International Council for the
Exploration of the Sea
Copenhagen, 1974

C.M. 1974/E:16
Fisheries Improvement
Committee/Ref. Shell-
fish and Benthos Cttee

GEOGRAPHICAL DISTRIBUTION OF CADMIUM AND ARSENIC[1] IN LOBSTER DIGESTIVE GLAND (HEPATOPANCREAS)

by

H. C. Freeman and J.F. Uthe

Environment Canada
Fisheries and Marine Service
Halifax Laboratory
1707 Lower Water Street
Halifax, Nova Scotia, Canada, B3J 2R3

SUMMARY

Cadmium levels were determined in the edible portions of lobsters from selected areas picked to sample the bulk of the lobster fishery in the four Atlantic provinces of Canada. Most of the cadmium in the lobster was in the digestive gland which is used for lobster paste and ranged from 2.82 to 16.73 ppm while muscle levels were less than 1.0 ppm. Calculated cadmium levels in the total edible portion ranged from 0.51 to 2.98 ppm. It was thought that most of the cadmium was of geologic origin.

Arsenic levels ranged from 1.04 to 37.29 ppm in flesh surveyed but indications are that the arsenic is present in a relatively non-toxic form.

Arsenic levels in lobster digestive gland ranged from 6.61 ppm from specimens obtained from Gaspé, P.Q. to 16.2 ppm in specimens obtained from Sambro, N.S. Little of the arsenic is present as inorganic toxic arsenic.

INTRODUCTION

Cadmium, a white metal used in a variety of industrial applications, especially electroplating is an extremely toxic element, believed by some toxicologists to be as toxic as methyl mercury[1]. Shellfish are known to be potent concentrators of metal ions. This effect is potentially serious, both to the survival of the animal itself as a species and also to mankind in his use of shellfish as foodstuff. Areas in which levels of cadmium above average are being added to the watershed, either geologically or through man's activities are to be carefully discovered and monitored.

Preliminary studies by the Inspection Service of Environment Canada showed that canned lobster paste (made up of digestive gland and lobster roe mainly) could contain levels of cadmium in a parts per million range. The Halifax Laboratory was called in to study this problem indepth. One part of this study dealt with the geographical distribution of cadmium in lobsters and is reported on in this paper.

The existence of high arsenic levels in certain fish and shellfish has been known for many years and levels of 25ppm are not uncommon. Early studies by Coulson *et al*, (2) showed that the arsenic present in shrimp is in a chemical combination which causes injested arsenic from shrimp to be rapidly excreted in the urine and therefore is relatively non-toxic. Recent work by Lunde (3) suggests that not only a variety of compounds of arsenic exists in marine organisms but that potentially toxic inorganic arsenic might also be present. A preliminary survey of arsenic levels in marine species and a geographical distribution of arsenic will be reported here.

MATERIAL AND METHODS

Sample Collection -

Lobsters (400-700g) each were purchased live. Each sample was composed ideally of thirteen males and thirteen females and were picked from traps within an area of about 15 kilometers. Weight, length and sex of each animal was recorded and the total digestive gland removed. The crusher claw and the tail section were also kept. All samples were frozen over dry ice for transport to the laboratory. In the lab, the claw and tail were steamed, the muscle removed and frozen until homogenized and analyzed. The digestive gland was homogenized by hand kneading in a plastic bag prior to analysis.

Total Arsenic Analysis -

The total arsenic contents of the samples were determined by the wet ash method of Uthe et al (4) using the reduction system described by Freeman and Uthe (5). The method involves digestion of the tissue (0.2 - 0.5 gm) in nitric acid (5 ml) in the presence of vanaduim pentoxide followed by fuming with sulfuric acid (10 ml) for 2 hrs to reconvert all forms of arsenic to inorganic arsenic. Conversion of inorganic arsenic to arsine for atomic absorption spectrophotometry was carried out by the method of Fernandez and Manning (6).

Total Cadmium -

Cadmium was determined in acid (5 ml H_2SO_4 - HNO_3; 4:1 v/v) digests of tissue (0.2 - 0.5 g) by atomic absorption spectrophotometry using a graphite furnace. Cadmium levels were calculated using the method of additions after this method was shown to give results equivalent to extraction of the cadmium as a chelate into organic solvents. The standard curve was linear between 0.01 and 0.2 ng Cd.

