

# The Carcinogenic Load of the Environment: Benzo(a)Pyrene in Sediments of Arctic Waters

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**ABSTRACT.** Baseline levels of the chemical carcinogen benzo(a)pyrene were measured in arctic sediments. Levels were highest in samples from the Mackenzie River delta and adjacent areas of the Beaufort Sea. The distribution of carcinogen did not correspond to the location of inhabited areas — a natural rather than a man-made source for polycyclic aromatic hydrocarbons in arctic sediments is indicated.

**RÉSUMÉ.** Les niveaux minimum de benzo(a)pyrènes "carcinogènes", étaient mesurés chimiquement dans les sédiments arctiques. Les plus hauts niveaux venaient d'échantillons en provenance du delta de fleuve Mackenzie et des parties adjacentes de la Mer de Beaufort.

La répartition des "carcinogènes" ne correspondait pas à la position des régions habitées; il y a une indication d'une source naturelle plutôt qu'artificielle pour les hydrocarbures aromatiques polycycliques dans les sédiments arctiques.

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## INTRODUCTION

Stimulated by the possibility of oil leakage and spills, considerable attention has been given to aliphatic hydrocarbons in the arctic environment. Their geographic distribution (NAS publication, 1975; McAuliffe, 1976) and accumulation in sediments (Shaw and Cheek, 1976) has been submitted to numerous careful examinations. Less work has been done on the occurrence of polycyclic aromatic hydrocarbons (PAH) in marine environments (Neff, 1979) although many of them are potent carcinogens and thus could represent a hazard to living organisms including man (IARC, 1972). It is widely assumed that PAH's in bottom sediments and sedentary organisms are associated with human activity (Dunn and Stich, 1976; Grimmer and Bohnke, 1975; Neff, 1979). Benzo(a)pyrene [B(a)P] which is one of the carcinogenic PAH's was observed in commercial and pleasure boat harbors, vicinities of urban or industrial discharges, and piers containing creosoted pilings.

In this paper we report the occurrence of B(a)P in shore sediments of what are generally considered to be pristine arctic waters. The observed concentrations of B(a)P can be used as a baseline useful for detecting man-made contaminations. These studies may help in recognizing naturally-occurring hot spots of chemical carcinogens which remain unrecognized because of our current emphasis on man-made contamination.

## MATERIAL AND METHODS

### *Sediment Samples*

Samples were obtained by collecting the top layers of sediment not exceeding 5 cm in depth. The samples were frozen within an hour of collecting and only

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thawed prior to B(a)P analysis. The sediment was kept in plastic bags which did not contribute any detectable amounts of PAH's to the samples.

#### *Analysis of Benzo(a)pyrene*

Techniques used for the extraction of polycyclic aromatic hydrocarbons and the removal of interfering materials have been described previously (Dunn, 1976). In brief, 50-100 g of sediment were refluxed with alcoholic KOH, then the sediment removed by decantation. Water was added to the alcoholic extract, and the hydrocarbons partitioned into iso-octane. Interfering materials were removed by column chromatography of Florisil and by partitioning the extract between iso-octane and DMSO. An internal standard of radioactively labelled benzo(a)pyrene was added to each sample before extraction in order to correct for losses during the procedures.

Benzo(a)pyrene was measured in one of two ways. For Alaska samples, and for Mackenzie/Beaufort Sea samples taken in 1977, benzo(a)pyrene was separated from other polycyclic aromatic hydrocarbons by thin-layer chromatography on cellulose acetate, and measured by fluorimetry (Dunn, 1976). For Mackenzie/Beaufort Sea samples taken in 1979, purified extracts of polycyclic aromatic hydrocarbons were subjected to high pressure liquid chromatography on a Perkin-Elmer HC-ODS column using a gradient of 60 to 99% acetonitrile in water. Chromatographic separations were similar to those reported by Ogan *et al.* (1979). Benzo(a)pyrene was measured using a UV absorption detector and a fluorescence detector in series. When samples of sediments were split and analyzed by both methods, analytical results generally agreed to within  $\pm 25\%$ . Because such analytical variability is less than the variability between different samples, no distinction is made in the tables between sediments analyzed by different procedures.

