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2,3,7,8-TCDD and 2,3,7,8-TCDF in Blue Crabs and American Lobsters from the Hudson-Raritan Estuary and the New York Bight

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The discovery in 1984 of dioxin contamination of soils at a former pesticide manufacturing site on the Passaic River in Newark, New Jersey prompted several studies of sediments and biota from the head of tide on the Passaic downstream into Newark Bay and the New York Bight (Figure 1) (Belton et al. 1985; Bopp et al. 1991). The studies found widespread contamination of sediments in the estuary with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and other dioxins and furans. Bopp et al. (1991) estimated that a total of 4-8 kg of 2,3,7,8-TCDD had been deposited in Newark Bay sediments since the late 1940s, one of the largest such releases ever documented.

One of these earlier studies (Belton et al. 1985) also found a variety of finfish and crustacea from the area to contain detectable levels of 2,3,7,8-TCDD. They included blue crabs from the Passaic River near the suspected source of the contamination, and blue crabs, American lobsters, and striped bass from areas closer to the downstream limit of the Hudson-Raritan estuary and from nearshore coastal waters. Since then, Rappe et al. (1991) have also found elevated levels of dioxins and furans in fish and crustaceans from the area. The present study was designed to better define the extent and seriousness of 2,3,7,8-TCDD and 2,3,7,8-tetrachlorodibenzo-p-furan (2,3,7,8-TCDF) contamination in blue crabs at the seaward limit of their migratory range, and in American lobsters throughout their migratory range in the New York Bight.

MATERIALS AND METHODS

Blue crabs (Callinectes sapidus) were collected in 1985 and 1986 by the use of crab pots, otter trawls and

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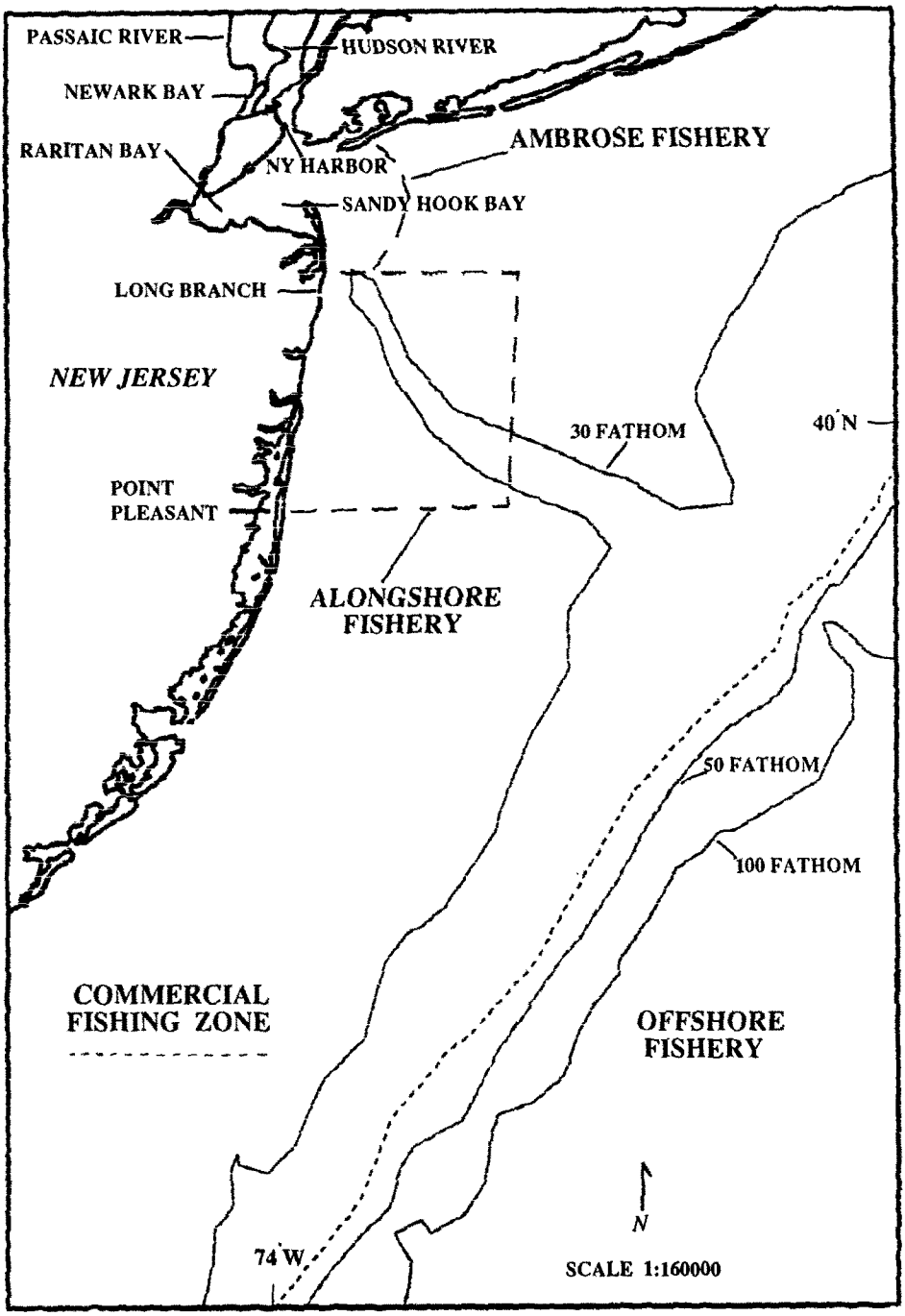