RESULTS AND DISCUSSION

The lobster collection sites are shown in Figures 1 and 2, and were selected in areas to sample the bulk of the lobster fishery. Preliminary analysis of a few of the sampling sites showed that essentially no difference in cadmium or arsenic levels existed between sexes. The distribution of cadmium levels within a sample from a site was distributed log normally on the basis of probit plots. In a like manner arsenic was normally distributed. For this reason all mean cadmium levels and standard deviations were calculated from log individual sample values. Arsenic means and standard deviations were calculated in the usual manner. Mean cadmium levels are shown in Table 1 along with standard deviations and range of values found. Means range from 2.82 ppm Cd to a high of 16.73 with many of the areas (12/24) having mean levels in excess of 10 ppm. These are very high levels of cadmium for a foodstuff. Levels in other foodstuff are generally below 1 part per million. The highest mean values for cadmium were found in lobsters taken from the north side of Prince Edward Island within the Gulf of St. Lawrence. The question of how much of this cadmium is present as a result of industrialization cannot easily be answered. Non-industrialized areas, away from sites of known St. Lawrence River deposition gave highest values while areas of deposition and industrialization (Chaleur Bay) gave relatively low values. It is likely that the majority of the cadmium is geological

INTRODUCTION

Cadmium, a white metal used in a variety of industrial applications, especially electroplating, is an extremely toxic element, believed by some toxicologists to be more toxic than mercury as toxic as methyl mercury[1]. Shellfish are known to be potent concentrators of trace metals ions. This effect is potentially serious, both to the survival of the animal as and itself and as a species and also to mankind in his use of shellfish as foodstuff. Areas in which levels of cadmium above average are being added to the watershed either geologically or through man's activities are to be carefully discovered and monitored.

Preliminary studies by the Inspection Service of Environment Canada showed that canned lobster paste (made up of digestive gland and lobster roe mainly) could contain levels of cadmium in a parts per million range. The Halifax Laboratory was called in to study this problem in depth. One part of this study dealt with the geographical distribution of cadmium in lobsters and is reported on in this paper.

The existence of high arsenic levels in certain fish and shellfish has been known for many years and levels of 25ppm are not uncommon. Early studies by Coulson et al, (2) showed that the arsenic present in shrimp is in a chemical combination which causes injested arsenic from shrimp to be rapidly excreted in the urine and therefore is relatively non-toxic. Recent work by Lunde (3) suggests that not only a variety of compounds of arsenic exists in marine organisms but that potentially toxic inorganic arsenic might also be present. A preliminary survey of arsenic levels in marine species and a geographical distribution of arsenic will be reported here.

MATERIAL AND METHODS

Sample Collection -

Lobsters (400-700g) each were purchased live. Each sample was composed ideally of thirteen males and thirteen females and were picked from traps within an area of about 15 kilometers. Weight, length and sex of each animal was recorded and the total digestive gland removed. The crusher claw and the tail section were also kept. All samples were frozen over dry ice for transport to the laboratory. In the lab, the claw and tail were steamed, the muscle removed and frozen until homogenized and analyzed. The digestive gland was homogenized by hand kneading in a plastic bag prior to analysis.

Total Arsenic Analysis -

The total arsenic contents of the samples were determined by the wet ash method of Uthe et al (4) using the reduction system described by Freeman and Uthe (5). The method involves digestion of the tissue (0.2 - 0.5 gm) in nitric acid (5 ml) in the presence of vanaduim pentoxide followed by fuming with sulfuric acid (10 ml) for 2 hrs. to reconvert all forms of arsenic to inorganic arsenic. Conversion of inorganic arsenic to arsine for atomic absorption spectrophotometry was carried out by the method of Fernandez and Manning (6).

Total Cadmium -

Cadmium was determined in acid (5 ml H_2SO_4 - HNO_3; 1:4 v/v) digests of tissue (0.2 - 0.5 g) by atomic absorption spectrophotometry using a graphite furnace. Cadmium levels were calculated using the method of additions after this method was shown to give results equivalent to extraction of the cadmium as a chelate into organic solvents. The standard curve was linear between 0.01 and 0.2 ng Cd.