Duplicate samples of sediments were dried at 80°C for 24 hours to determine their moisture content. Dried samples were then heated at 500°C for 6 hours for determination of the ashable organic content by weight loss during ignition. Data in tables are expressed in micrograms benzo(a)pyrene per kg wet sediment, per kg dry sediment, and per kg organic content (determined by ignition at 500°). For example, if a 100 g wet sample is found to contain 1  $\mu\text{g}$  benzo(a)pyrene, and analysis of a duplicate sample reveals a dry weight of 50 grams and a loss during ignition of 5 grams, the contamination of the sample is 10  $\mu\text{g}/\text{kg}$  wet weight, 20  $\mu\text{g}/\text{kg}$  dry weight, and 200  $\mu\text{g}/\text{kg}$  organic content.

## RESULTS

Bottom sediments were collected from areas of three geographically distinct regions: (1) Kotzebue and Nome area (Alaska); (2) Mackenzie delta and its vicinity extending westwards to Herschel Island and eastwards till Franklin Bay (Northwest Territories, Canada); and (3) Devon Island (High Arctic Canada). Most sampling sites are shown in Figures 1 and 2. The samples were taken at the water edge during a regular low tide period.

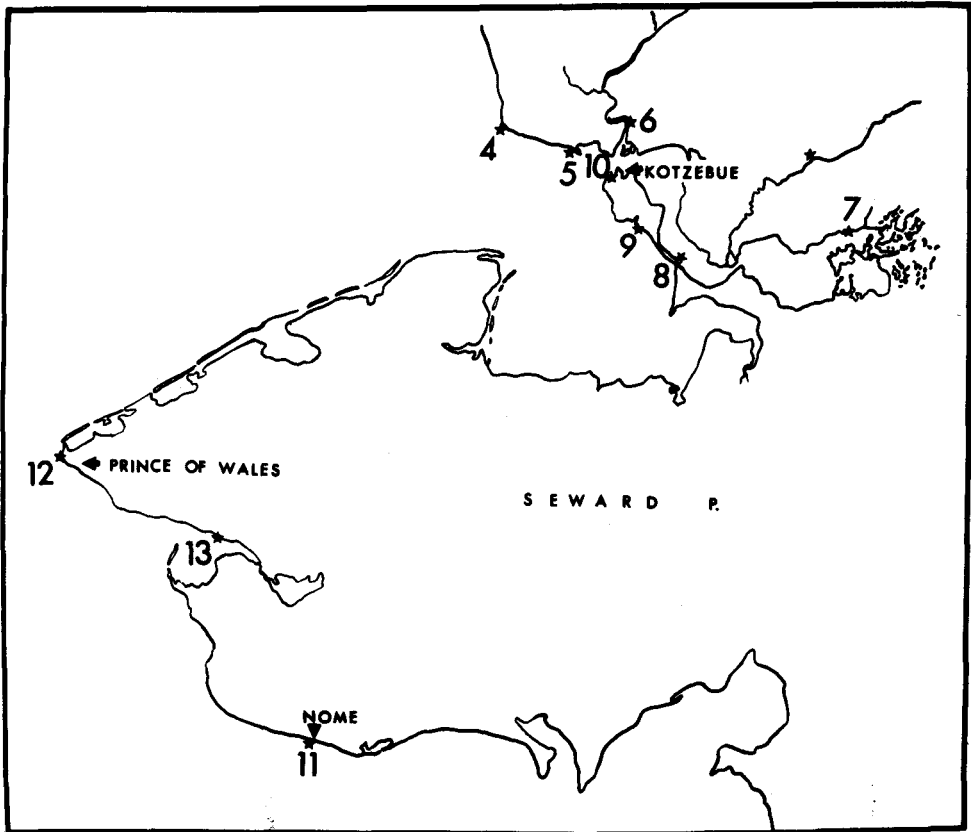


Fig. 1. Alaska study areas.

