TOXAPHENE IN ESTUARINE FISH DECREASES AFTER REMOVAL OF CONTAMINATED SEDIMENTS

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Introduction

Hercules Inc. produced technical toxaphene (TTX), a broad spectrum biocide consisting of hundreds of individual chlorinated monoterpene compounds[1], at its Brunswick (Georgia, USA) facility from 1948-1980. Discharge of toxaphene via the plant's cooling water canal has resulted in widespread contamination of the local estuarine marsh ecosystem. Early reports indicated contamination levels in local aquatic biota to be in the ppm range[2]. In 1997, a study to determine the levels of trace contaminants, including toxaphene, in edible tissue composites of multiple species of fin- and shellfish was conducted[3]. Toxaphene residue levels ranged up to 25 μg/g in certain species collected closest to the plant discharge[4]. Moreover, the "weathered" congener profile in these samples indicated the primary source of toxaphene contamination is marsh sediment[4,5]. Thus, almost 20 years after production of TTX at this location ceased, residue levels in local aquatic species remain elevated, warranting the issuance of local fish consumption advisories.

In the year 2000, remedial action was undertaken to reduce the toxaphene mass inventory associated with contaminated sediments by selective dredging. To assess the effectiveness of this strategy, we report the results of a post-dredging study conducted in 2001 to characterize the extent and levels of toxaphene in edible fish from the impacted area. To ensure data comparability, this study was similar to the pre-dredging (1997) study in terms of design and toxaphene analytical protocols utilized.

Materials and Methods

Specimens of similar size for each of 6 species -- striped mullet (*Mugil cephalus*) (13), spotted seatrout (*Cynoscion nebulosus*) (12), spot (*Leiostomus xanthurus*) (8), Atlantic croaker (*Micropogonias undulatus*) (8), mummichogs (*Fundulus* sp.) (4) and Southern kingfish (*Menticirrhus americanus*) (6) -- were collected in each of 4 areas representing a spatial gradient away from the Hercules Inc. plant during August-September 2001[6]. Area 1 was Dupree Creek (closest to the plant); Areas 3 and 4 were in the Back River (furthest from the plant) and are connected to Dupree Creek by Terry Creek (Area 2). The approximate areal coverage for this study was 20 km^2. A total of 51 composites were analyzed with a breakdown by species given in parentheses in a previous sentence. Edible tissue (skin-on, scaled fillets) was removed from 5 of the 6 species tested; whole body tissue was composited for *Fundulus*, a small forage fish. Tissues were homogenized using a stainless steel blender, extracted with CH_2Cl_2 at elevated temperature and pressure using accelerated solvent extraction (ASE), and fractionated using Florisil column chromatography. Toxaphene-containing fractions (1 and 2) were reduced and exchanged to hexane and analyzed by narrow-bore capillary gas chromatography with electron capture detection

(GC-ECD). Extractable lipid content was determined gravimetrically and reported on a wet weight basis. Total toxaphene concentration (ΣTOX) was estimated using a modified "area under the curve" approach after pre-separation of other prominent organochlorine contaminants (e.g. PCBs) (Figure 1). Integrated peaks observed in ECD chromatograms were subject to confirmation as chlorinated terpene (i.e. toxaphene) residues using GC- negative chemical ionization mass spectrometry (NCI-MS). Comprehensive, research grade quality assurance/quality control (QA/QC) measures, including the analysis of procedural blanks and spiked tissue, were implemented to ensure data of the highest quality. Statistical tests (*t*-test, single factor ANOVA) on untransformed data were performed using Microsoft Excel 2002 version SP-1.

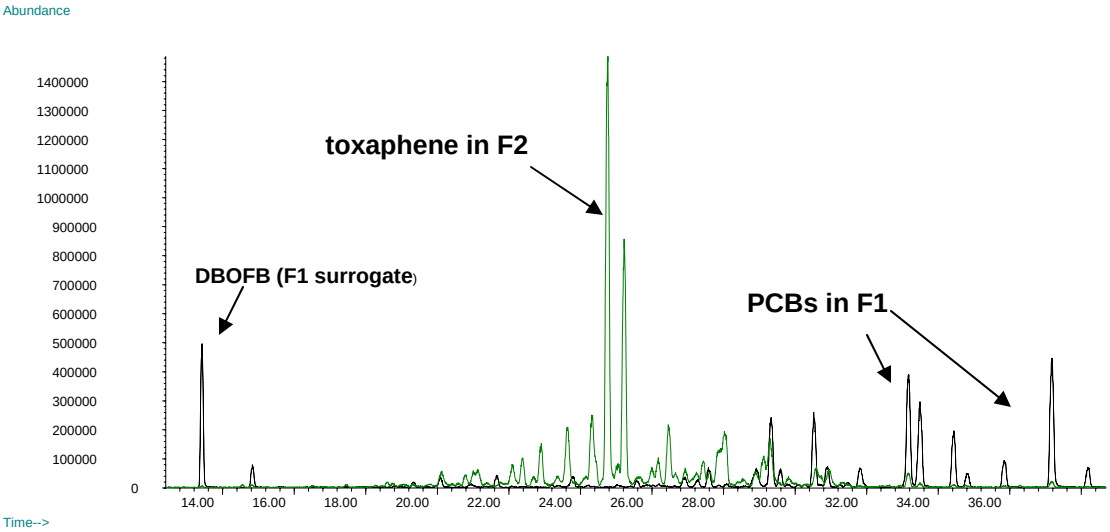

Figure 1. Superimposed ECD chromatograms of F1 and F2 extracts (spot, Area 2) show that pre-separation of non-polar, co-occurring contaminants (PCBs) is essential for accurate toxaphene quantitation.