Figure 1. Commercial Lobster Sub-Fisheries in the Hudson-Raritan Estuary and the New York Bight

purchases from commercial crabbers. Sites sampled included locations from Raritan Bay, Sandy Hook Bay and upper New York Harbor. American lobsters (Homarus americanus) were collected in lobster pots and otter trawls for Raritan and Sandy Hook Bays or purchased from commercial lobstermen for deepwater areas. Lobster catch locations were sub-divided into three fisheries as defined by the National Marine Fisheries Service (Andrews 1980; Figure 1). The Ambrose fishery includes Raritan and Sandy Hook Bays, and extends to a 7-naut-mi radius from Ambrose Light, near the entrance to New York Harbor. This area also includes the blue crab sampling locations previously mentioned. The Alongshore fishery is a box-like area extending from Long Branch, New Jersey to Point Pleasant, New Jersey and extends offshore approximately 25 naut mi following the Hudson Canyon. This area includes the ocean water disposal sites for dredge spoils, fly ash and sewage sludge. (The sewage sludge dumpsite has been closed since 1988.) The Offshore fishery extends eastward from the 50-fm line to the 100-fm line approximately 100 mi seaward to the edge of the continental shelf. Blue crab and lobster control samples were obtained from Delaware Bay and the Gulf of Maine, respectively.

Samples for analysis consisted of standardized edible portions including the thoracic, claw, leg and tail meat as well as the hepatopancreas. Tissue from five organisms of similar size and weight was composited and homogenized in a food processor to generate comparable amounts of material, which were then held frozen for periods ranging from 1 month to just over a year until extraction. Separate muscle and hepatopancreas samples from seven individual lobsters were also prepared and analyzed.

Tissue analyses were performed using a modified EPA method (U.S. Environmental Protection Agency 1983) with high resolution gas chromatography and low resolution mass spectroscopy. Before clean-up the samples were fortified with ^{13}C-labelled 2,3,7,8-TCDD and 2,3,7,8-TCDF as an internal standard. The sample preparation steps of the method were as follows: (1) saponification of the sample with ethanol and aqueous KOH in a reflux apparatus, with the sample completely hydrolyzed before termination of the saponification step; (2) extraction with nanograde hexane, followed three times by removal of the lower aqueous layer and re-extraction of that layer, for a total of four extracts; (3) washing of the combined extracts with water and with concentrated H_2SO_4; (4) concentration under dry nitrogen; (5) initial cleanup via passage of the extract through a dual macro-column system with effluent solvent evaporation using

ultra-pure nitrogen (top column: 1 g silica over 4 g 44% H_2SO_4/silica; bottom column: 2 g 33% 1 N NaOH/silica over 1 g silica); (5) second cleanup with another dual column system (top column: 1.5 g 10% $AgNO_3$/silica; bottom column: 5 g basic alumina), rinsing the vial with hexane after draining the system to bed level and repeating this rinsing two additional times; (6) elution with hexane, followed by removal of the top column; (7) elution of the bottom column with CCl_4/hexane; (8) discarding of the hexane and CCl_4/hexane extracts, and elution of chlorinated dioxins/furans with $CHCl_2$/hexane; (9) final cleanup using an activated Carbopak C/Celite 545™ mix in a 2-cm column, with sequential elutions with hexane, cyclohexane/methylene chloride, and methylene chloride/methylene/benzene; (10) final elution of analytes with toluene.

