Bull. Environ. Contam. Toxicol. (1986) 37:730–738

Bulletin of Environmental Contamination and Toxicology

Polycyclic Aromatic Hydrocarbon Contamination of American Lobster, *Homarus americanus*, in the Proximity of a Coal-Coking Plant

J. F. Uthe and C. J. Musial

Fisheries and Environmental Sciences, Department of Fisheries and Oceans, Halifax Fisheries Research Laboratory, P.O. Box 550, Halifax, Nova Scotia, Canada B3J 2S7

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental contaminants resulting predominantly from anthropogenic pyrolytic and combustion processes (NRCC 1983). In addition to the usual methods of aerial and aqueous transport to the coastal marine environment substantial amounts of PAH are added through the use of products such as creosote, coal tar and coal tar pitch as preservative and antifouling agents in the marine environment. Many of the compounds comprising PAH are known carcinogenic agents or are suspected of playing other roles in the carcinogenic process (NAS 1972). PAH are rapidly taken up by both fish and shellfish from water. Teleosts metabolize and excrete PAH compounds fairly rapidly while crustaceans and bivalves tend to accumulate PAH to relatively high levels in their tissues and metabolize them only slowly (Uthe 1979, NRCC 1983). As desirable human foodstuffs many of these shellfish species warrant monitoring for PAH.

Dunn and Fee (1979) reported that PAH concentrations in American lobster (Homarus americanus) muscle and digestive gland tissues were elevated following holding of the live animals in tidal impoundments which had utilized creosoted timbers in their construction. Further studies indicated that PAH levels in these lobsters could not be reduced to safe levels by holding in clean water (Uthe et al. 1984), and pound owners were advised to replace creosoted timbers.

A similar study of PAH in lobster tissues has been carried out using lobsters captured in Sydney Harbour, Nova Scotia, Canada. Two coal-coking ovens have been located on the shore of the harbour for many years and have discharged their liquid effluents through a pond into the harbour. In 1982 the South Arm of the harbour (nearest the discharge from the plant) was closed to commercial lobster fishing due to the presence of PAH in the animals. One of the coking ovens was shut down in November 1981, the other in November 1983. Lobsters were sampled and analyzed for PAH in 1982 and 1984.

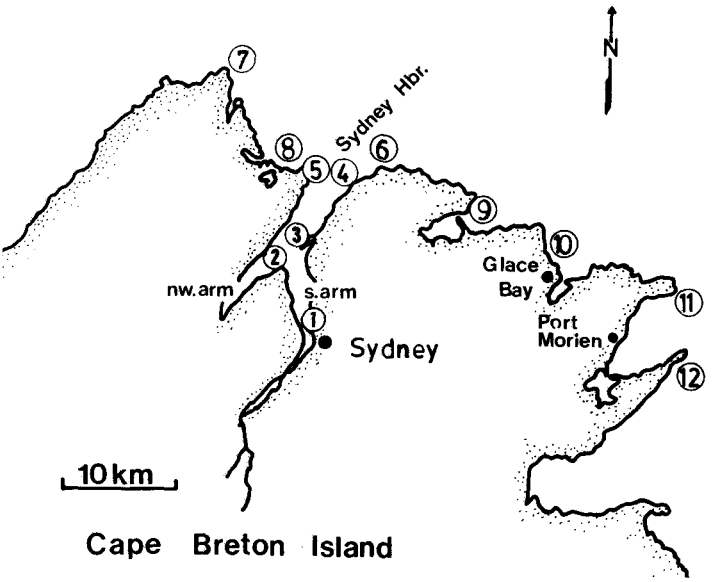

Figure 1. Map showing sampling sites, Cape Breton Island, Nova Scotia, Canada

MATERIALS AND METHODS

Lobsters (generally 10) were captured at the sites shown in Figure 1 using standard commercial traps and transported live to the laboratory where the intact digestive gland (hepatopancreas, mid-gut gland) and the tail muscle were removed, weighed and frozen. For analysis, pools of tissues from 5 animals were prepared from equal weights of tissues. Two g digestive gland or 8.0 g tail muscle was taken for saponification. Following alcoholic saponification PAH were extracted into isooctane. In the 1982 study the extracts were cleaned up by partitioning and column chromatography on Florisil (Sirota et al. 1984) while in the 1984 study size-exclusion chromatography on Biobeads SX-3 was used. Non-alkylated PAH compounds were determined by reverse-phase high performance liquid chromatography (Musial and Uthe 1986). A number of lobsters from the 1984 sample were retained and held in the laboratory aquarium for a period of twelve months, after which they were analysed for PAH. During the holding period, lobsters were fed the normal aquarium diet of herring.