RESULTS AND DISCUSSION

The lobster collection sites are shown in Figures 1 and 2, and were selected in areas to sample the bulk of the lobster fishery. Preliminary analysis of a few of the sampling sites showed that essentially no difference in cadmium or arsenic levels existed between sexes. The distribution of cadmium levels within a sample from a site was distributed log normally on the basis of probit plots. In a like manner arsenic was normally distributed. For this reason all mean cadmium levels and standard deviations were calculated from log individual sample values. Arsenic means and standard deviations were calculated in the usual manner. Mean cadmium levels are shown in Table 1 along with standard deviations and range of values found. Means range from 2.82 ppm Cd to a high of 16.73 with many of the areas (12/24) having mean levels in excess of 10 ppm. These are very high levels of cadmium for a foodstuff. Levels in other foodstuff are generally below 1 part per million. The highest mean values for cadmium were found in lobsters taken from the north side of Prince Edward Island within the Gulf of St. Lawrence. The question of how much of this cadmium is present as a result of industrialization cannot easily be answered. Non-industrialized areas, away from sites of known St. Lawrence River deposition gave the highest values while areas of deposition and industrialization (Chaleur Bay) gave relatively low values. It is likely that the majority of the cadmium is geological

in nature and results from erosion. There many known deposits of cadmium containing ores, such as zinc ores, and the fish in some of the areas studied are directly affected by the mine effluents.

The effect of these findings on the lobster fishery is unknown. The preliminary studies indicate that cadmium content in the digestive gland increases as the animal grows. The bulk of the cadmium in the lobster is in the digestive gland. Muscle, both claw and tail, have cadmium levels between 0.05 and 0.1 ppm and the hemolymph has essentially none. The digestive gland represents slightly more than 5% of the lobster's total weight (8) and as a lobster dresses at about 30%, the digestive gland represents about 20% of the edible portion. Assuming that 98% of the cadmium in the edible portion is in the digestive gland fraction, an average cadmium content of the edible portion can be calculated. This is shown in Table 2. While these levels are much lower than levels in the digestive gland, they are still in excess of the 0.5 - 1 ppm level. If cadmium is as toxic as mercury it seems reasonable to expect allowable cadmium levels to be set at around 1 ppm. However, the lobster is a rather exotic foodstuff and it would seem to be an instance where a level could be set based on an allowable weekly intake of cadmium. A maximum weekly intake of 0.4 - 0.5 mg Cd has been suggested (1). A 0.5 - 1.0 kg lobster yields about 150-300 gms of edible portion. Assuming an average level of 2 ppm, eating this much would give an intake of 0.3 - 0.6 mg Cd. Due to the limited intake of lobster by the average person, a higher tolerance for Cd appears reasonable. The situation with very large lobsters is, of course, different, as cadmium levels will be much higher. Products such as lobster paste will also need research for cadmium removed prior to canning.

Arsenic is a much less serious problem in lobster than is cadmium, but is a more widespread contaminant than cadmium. Table 3 shows arsenic levels in a wide variety of marine species. It must be kept in mind that the bulk of this arsenic is probably present in a non-toxic form. The geographical distribution of arsenic has been determined based on a selected number of sampling sites from the cadmium distribution study. These results are shown in Table 4. The pattern which emerges suggests that levels just off the east coast of Nova Scotia (Sambro, Tangier, Arichat) are about twice those found in areas surrounding the Gulf of St. Lawrence. Individual specimens have been found with arsenic levels in excess of 100 ppm. With such high levels even though it is known that a lot of the arsenic is present in relatively non-toxic forms it is possible that smaller percentages of the arsenic may be present as the very toxic arsenite form. With this in mind, a method of determining only arsenite has been developed and preliminary experiments have suggested that very little arsenite is present in these arsenic containing fish.

REFERENCES

F.A.O. Nutrition Meetings Report Series No. 51A, Food and Agriculture Organization of the United Nations, Rome (1973).

COULSON, E.J., R.E. REMINGTON and K.M. LYNCH. J. Nutrition 10, 255 (1935).

LUNDE, G. J. Sci. Food Agric 24, 1021, (1973)

UTHE, J.F., H.C. FREEMAN, J.R. JOHNSTON and P. MICHALIK. J. of the AOAC, in press (1974).

FREEMAN, H.C. and J.F. UTHE. Atomic Absorption Newsletter 13, 75 (1974).

FERNANDEZ, F.J. and D.C. MANNING. Atomic Absorption Newsletter 10, 86 (1971)

LORING, D.H. and D.J.G. NOTA. Morphology and sediments of the Guld fo St. Lawrence. Bull. Fish. Res. Bd. Canada, Number 182, Ottawa (1973).