The concentrations of B(a)P per kg wet or dry sample weight are given in Table 1. When comparing the contamination of samples from a given area, it was apparent that there was to some degree a positive correlation between levels of B(a)P, and levels of organic material in the sediments. A linear regression analysis for 19 Mackenzie delta and Beaufort Sea samples taken in 1977 indicated a correlation coefficient of 0.479 (significant at the 5% confidence level). To help in the interpretation of the data, levels of B(a)P were also expressed in terms of the organic content of the samples (Table 1, last column). This latter figure gives an indication of the contamination of the organic fraction of the sediment, independent of the proportion of mineral material (sand, pebbles, etc.) in the sample. The results show considerable geographic differences in B(a)P concentrations. Relatively high concentrations were only observed in sediments of the Mackenzie delta (N.W.T.) and towards the area of the Smoking Hills (N.W.T.). Samples from Alaska and Devon Island contained low B(a)P levels.

Of particular interest is the observation that the B(a)P contents of sediments close to cities (e.g. Kotzebue and Nome in Alaska, Inuvik and Aklavik in Canada) did not show any significant increase above those found in the neighbouring areas. Similarly, the B(a)P levels of beaches with motorboat traffic (e.g.

Table 1. Concentration of benzo(a)pyrene in marine sediments of arctic waters

Map Nos.	Location	No. of Samples	Average B(a)P $\mu\text{g}/\text{kg}$ Wet Weight	Average B(a)P $\mu\text{g}/\text{kg}$ Dry Weight	Average B(a)P $\mu\text{g}/\text{kg}$ Organic Content
<b>ALASKA</b>					
4	Cape Krusenstern	1	0.02	0.02	2
5	Sheshalik	7	0.03	0.8	18
6	Noatak	2	0.04	0.65	10
7	Selavik	1	1.1	1.5	132
Baldwin Peninsula					
8	Arctic Shelter Cabin	2	0.4	1.2	26
9	Reindeer Corral	1	0.3	1.0	4
10	Kotzebue	2	0.4	0.5	34
11	Nome	4	0.8	1.0	75
12	Prince of Wales	3	0.3	0.5	10
13	Teller Reindeer Station	2	0.04	0.04	3
<b>NORTHWEST TERRITORIES—CANADA</b>					
14	Herschel Island	1	0.5	0.6	46
15	Stoke Point	1	0.5	0.6	72
16	Kay Point	2	7.5	10.1	442
17	King Point	2	1.9	2.3	181
18	Shingle Point	2	2.4	3.3	36
19	Inuvik Channel	2	5.3	10.0	113
20	Mackenzie Delta	1	5.4	8.6	151
21	Mackenzie Delta	1	1.8	2.3	67
22	Mackenzie Delta	1	14.0	23.0	461
23	Mackenzie Delta	1	20.0	33.1	539
24	Mackenzie Delta	1	7.6	2.2	30
25	Aklavik	1	15.6	25.0	413
26	Kittigazuit Bay	1	16.7	22.0	582
27	Kittigazuit	1	19.4	24.3	1637
28	Naparotalik Spit	1	0.6	0.7	86
29	Tuktoyaktuk	6	1.0	1.5	66
30	Hutchison Bay	1	1.9	2.2	247
31	McKinley Bay	1	0.2	0.2	31
32	Nicholson Point	1	1.4	1.6	97
33	Wood Bay	2	7.4	9.5	122
34	Maitland Point		3.4	4.9	64
35	Franklin Bay	1	8.5	13.4	130
<b>DEVON ISLAND</b>					
37	Thomas Lee Inlet	2	0.3	0.4	29

the Eskimo settlements at Sheshalik, Selavik or Tuktoyaktuk) were comparable to those seen in areas devoid of human activity. The B(a)P concentrations in bottom sediments of the Eskimo settlement of Tuktoyaktuk, which has an active airport, shipping activity, and large storage depots of oil drums, are considerably lower than in the Mackenzie delta (map locations #20 to 24) or the vicinity of the Smoking Hills (map locations #33, 34 and 35) which are completely devoid of human settlements.

