reported here and decreased by a factor of 5 between 1981 and 1997. Interestingly, B8-1413 (P-26) and 2,2,5,5,8,9,10,10-octaCB (B8-786 or P-51) were reported to have increased in relative abundance during the 16-year study period, whereas B8-1945 (P-41), B9-1679 (P-50) and several others decreased. B8-1414 (P-40) appeared to remain in proportion to B8-1413, whereas B9-1025 (P-62) and B9-2206 (P-63) were nondetectable in later years. One disadvantage to the XLB stationary phase used in this study is the very low response of B8-786 and B9-1025 (Smalling and Maruya 2001). However, that B8-786 increased with time in tern eggs (Witte *et al.* 2000) is curious because B8-786 contains two pairs of geminal chlorine atoms on the six-carbon bornane skeleton (positions C-2 and C-5) and thus is not expected to persist in the environment (Vetter and Scherer 1999). Moreover, it has not been reported as a major residue congener in any previous study. A further complication is that B8-786 elutes in the region of the several unidentified Cl_8 monoterpenes that persist in other biota including B8-1412 (Vetter *et al.* 2001; Maruya *et al.* 2001).

This is the first report of increased concentrations of B8-806 (P-42a) in avian tissue, possibly because the analytic system employed here (GC-ECNI-MS-SIM with 60-m DB-XLB) was

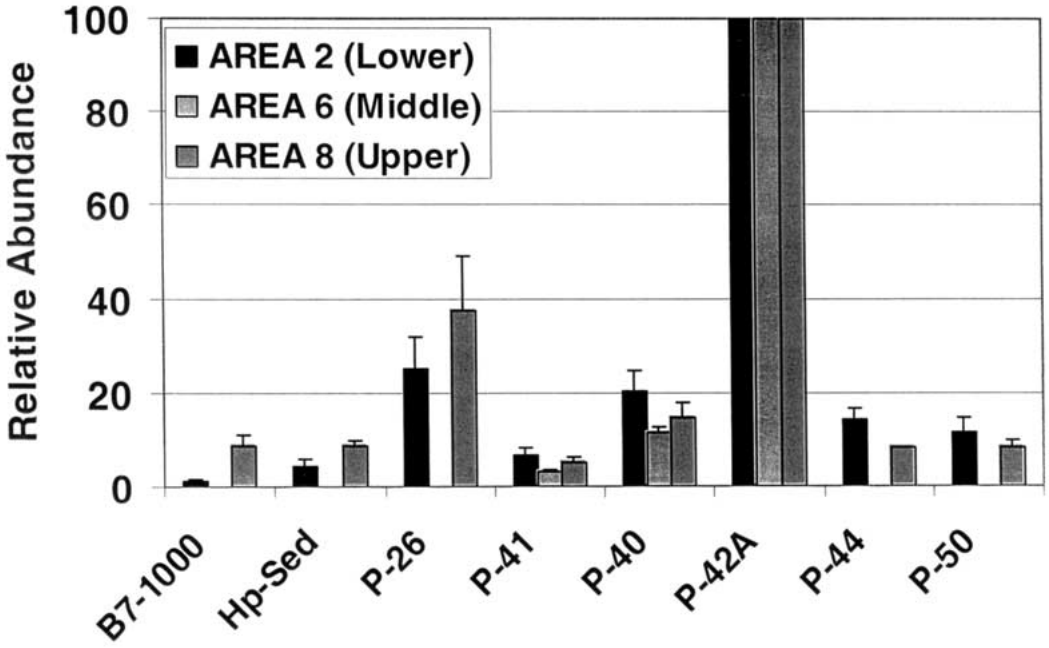

Fig. 5. The toxaphene residue congener distribution in livers from *Petrochelidon* spp. is relatively invariant throughout the Rio Grande. Only 3 of 10 congeners were detectable (method detection limit approximately 1.3 ng/g lipid) in samples collected near Laredo, TX (area 6). Error bars represent 1 SD

able to adequately separate the enantiomer pair B8-806/809 (P-42a/b) from its closely eluting homologs B8-1414 (P-40), B8-1945 (P-41), and B8-2229 (P-44). For nonpolar ''DB5-like'' stationary phases and other alternatives such as HT-8 (Witte *et al*. 2000), adequate resolution of these environmentally relevant congeners has not been achieved. Although a major component of technical toxaphene, B8-806 is reported only as a minor residue congener (or not at all) in remote polar ecosystems. Thus, its abundance in Rio Grande swallow livers suggests (1) a local regional source enriched in B8-806 such as technical toxaphene and/or (2) preferential accumulation and/or inability of *Petrochelidon* spp. to biotransform this congener. Future sampling and congener-specific analysis of preferred *Petrochelidon* prey (flying insects) would address hypothesis 1, whereas uptake and biotransformation studies with avian species and tissue are needed to address hypothesis 2.

B8-806 notwithstanding, congener profiles for *Petrochelidon* spp. livers (this study) were not wholly inconsistent with those in seabirds (Vetter *et al*. 2001) and seabird eggs (Witte *et al*. 2000). That B8-806 is rarely, if ever, reported in samples from polar regions suggests it possesses a relatively short half-life in atmospheric and cold oceanic environments. It remains possible, however, that B8-806 is masked by other closely eluting Cl_8 toxaphene homologs (e.g., B8-1414, -1945, and -2229) using 1% to 5% phenyl-substituted polysiloxane GC stationary phases, particularly in samples with ultra-low concentrations. Regardless, the accurate determination of B8-806 (P-42a) in environmental samples that are geographically ''close'' to residual toxaphene sources and that represent species with limited chlorobornane biotransformation capability needs to be stressed in future studies.

Toxaphene residue concentrations in *Petrochelidon* spp. were highest in the LRGV. However, $\sum$TOX in the agriculturally dominated areas of Hidalgo and Cameron counties (Texas) were lower than DDE and other legacy OCs as measured in several bird species and other sentinel organisms (Mora 2001). Toxaphene concentrations in swallow livers were much lower than those reported in green heron (*Butorides virescens*) eggs also collected in the LRGV in 1997 (Wainwright *et al.* 2001). Toxaphene residues as high as 24 μg/g ww were reported in green heron carcasses from Louisiana oxbow lakes during the 1980s (Niethammer *et al*. 1984). Tissue-specific metabolism and rapid excretion of toxaphene residues could explain the higher egg concentrations in *B. virescens* relative to *Petrochelidon* spp. liver as well as the conclusion of low (adult) toxicity based on bioaccumulation potential (Eisler and Jacknow 1985). However, concentrations at which toxaphene residues begin to affect reproduction and/or growth for avian species such as *Petrochelidon* spp. remain unknown. Based on the geographic trends and residue congener patterns observed here, these insectivorous birds are thus valuable as avian bioindicators of toxaphene and other OC contaminants in this and other watersheds. Moreover, incorporation of these data can be used to update and assess risks associated with a broader category of persistent OC contaminants that include residues of toxaphene.

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