STEWART, J.E., J.W. CORNICK, D.M. FOLEY, M.F. LI, and C.M. BISHOP. J. Fish. Res. Bd. Canada 24, 2339 (1967).

in nature and results from erosion. There many known deposits of cadmium containing ores, such as zinc ores, and the fish in some of the areas studied are directly affected by the mine effluents.

The effect of these findings on the lobster fishery is unknown. The preliminary studies indicate that cadmium content in the digestive gland increases as the animal grows. The bulk of the cadmium in the lobster is in the digestive gland. Muscle, both claw and tail, have cadmium levels between 0.05 and 0.1 ppm and the hemolymph has essentially none. The digestive gland represents slightly more than 5% of the lobster's total weight (8) and as a lobster dresses at about 30%, the digestive gland represents about 20% of the edible portion. Assuming that 98% of the cadmium in the edible portion is in the digestive gland fraction, an average cadmium content of the edible portion can be calculated. This is shown in Table 2. While these levels are much lower than levels in the digestive gland, they are still in excess of the 0.5 - 1 ppm level. If cadmium is as toxic as mercury it seems reasonable to expect allowable cadmium levels to be set at around 1 ppm. However, the lobster is a rather exotic foodstuff and it would seem to be an instance where a level could be set based on an allowable weekly intake of cadmium. A maximum weekly intake of 0.4 - 0.5 mg Cd has been suggested (1). A 0.5 - 1.0 kg lobster yields about 150-300 gms of edible portion. Assuming an average level of 2 ppm, eating this much would give an intake of 0.3 - 0.6 mg Cd. Due to the limited intake of lobster by the average person, a higher tolerance for Cd appears reasonable. The situation with very large lobsters is, of course, different, as cadmium levels will be much higher. Products such as lobster paste will also need research for cadmium removed prior to canning.

Arsenic is a much less serious problem in lobster than is cadmium, but is a more widespread contaminant than cadmium. Table 3 shows arsenic levels in a wide variety of marine species. It must be kept in mind that the bulk of this arsenic is probably present in a non-toxic form. The geographical distribution of arsenic has been determined based on a selected number of sampling sites from the cadmium distribution study. These results are shown in Table 4. The pattern which emerges suggests that levels just off the east coast of Nova Scotia (Sambro, Tangier, Arichat) are about twice those found in areas surrounding the Gulf of St. Lawrence. Individual specimens have been found with arsenic levels in excess of 100 ppm. With such high levels even though it is known that a lot of the arsenic is present in relatively non-toxic forms it is possible that smaller percentages of the arsenic may be present as the very toxic arsenite form. With this in mind, a method of determining only arsenite has been developed and preliminary experiments have suggested that very little arsenite is present in these arsenic containing fish.

REFERENCES

F.A.O. Nutrition Meetings Report Series No. 51A, Food and Agriculture Organization of the United Nations, Rome (1973).

COULSON, E.J., R.E. REMINGTON and K.M. LYNCH. J. Nutrition 10, 255 (1935).

LUNDE, G. J. Sci. Food Agric 24, 1021, (1973).

UTHE, J.F., H.C. FREEMAN, J.R. JOHNSTON and P. MICHALIK. J. of the AOAC, in press (1974).

FREEMAN, H.C. and J.F. UTHE. Atomic Absorption Newsletter 13, 75 (1974).

FERNANDEZ, F.J. and D.C. MANNING. Atomic Absorption Newsletter 10, 86 (1971).

LORING, D.H. and D.J.G. NOTA. Morphology and sediments of the Guld fo St. Lawrence Bull. Fish. Res. Bd. Canada, Number 182, Ottawa (1973).

STEWART, J.E., J.W. CORNICK, D.M. FOLEY, M.F. LI, and C.M. BISHOP. J. Fish. Res. Bd. Canada 24, 2339 (1967).