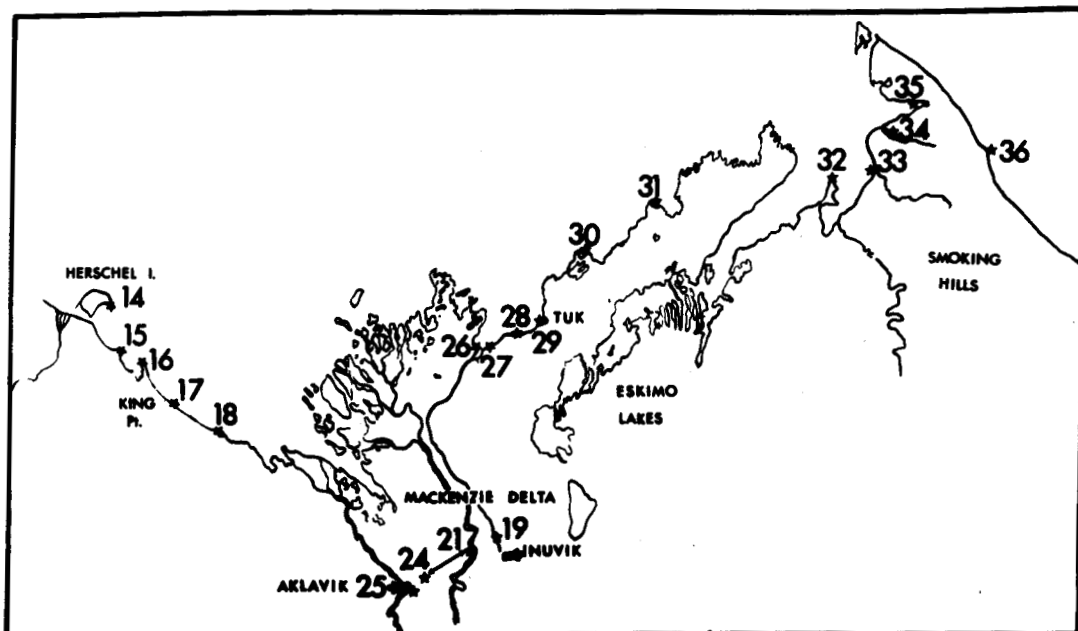


Fig. 2. Arctic Canada study areas.

Table 2. Variation of benzo(a)pyrene concentrations within a location

Location	Sample Description	B(a)P $\mu\text{g/kg}$ Wet Weight	B(a)P $\mu\text{g/kg}$ Dry Weight	B(a)P $\mu\text{g/kg}$ Organic Content
Sheshalik	off shore, coarse sand	0.2	0.2	22
	off shore, fine sand	0.2	0.2	27
	shoreline, mud	0.4	0.4	44
	shoreline, mud with plant roots	0.6	1.9	11
	slough at shore	0.3	1.0	6
	soil at shore	0.4	0.8	4
	soil at shore	0.3	1.4	10
	Prince of Wales	off shore	0.9	1.1
water edge at low tide		0.02	0.02	3
10 m from water edge		0.02	0.02	2
lagoon at shore		0.2	0.2	70
slough with roots		0.2	0.4	8
Tuktoyaktuk	peninsula, fine sand	0.1	0.1	12
	city edge, fine sand	1.2	1.2	160
	city centre, fine sand	1.1	1.3	80
	city centre, black material	2.0	4.4	17
	at oil drum deposit	0.9	1.0	49
	inside harbour	1.0	1.2	79

The variation in B(a)P levels between different samples from the same sampling area is shown in Table 2. There is considerable variability, suggesting that multiple samples are necessary to accurately assess the level of contamination in a given area. At the same time, it was found that the range of concentration in the

Table 3. Concentration of benzo(a)pyrene in marine sediments taken in 1977 and 1979

Location		Time	B(a)P $\mu\text{g}/\text{kg}$ Wet Weight	B(a)P $\mu\text{g}/\text{kg}$ Dry Weight	B(a)P $\mu\text{g}/\text{kg}$ Organic Content
Tuktoyaktuk	inside harbour	1979	1.0	1.2	79
	inside harbour	1977	1.3	1.8	107
Beluga Point	off shore	1979	0.5	0.7	86
	off shore	1977	0.2	0.2	23
Mackenzie Delta	east channel	1979	17.1	22.9	398
	east channel	1977	14.0	23.0	461
	west channel	1979	11.6	22.0	179
	west channel	1977	20.6	33.1	539

most contaminated sites and the least contaminated sites did not overlap — single samples may therefore be useful in a preliminary assessment of the contamination of an area. Three locations were sampled both in 1977 and in 1979. The analytical results (Table 3) indicate that within the limitations imposed by sample variability there were no changes in the B(a)P content of the sediments within this period.