RESULTS AND DISCUSSION

Two pooled samples per site were analyzed. The pool approach was taken following analysis of individual animal tissues (Table 1). The inter-animal relative standard deviation in PAH concentrations in both digestive gland and tail muscle was very large, ranging 48-86% for digestive gland and 40-70% for tail muscle. Thus it is not surprising that the agreement between the results for the two pooled samples from each site is not particularly good (Table 2). The results from the most contaminated area of the harbour, the South Arm, are shown for 1982 and 1984 along with the results for

Table 1. PAH concentrations (ng/g wet wt) in individual lobster digestive gland following 3 month exposure to creosoted timbers and transfer to clean water for 13 days.

Number	1	2	3	4	5	6	7	8	9	10	RSD*
						Digestive Gland					
Fluoranthene	3800	6700	3400	2100	3400	10300	6500	7100	10600	18500	48
Pyrene	1300	3000	1200	420	1400	5500	1800	2400	2700	3500	63
Benz[a]anthracene	6200	8100	4900	2000	4500	20000	9500	17500	19400	19600	64
Chrysene	5600	5300	3600	1800	3100	17800	7200	16100	16700	17600	70
Benzo[e]pyrene	1200	500	360	210	250	1600	780	1200	1400	1200	59
Benzo[b]fluoranthene	790	630	440	370	390	2000	950	2100	1800	1800	63
Benzo[k]fluoranthene	200	160	110	100	100	530	250	520	450	440	63
Benzo[a]pyrene	220	150	140	100	140	860	270	830	680	740	78
Benzo[ghi]perylene	340	240	240	140	240	1600	400	1700	1300	1400	86
Indeno[1,2,3-cd]pyrene	1000	690	560	390	500	4300	1300	4300	2900	3300	83
						Tail Muscle					
Fluoranthene	90	97	180	99	67	180	200	210	230	240	40
Pyrene	10	35	56	22	29	83	47	57	61	78	47
Benz[a]anthracene	200	210	260	130	100	370	410	560	310	370	46
Chrysene	190	130	160	110	60	290	280	430	200	250	50
Benzo[e]pyrene	30	14	20	10	10	36	30	45	22	30	45
Benzo[b]fluoranthene	30	20	26	27	9	42	46	72	31	35	48
Benzo[k]fluoranthene	7	4	7	7	2	11	13	19	9	10	51
Benzo[a]pyrene	8	5	10	12	4	21	19	32	15	16	57
Benzo[ghi]perylene	15	8	15	17	6	39	29	59	24	25	64
Indeno[1,2,3-cd]pyrene	45	21	34	44	12	100	78	170	60	59	70

* - relative standard deviation

the digestive glands from the control site animals. PAH concentrations in control lobster tail muscle were at or below our detection limit. With the exception of fluoranthene and pyrene the South Arm tissue levels of PAH appear to have decreased only slightly, if at all, between 1982 and 1984. Levels of benz[a]anthracene appear to have dropped precipitously between 1982 and 1984, however, since the same relative drop was observed in the control animals it is likely that the drop was due to some other factor. Consideration of the chromatograms from the two years suggested that the amount of benz[a]anthracene present in the 1982 standard was only one-tenth of the amount believed to be present. It is likely that the real change in benz[a]anthracene levels between 1982 and 1984 is less than the drop observed for pyrene. The magnitude of the difference in levels of PAH in the two tissue pools makes it impossible to accurately estimate the change in average tissue levels over the two year interval. Fluoranthene and pyrene levels have decreased, possibly along with benz[a]anthracene but the levels of the other PAH have not changed substantially. As mentioned above, there are two coal-coking ovens located near the harbour, one of which was shut down in November 1981. After 1981 the second oven ran at half-capacity until shut down in November 1983. When one considers the greater water solubility and vapour pressure of pyrene and fluoranthene compared to the other PAH studied here it is easy to postulate a mechanism based on these chemical properties by which an aging PAH source would result in the observed results. The relatively small changes observed in concentrations of the higher molecular weight PAH between 1982 and 1984 predict a long-term lobster contamination problem with relatively slow changes in PAH concentrations in lobster tissue over time. Since many of these higher molecular weight PAH are cancer-causing (NAS 1972) it is probable that the harbour will remain closed to the commercial fisheries for a long time unless action is taken to remove or isolate the source of PAH.