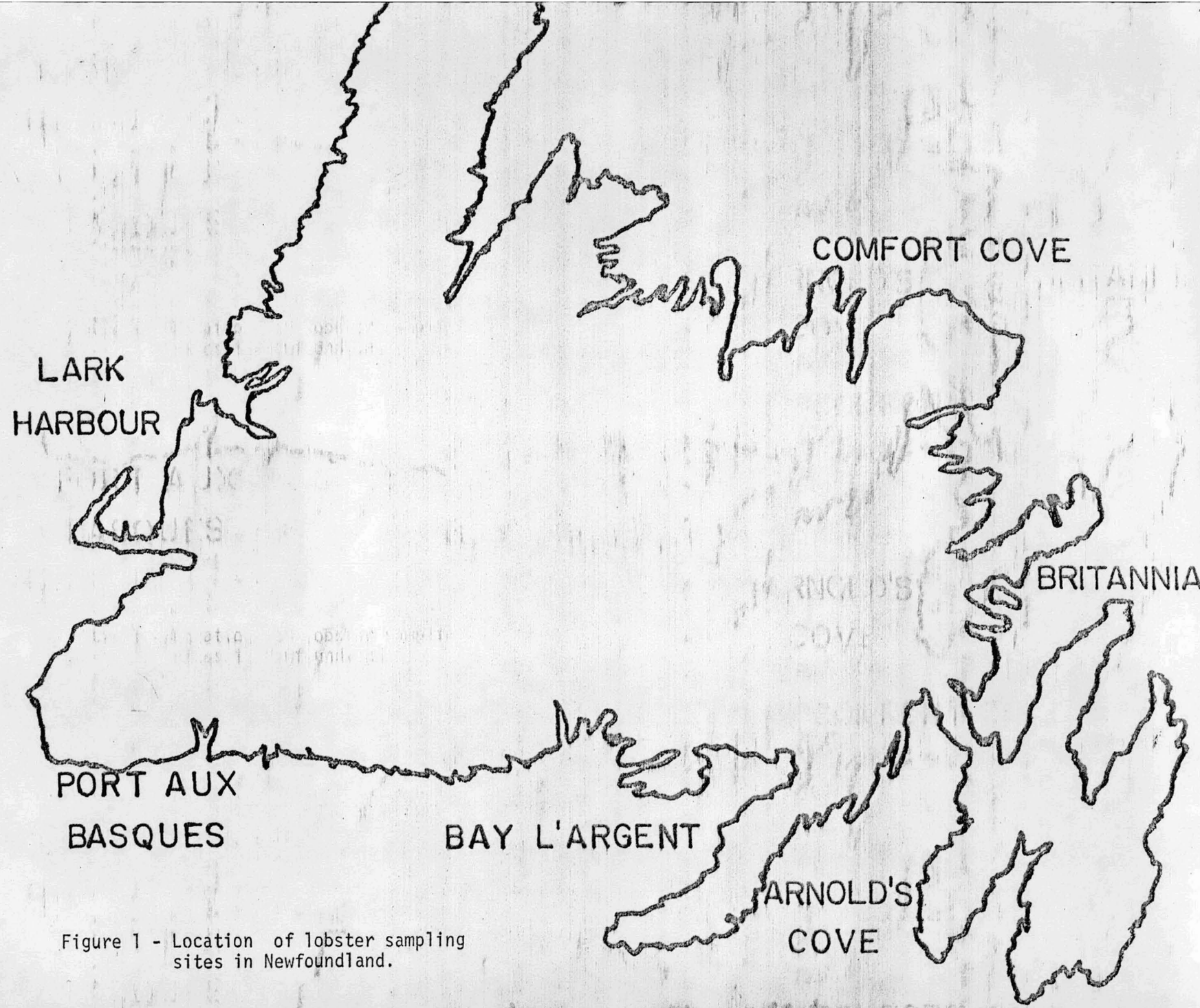

Figure 1 - Location of lobster sampling sites in Newfoundland.