For comparative purposes, levels of benzo(a)pyrene in sediment samples taken from harbour and non-harbour sites outside the Arctic are shown in Table 4. Median values rather than means are used, since occasional extremely high contamination levels are encountered in harbour areas near sources of pollution, and these values have a disproportionate effect on mean values of contamination. In 20 samples taken from 9 separate non-harbour sites on the Pacific Coast of North America (Oregon to British Columbia), the median value of contamination by benzo(a)pyrene was only  $0.4 \mu\text{g}/\text{kg}$ . This value is comparable to levels found in Alaskan sediments and Devon Island samples, but is considerably less than levels encountered in sediments from the Mackenzie River and Beaufort Sea areas (median value  $4.4 \mu\text{g}/\text{kg}$  for 22 sites in Table 1). This difference is not due to any difference in the organic content of Pacific samples compared with Arctic samples. Although the levels in the Mackenzie and Beaufort samples are higher than the baseline levels seen elsewhere, they are still considerably less than the levels which are commonly encountered in polluted areas such as harbours (Table 4). Contamination in these latter areas probably results from a combination of petroleum discharges, urban runoff and sewage discharges, fallout from urban air pollution, and leaching of creosote from treated pilings used in wharf structures.

#### DISCUSSION

PAH's in marine and freshwater environments originate from a great variety of different sources (Neff, 1979; Shabad, 1973). A sharp gradient of B(a)P towards a sewage treatment plant (Dunn and Stich, 1976), a higher concentration of B(a)P at the settled northern shore of the Ploner Sea than at the non-inhabited

Table 4. Concentration of benzo(a)pyrene in harbour and non-harbour areas

Location	No. of Samples	Median B(a)P $\mu\text{g}/\text{kg}$ Wet Weight	Median B(a)P $\mu\text{g}/\text{kg}$ Dry Weight	Median B(a)P $\mu\text{g}/\text{kg}$ Organic Content
Pacific Coast, North America 9 sites, non-harbour	20	0.4	—	—
Pacific Coast, North America 9 sites, harbour	22	105	—	—
Hakodate Harbour, Japan	14	3	6.7	91
Hong Kong Harbour	3	34	—	—
Wilhelmshaven Harbour, Germany	13	19	24	1435
Vancouver Harbour, Canada	9	200	288	7321

southern shore (Grimmer and Bohnke, 1975), an increase of B(a)P in core samples of recent origin (Müller *et al.*, 1977; Hites *et al.*, 1977) indicate an anthropogenic origin of PAH's.

There was a significant positive correlation between levels of organic material in sediments, and levels of benzo(a)pyrene. Means *et al.* (1979) have indicated that the absorptive properties of sediments for polycyclic aromatic hydrocarbons depend mainly on their organic carbon content. A positive correlation between organic content and B(a)P levels in sediments could result from the ability of organic material in sediments to remove B(a)P from the water column. Alternatively, B(a)P and sediment organic material might originate from the same basic source, and be found in association with each other.

The relatively high concentrations of B(a)P in bottom sediments of the Mackenzie delta, the neighbouring shores of the Beaufort Sea and the vicinity of Smoking Hills (N.W.T.) do not fit this pattern. It is difficult to trace this contamination to a man-made activity. There is no increase of B(a)P in the vicinity of small cities or settlements as seen in the case of Nome, Aklavik, Inuvik and Tuktoyaktuk. Oil seepage could conceivably be an important factor. However, high pressure liquid chromatograph fingerprint patterns of polycyclic aromatic hydrocarbons from Athabasca tar sands differ considerably from those from bottom sediments of the Mackenzie delta (unpublished results). At present we consider forest fires or tundra fires (Wein, 1976) as the most likely source of B(a)P in the marine sediments of arctic waters. There seems to be little doubt that forest and grass fires are a natural pyrolytic source of atmospheric PAH (Youngblood and Blumer, 1975; Farrington and Meyers, 1975; Suess, 1976). A relatively high concentration of B(a)P in prehistoric layers of permafrost soil also indicates a natural origin of PAH's (Jenitsky *et al.*, 1979). However, an anthropogenic source cannot be completely excluded considering that PAH's can be carried over long distances (Bjorseth *et al.*, 1979).

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