Using fluoranthene and benzo[a]pyrene as PAH markers (Table 3) the geographical distribution of PAH in lobsters within and around Sydney Harbour is apparent. As expected, levels decreased from the South Arm to the mouth of the harbour and beyond until the lowest levels at sites 7 and 12, furthest from the harbour and other coastal urban areas (sites 9 and 10). The results of the analyses of the lobster sub-sample which had been held live at the laboratory facilities are given in Table 4. Even after holding in a relatively clean environment for one year, these lobsters did not lose substantial amounts of all PAH which were determined. The compounds whose concentrations decreased the most were those with the greatest water solubility. An average overall of 85% of the most water soluble compound, fluoranthene, was lost from the digestive glands, and as little as 6% of chrysene, whose solubility is much less than that of fluoranthene (Futoma et al 1981). Figure 2 shows the relationship between PAH losses and water solubilities. The curve was calculated with a Hewlett-Packard 97 programmable calculator using the Standard Pac curve fitting program and is described by the equation:

Table 2. Polycyclic aromatic hydrocarbon (PAH) levels (ng/g wet wt) in lobster captured in May in the South Harbour (Site 1) compared to Port Morien lobsters (control).

	South Arm							
	Digestive Gland				Tail Muscle			
	1982		1984		1982		1984	
PAH								
Fluoranthene	15200	12400	4220	5240	420	442	68	68
Pyrene	13100	9150	3180	2910	333	70	59	63
Benz[a]anthracene	32700	18000	762	1150	678	900	17	19
Chyrsene	1030	252	770	1240	20	15	24	24
Benzo[e]pyrene	3600	1990	1550	2870	35	35	36	36
Benzo[b]fluoranthene	3820	2460	1020	1550	835	72	29	35
Benzo[k]fluoranthene	955	640	502	813	26	19	15	19
Benzo[a]pyrene	1430	930	711	1260	43	33	27	37
Benzo[ghi]perlyene	769	479	232	459	20	10	10	18
Indeno[1,2,3-cd]pyrene	739	525	486	931	40	30	12	21
	Port Morien							
	Digestive Gland				Tail Muscle			
	1982		1984		1982		1984	
Fluoranthene	156	162	93	90	6	34	-	
Pyrene	42	46	38	35	-*	22	-	
Benz[a]anthracene	79	74	6	6	6	17	-	
Chyrsene	7	2	26	43	-	-	-	
Benzo[e]pyrene	17	15	22	29	2.5	3.6	-	
Benzo[b]fluoranthene	10	7	16	13	0.5	0.8	-	
Benzo[k]fluoranthene	2.8	1.9	8	6	0.5	0.8	-	
Benzo[a]pyrene	2.5	1.6	8	5	0.5	1.6	-	
Benzo[ghi]perlyene	2.4	3.8	10	10	0.8	-	-	
Indeno[1,2,3-cd]pyrene	2.1	2.5	5	trace	0.8	-	-	

* - not detected

(difference in average concentration at beginning and end of holding period divided by average concentration at beginning) x 100 = % change in average concentration = 109 + 14 ln water solubility in mg/kg (coefficient of determination = 0.8457). Solubility data were available for only five of the PAH studied (Futoma et al. 1981), and while the published data refer to distilled water and not seawater, the information in Figure 2 is generally consistent with the decrease in the concentrations of the more water soluble PAH in Sydney Harbour lobsters during the 1982 - 84 period when the coking plant was inoperative. It should be noted that the curve in Figure 2 is based on a limited

Table 3. Fluoranthene and benzo[a]pyrene concentrations (ng/g wet wt) in digestive glands from lobsters captured at various sites in and around Sydney Harbour, Nova Scotia in May 1982.

Sample Site	Fluoranthene		Benzo[a]pyrene	
1	15200	12400	1430	930
2	8200	2320	134	147
3	2590	1920	81	80
4	648	2330	60	131
5	1290	533	37	20
6	1100	1200	60	4.5
7	30	33	0.1	0.5
8	350	320	8.4	2.0
9	340	256	7.0	2.5
10	460	381	19	22
11	742	46	2.5	1.6
12	46	90	0.4	1.0

Table 4. Polycyclic aromatic hydrocarbon (PAH) levels in lobster from South Arm of Sydney Harbour immediately after capture (1984) and after live holding in laboratory facilities for twelve months.