The extracts were analyzed using an electron impact GC/MS instrument with a direct capillary interface, and a 50 or 60-m isomer-specific fused silica capillary column with an inner diameter of 0.22 mm. The carrier gas was helium, and the temperature program ran from 40°C to 235 or 240°C at 25°C/min, with the final temperature held for 24 or 25 min. If 2,3,7,8-TCDD or 2,3,7,8-TCDF was not detected, a detection limit was calculated based on a 2.5 times signal-to-noise ratio at the retention time of the respective contaminant and the ^{13}C-labelled internal standard.

The QA/QC procedures followed EPA guidelines (U.S. Environmental Protection Agency 1979) and included spiking tissue of each species with appropriate standards (native 2,3,7,8-TCDD: 99+%, EPA Lot No. 20603-01/83; labelled ($^{13}C_{12}$): 98+%, KOR, Inc., Lot No. J-2-70; labelled ($^{37}Cl_4$): 99%, KOR, Inc., Lot No. SSY-G-123), analyzing replicate and blind control samples and demonstrating the proper isomer specificity and ion ratios. The mean percent recovery for spiked samples with internal standards was 96.8% with 9±1 % error for the full range of analyses. The measured values reported in the tables are not corrected for recovery.

Arithmetic means and standard deviations are reported. Results reported by the laboratory as "below detection limit" were treated in data reduction as equal to one-half the reported detection limit for the analysis in question.

Measured concentrations of 2,3,7,8-TCDF were converted to 2,3,7,8-TCDD equivalents via the Toxic Equivalency Factor (TEF) approach often used by regulatory agencies in the U.S. and elsewhere (Kutz et al. 1990). The TEF approach allows reduction of data on concentrations of

various TCDD and TCDF isomers to a single value for 2,3,7,8-TCDD equivalents by assigning weights to each isomer based on its toxicity relative to that of 2,3,7,8-TCDD, which is assigned a weight of 1. (2,3,7,8-TCDF has a weight of 0.1.) Measured 2,3,7,8-TCDD concentrations and TCDD equivalents calculated using the TEF approach were compared to guideline levels of the U.S. Food and Drug Administration (FDA). (The State of New Jersey has no separate guideline levels of its own, and relies on the FDA levels.)

RESULTS AND DISCUSSION

Combined muscle/hepatopancreas samples for blue crabs from Raritan Bay and the lower Hudson River (Table 1) had a mean 2,3,7,8-TCDD concentration of 71.5 pg/g (range ND-260 pg/g) and a mean 2,3,7,8-TCDF concentration of 67.1 pg/g (range ND-110 pg/g). Conversion of measured levels of 2,3,7,8-TCDF to 2,3,7,8-TCDD equivalents yielded a mean total concentration (in TCDD equivalents) of 78.2 pg/g. Both the mean 2,3,7,8-TCDD concentration and the mean concentration in TCDD equivalents exceeded the FDA guideline levels for "limited consumption" (25 pg/g) and "no consumption" (50 pg/g). A large percentage of the captured animals tested positive for 2,3,7,8-TCDD (53%) and 2,3,7,8-TCDF (67%). Combined muscle/hepatopancreas samples from both control blue crabs from Delaware Bay (n(composites) = 5) and control lobsters from the Gulf of Maine (n(composites) = 3; n(single-animal samples) = 2) showed no detectable levels of either contaminant.

Levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in combined muscle/hepatopancreas samples for American lobsters were similar in animals from the Ambrose fishery and those from the Alongshore fishery (Table 1; Figure 1), with mean concentrations of both contaminants in both areas between 34 and 41 pg/g. Mean total concentrations (in TCDD equivalents) were 38.5 pg/g for the Ambrose fishery and 44.4 pg/g for the Alongshore fishery. Mean 2,3,7,8-TCDD and TCDD equivalent levels thus fell between the two FDA guideline levels. Approximately 40% of the lobsters from both the Ambrose and Alongshore fisheries had detectable levels of 2,3,7,8-TCDD, but only 26% of the lobsters from both areas had detectable levels of 2,3,7,8-TCDF. None of the lobsters from the Offshore fishery contained detectable levels of either contaminant. The calculated mean concentrations (based on one-half the reported detection limits) were lower than those for the other areas, as was the calculated total mean concentration (18.7 pg/g in TCDD equivalents). The 2,3,7,8-TCDD and TCDD equivalent levels for the Offshore fishery fell below the FDA guideline levels.