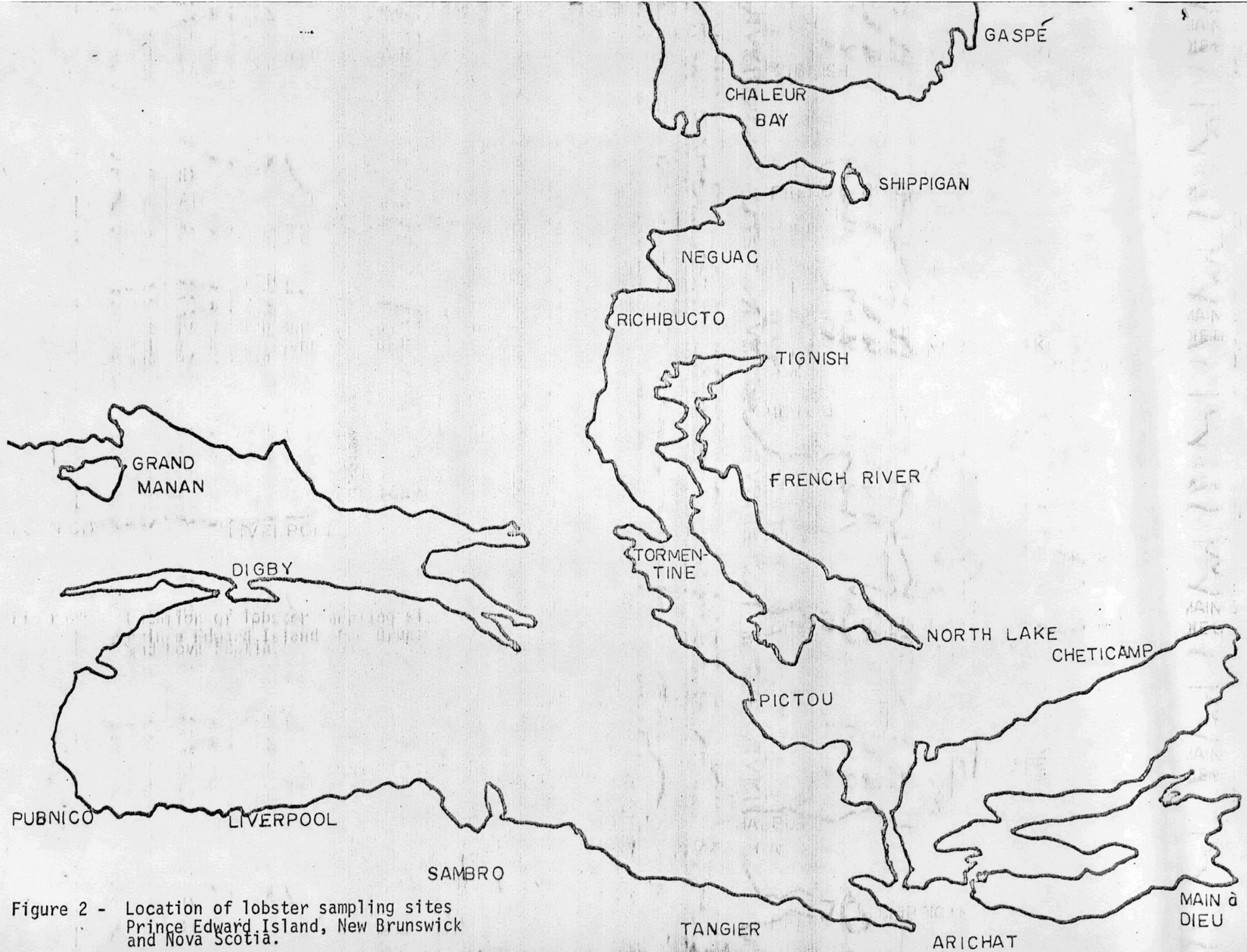

Figure 2 - Location of lobster sampling sites Prince Edward Island, New Brunswick and Nova Scotia.

TABLE 1. MEAN CADMIUM CONCENTRATION IN LOBSTER DIGESTIVE GLAND (UG Cd/G WET WEIGHT) FROM VARIOUS AREAS IN THE CANADIAN LOBSTER FISHERY.