	Digestive Gland ng/g wet weight				Tail Muscle ng/g wet weight			
	1984		1985		1984		1985	
Fluoranthene	4220	5240*	706	706**	68	68*	11	6**
Pyrene	3180	2910	909	523	59	63	34	22
Benz[a]anthracene	762	1150	388	214	17	19	5	2
Chrysene	770	1240	988	907	24	24	32	14
Benzo[e]pyrene	1550	2870	1070	934	36	36	40	17
Benzo[b]fluoranthene	1020	1550	1260	567	29	35	33	10
Benzo[k]fluoranthene	502	813	742	356	15	19	21	6
Benzo[a]pyrene	711	1260	866	449	27	37	39	11
Benzo[ghi]perylene	232	459	119	125	10	18	6	2
Indeno[1,2,3-cd]pyrene	486	931	451	256	12	21	26	7

* - two pools, each of equal weights of 5 animals
** - two pools, each of equal weights of 3 animals

data set for which it was impossible to obtain estimates of the variances. Therefore the curve should be considered as a broad representation. It should also be noted that a portion of the apparent decrease would have resulted from dilution caused by growth of the animals over the holding period. In an earlier

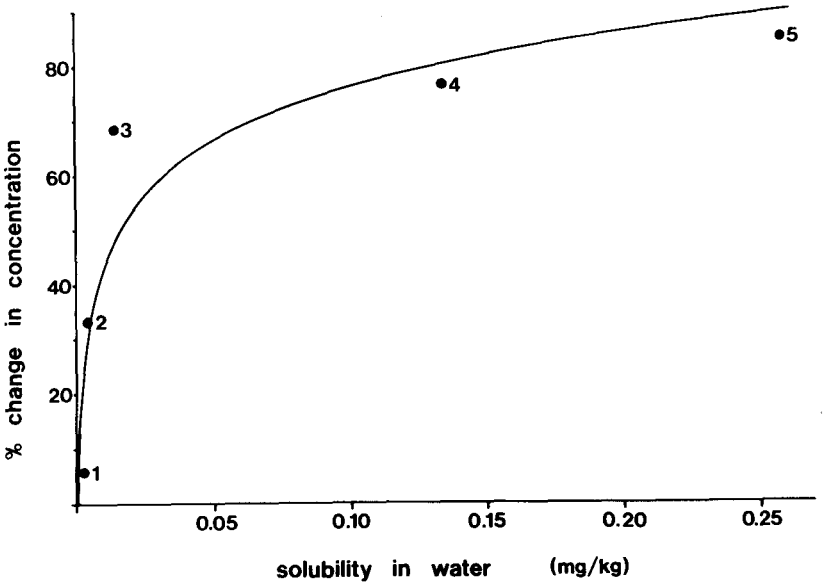

Figure 2. Plot of % change in average concentration of PAH in lobster digestive glands vs water solubility in mg/kg. Solubility data from Futoma et al. (1981). 1- chrysene, 2 - benzo[a]pyrene, 3 - benz[a]anthracene, 4 - pyrene, 5 - fluoranthene.

study (Uthe et al. 1984) losses of PAH from digestive glands of contaminated lobsters transferred to a clean environment ranged 31 - 77% over a five week winter holding period. In comparing these results, it should be noted that in the earlier study the lobsters had accumulated PAH in a relatively short period of time in contrast to the resident lobsters in Sydney Harbour, the diet was not specified, and that differences in water quality at the two holding facilities are probable. The results of both studies indicate that depuration of highly contaminated animals is impractical.

Both lobster digestive gland and tail muscle are viewed as highly desirable portions by many consumers. Digestive gland is utilized by the industry in preparing a canned product known as "lobster paste". It is therefore interesting to compare PAH concentrations in Sydney Harbour lobsters with PAH concentrations found in other foodstuffs. It should be noted that the usual