Table 1. 2,3,7,8-TCDD and 2,3,7,8-TCDF (pg/g, wet weight) in Combined Muscle/Hepatopancreas Samples (Five-Animal Composites; Weights in g)

Species	Location[a]	N[b]	Weight[c] (mean±sd[d])	TCDD/TCDF (mean±sd)	Range	Detection limit	#>DL[e]
			2,3,7,8-TCDD				
Blue crab	Ambrose	15	237±61	71.5±87.2	ND-260	10-22	8
Lobster	Ambrose	19	344±108	34.4±30.2	ND-100	7-90	7
	Alongshore	19	412±180	40.8±16.5	ND-83	40-90	8
	Offshore	17	499±154	15.9±12.3	ND	7.7-78	0
			2,3,7,8-TCDF				
Blue crab	Ambrose	15	237±61	67.1±33.8	ND-110	9-87	10
Lobster	Ambrose	19	344±108	40.8±28.7	ND-120	17-89	5
	Alongshore	19	412±180	36.4±16.3	ND-86	30-77	5
	Offshore	9	465±124	28.1±21.3	ND	13-140	0

[a] See text for definitions of locations.
[b] N = number of composite samples analyzed; each composite sample consisted of muscle and hepatopancreas tissue from five animals (except one lobster sample from the Alongshore fishery and one from the Offshore fishery)
[c] Weight statistics are for all individual organisms that made up the composites at a given location.
[d] sd = standard deviation
[e] #>DL = number of samples with detectable contaminant concentrations

Table 2. 2,3,7,8-TCDD and 2,3,7,8-TCDF (pg/g, wet weight) in Muscle or Hepatopancreas of Individual Lobsters, with Whole-Body Weights (g) (NA=no analysis)

Location	Weight	Tissue	TCDD	TCDF
Ambrose	450.5	Hepatopancreas	<26	<35
		Muscle	<20	<25
Alongshore	950.6	Hepatopancreas	410	380
		Muscle	<20	<10
"	807.5	Hepatopancreas	170	260
		Muscle	<10	<10
Offshore	1280.2	Hepatopancreas	<31	<33
		Muscle	<19	<13
"	1637.5	Hepatopancreas	31	NA
		Muscle	<13	NA
"	1768.5	Hepatopancreas	<30	NA
		Muscle	<6	NA
"	1068.5	Hepatopancreas	<39	NA
		Muscle	<9.5	NA

Analyses of separate muscle and hepatopancreas samples from individual lobsters (Table 2) yielded detectable levels of both contaminants only in the hepatopancreas (<26 to 410 pg/g for 2,3,7,8-TCDD; <33 to 380 pg/g for 2, 3, 7, 8-TCDF). The concentration of 2,3,7,8-TCDD in the hepatopancreas of the two Alongshore lobsters exceeded the FDA "no consumption" guideline level, and the level in the hepatopancreas of one of the four Offshore lobsters exceeded the lower "limited consumption" guideline level. Concentrations in samples of lobster muscle tissue were all below the detection limit, which ranged from 6 to 20 pg/g for 2,3,7,8-TCDD and from 10 to 25 pg/g for 2,3,7,8-TCDF. Rappe et al. (1991) reported similar findings for blue crabs collected near the suspected contamination source on the Passaic River, and for lobsters from the New York Bight.

Two important limitations of the data set should be noted. First, many of the samples were obtained from commercial sources. While there is no evidence that the reliability of those sources should be questioned, it remains true that the origin of those samples could not be documented or verified first-hand. Second, the usefulness of the data set is limited by the extremely

high detection limits for many of the samples. As shown in Table 1, TCDD detection limits for samples with "below detection limit" results were as high as 90 pg/g. This is two orders of magnitude above detection limits for biological samples reported in the dioxin literature (Dolan et al. 1990; O'Keefe et al. 1990), and over three times the lower of the two FDA guideline levels. The variability in detection limits also contributed to the significant variability in the overall results.

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