SAMPLE SITE	N*	CADMIUM LEVEL ± STANDARD DEVIATES	RANGE
NEWFOUNDLAND			
ARNOLD'S COVE	50	8.82±1.96	2.5 -48.9
BRITANNIA	20	12.63±1.61	4.8 -30.3
COMFORT COVE	21	2.82±1.42	1.7 - 6.9
LARK HARBOUR	25	10.89±1.66	3.8 -33.6
PORT AUX BASQUES	27	10.70±1.71	4.3 -45.0
BAY L'ARGENT	26	10.83±1.46	4.6 -20.2
NEW BRUNSWICK			
GASPÉ (QUEBEC)		10.53±2.15	4.2 -46.7
CHALEUR BAY	26	4.30±1.59	1.8 -10.7
SHIPPEGAN	26	3.79±1.68	1.6 -11.3
NEGUAC	26	4.72±1.46	2.5 -28.7
RICHIBUCTO	26	6.26±1.53	3.8 -14.4
TORMENTINE	24	10.90±1.53	4.1 -22.4
GRAND MANAN	26	6.93±1.98	2.6 -31.5
PRINCE EDWARD ISLAND			
TIGNISH	25	14.03±1.66	5.5 -37.8
FRENCH RIVER	26	11.95±2.15	2.3 -48.2
NORTH LAKE	24	16.73±1.74	7.2 -53.4
NOVA SCOTIA			
PICTOU	26	14.36±2.03	3.7 -79.1
CHETICAMP	23	9.14±2.23	2.1 -36.3
MAIN À DIEU	26	12.58±1.75	4.9 -47.2
ARICHAT	25	7.87±1.76	3.2 -31.7
TANGIER	26	6.53±1.94	2.4 -20.0
SAMBRO	25	8.03±1.60	2.0 -18.0
LIVERPOOL	26	5.19±1.75	1.3 -16.7
PUBNICO	20	10.68±1.09	5.2 -21.4
DIGBY	26	6.50±2.02	2.9 -15.4

* NUMBER SAMPLED

TABLE 2. AVERAGE CADMIUM CONTENT IN LOBSTER EDIBLE PORTION ASSUMING 98% OF THE CADMIUM IS IN THE DIGESTIVE GLAND AND THE LOBSTER DRESSES AT 30% INCLUDING DIGESTIVE GLAND.

SAMPLE SITE	TOTAL AV. WT. (G)	AV. DIGESTIVE GLAND WEIGHT (G)	AV. Cd/EDIBLE PORTION (UG/G)
NEWFOUNDLAND			
ARNOLD'S COVE	532	32.1	1.81
BRITANNIA	639	33.1	2.23
COMFORT COVE	538	28.7	0.51
LARK HARBOUR	631	28.5	1.67
PORT AUX BASQUES	476	29.5	2.26
BAY L'ARGENT	559	32.9	2.17
NEW BRUNSWICK			
GASPÉ (QUEBEC)	561	27.3	1.74
CHALEUR BAY	436	25.0	0.84
SHIPPEGAN	478	25.6	0.69
NEGUAC	350	21.2	0.97
RICHIBUCTO	460	22.2	1.03
TORMENTINE	561	27.0	1.78
GRAND MANAN	530	26.8	1.19
PRINCE EDWARD ISLAND			
TIGNISH	538	27.3	2.42
FRENCH RIVER	491	24.5	2.03
NORTH LAKE	599	31.4	2.98
NOVA SCOTIA			
PICTOU	482	23.1	2.34
CHETICAMP	613	34.4	1.74
MAIN À DIEU	552	30.8	2.39
ARICHAT	536	26.0	1.30
TANGIER	495	24.5	1.10
SAMBRO	680	30.1	1.21
LIVERPOOL	547	26.5	0.86
PUBNICO	475	24.5	1.87
DIGBY	467	22.3	1.06

TABLE 3. ARSENIC LEVELS (UG As/G WET WEIGHT) IN A VARIETY OF MARINE SPECIES.

SAMPLE	ARSENIC CONTENT
WHOLE CLAMS	2.70±0.20
COD MUSCLE	3.75±0.02
HADDOCK MUSCLE	6.67±0.11
HALIBUT MUSCLE	4.55±0.02
LOBSTER TAIL MUSCLE	4.95±0.16
LOBSTER HEPATOPANCREAS	5.94±0.99
SHRIMP MUSCLE	37.29±0.49
SKATE MUSCLE	34.02±0.25
SOLE MUSCLE	13.12±0.19
SWORDFISH MUSCLE	1.04±0.08
BROOK TROUT MUSCLE	1.26±0.06

TABLE 4. GEOGRAPHICAL DISTRIBUTION OF ARSENIC IN LOBSTER DIGESTIVE GLAND (UG As/G WET WEIGHT).

SAMPLING SITE	N*	ARSENIC CONTENT
GASPE, QUE.	26	6.61±2.38
ARNOLD'S COVE, NFLD.	47	9.57±2.53
FRENCH RIVER, P.E.I.	26	5.94±0.99
MAIN À DIEU, N.S.	26	8.71±2.73
ARICHAT, N.S.	25	10.56±2.84
TANGIER, N.S.	26	11.54±3.78
SAMBRO, N.S.	25	16.20±4.47

* NUMBER SAMPLED