method of cooking lobsters, i.e. boiling or steaming the intact animal resulted in elevated PAH levels in the cooked tail meat, presumably from the digestive gland (Sirota et al. 1984). Comparison of PAH levels presented in this report with levels reported by other investigators must be viewed with some degree of caution due to the likelihood of sytematic error between the laboratories. (Uthe and Musial 1985; MacLeod et al. 1982; Law and Portman 1982). PAH levels in foodstuffs have been reviewed by a number of individuals (e.g. Howard and Fazio 1980; Lo and Sandi 1978) and it is instructive to compare reported levels of benzo[a]pyrene with our findings. Lo and Sandi (1978) concluded that most foodstuffs contain low levels of PAH unless pyrolytic reactions are involved in the preparation of the item (e.g. broiling and smoking). These authors note that shellfish are a notable exception since they appear to concentrate PAH and are unable to metabolize them. Benzo[a]pyrene levels in shellfish are reported to range up to 6 ng/g wet wt. Howard and Fazio (1980) in their review of PAH concentrations in foodstuffs reported that levels of benzo[a]pyrene in commercial shellfish were as high as 9.4 ng/g wet wt. in oysters from a contaminated bay. Dunn and Stich (1976) reported benzo[a]pyrene concentrations up to 45 ng/g wet wt. in mussels from creosoted timbers. Dunn and Fee (1979) reported benzo[a]pyrene concentrations up to 2300 ng/g in digestive gland and 281 ng/g wet wt. in tail meat from impounded lobsters and stated that these values are the highest that have ever been reported for any foodstuff. Our results in Sydney Harbour confirm the ability of lobsters to accumulate extremely high amounts of PAH in their tissues.

Acknowledgments

Thanks are extended to Drs. R. Mohn and D. Scarratt for reviewing the manuscript, to K. Deagle for art work and to V. Clayton and C. Holman for word processing.

REFERENCES

Dunn BP, Fee J (1979) Polycyclic aromatic hydrocarbon carcinogens in commercial seafoods. J Fish Res Bd Can 36:1469-1476

Dunn BP, Stich HF (1976) Release of the carcinogen benzo[a]pyrene from environmentally contaminated mussels. Bull Environ Contam Toxicol 15:398-401

Futoma DJ, Smith SR, Smith TE, Tanaka J (1981) Polycyclic Aromatic Hydrocarbons in Water Systems. CRC Press, Inc., Boca Raton, FA. 33431 p 16

Howard JW, Fazio T (1980) Analytical methodology and reported findings of polycyclic aromatic hydrocarbons in foods. J Assoc Off Anal Chem 63:1077-1104

Law RJ, Portman JE (1982) Report on the first ICES intercomparison exercise on petroleum hydrocarbon analyses in marine samples. ICES Coop Res Rep 117 p 55

Lo MT, Sandi E (1978) Polycyclic aromatic hydrocarbons (polynuclears) in foods. Residue Rev 69:35-86
MacLeod WD, Prohaska PG, Gennero DG, Brown DW (1982) Interlaboratory comparisons of selected trace hydrocarbons from marine sediments. Anal Chem 54:386-392
Musial CJ, Uthe JF (1986) A rapid, semi-micro method for the determination of polycyclic aromatic hydrocarbons in shellfish by automated gel permeation/high performance liquid chromatography. J. Assoc Off Anal Chem - in press
National Academy of Sciences (USA) (1972) Particulate polycyclic organic matter. US National Academy of Sciences, Washington, D.C. p 361
National Research Council of Canada (1984) Polycyclic aromatic hydrocarbons in the aquatic environment: Formation, sources, fate and effects on aquatic biota. Ass. Comm. Sci. Crit. for Environ. Qual. Ottawa, Canada No. NRCC 18981 p 209
Sirota GR, Uthe JF, Robinson DG, Musial CJ (1984) Polycyclic aromatic hydrocarbons in American lobster (Homarus americanus) and blue mussels (Mytilus edulis) collected in the area of Sydney Harbour, Nova Scotia. Can MS Rep Fish Aquat Sci 1758: 22 p
Uthe JF, Musial CJ (1985) Report on the intercomparative study 03/HC/BT on the determination of polycyclic aromatic hydrocarbons in biological tissue. ICES Statutory meeting. Paper C.M 1985/E:46
Uthe JF, Sirota GR, McLeese DW, Burridge L (1984) The uptake and depuration of polycyclic aromatic hydrocarbons (PAH) by American lobster (Homarus americanus) held in a tidal pound. Can Tech Rep Fish Aquat Sci 1059: 10 p
Uthe JF (1979) The environmental occurrence and health aspects of polycyclic aromatic hydrocarbons. Fish Mar Ser Tech Rep 914: 30 p
Received December 19, 1985; accepted March 3, 1986.