Results and Discussion

ΣTOX (mean±sd) for the entire sample set (n=51) was 1200±3000 ng/g wet weight. ΣTOX for individual composite samples ranged from ≤ 18 ng/g for area 4 spotted seatrout to 18000 ng/g for area 1 spot, a 1000-fold difference. Percent lipid ranged from 0.23 to 19 with a mean±sd of 3.6±4.5%. Expressed on a lipid basis, mean total toxaphene was 28 ± 41 μg/g lipid. Lipid normalization of ΣTOX reduced the range of concentrations observed by a factor of 7. A significant positive association (R^2=0.47; p<<0.001) between lipid content and ΣTOX wet was observed.

The mean ΣTOX for Area 1 samples was statistically greater than for all other areas (ANOVA; p<0.001) (Figure 2). Spot contained the highest mean ΣTOX (4900 ng/g), which was significantly greater (p<0.05) than that for *Fundulus* (600 ng/g), Southern kingfish (120 ng/g) and spotted seatrout (69 ng/g). Mean ΣTOX for Atlantic croaker and striped mullet were 1200 and 660 ng/g,

Table 1. Pre- (1997) and post- (2001) dredging levels of total toxaphene (ΣTOX) and lipid content (mean±sd) in edible fish tissue.

Year	ΣTOX, wet (μg/g)	ΣTOX, lip (μg/g)	% Lipid
1997	5.2 ± 6.4	50 ± 56	7.44 ± 5.63
2001	1.2 ± 3.0	28 ± 41	3.60 ± 4.47
Ratio[1]	0.23	0.57	0.48
% Change	-78	-43	-52

[1] 2001/1997 mean values

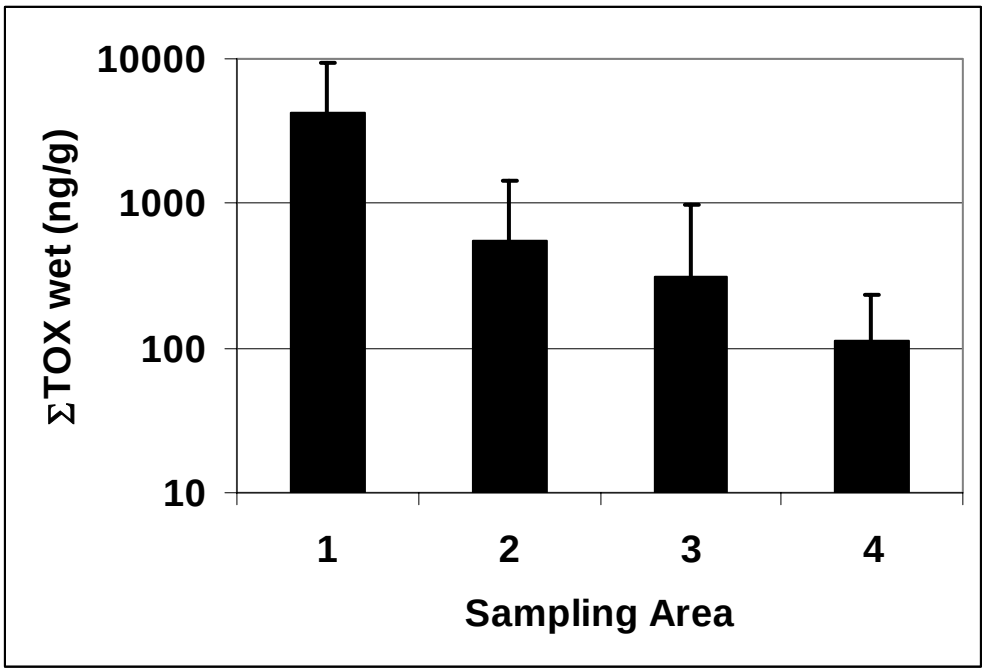

Figure 2. Mean total toxaphene (ΣTOX wet) for edible fish tissue collected along a gradient away from the former toxaphene plant. Area 1 (Dupree Creek) is closest to the plant, Area 4 (Back River) is furthest from the plant.

respectively. The trend in lipid content for the 6 species was similar to that for ΣTOX: spot (11.4%) > croaker (5.83%) > mullet (2.21%) > kingfish (1.29%) > mummichog (0.91%) > seatrout (0.49%). Mean lipid content was highest for area 4, indicating that lipid content alone could not explain the spatial differences in ΣTOX noted above.

The mean ΣTOX for finfish (*n*=38) collected in 1997 in the same general vicinity and analyzed using similar methods was 4.3 times greater (5200 ng/g) than that reported herein (Table 1). Lipid content, however, was only 2.1 times greater in the 1997 study, suggesting another explanation for the reduced toxaphene body burdens. Mean ΣTOX and lipid content in fish from Dupree Creek (Area 1) were not significantly different between 1997 and 2001, however, these same parameters were significantly different in Terry Creek (Area 2). Significant differences in ΣTOX and lipid content were noted for some species. With the exception of spot, ΣTOX and lipid content were both lower in all species collected in 2001.

The most striking comparison between 1997 and 2001 is that lipid normalized ΣTOX decreased by a factor of 1.8 (Table 1), suggesting that the remedial dredging action undertaken in 2000 had the desired effect in reducing overall concentrations of toxaphene residues in resident fish. Certain species, such as spot, croaker and mummichogs, did not exhibit reduced toxaphene burdens on a lipid basis in Area 1 suggesting additional remaining "hotspots" near the historical toxaphene discharge. In future monitoring efforts, selection of 2 or 3 sentinel fish species and a fixed collection schedule (i.e. pre- or post spawning) is recommended to minimize potential short term and/or seasonal ecological/physiological influences on toxaphene residue levels.

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