

**EVALUATION OF GULFWATCH 1994:
FOURTH YEAR OF THE
GULF OF MAINE ENVIRONMENTAL MONITORING PLAN**

**Gulf of Maine Council on the Marine Environment
December, 1996**

By : Margo Chase¹, Glenn Atkinson², Karen Coombs³, Robert Crawford⁴, Gareth Harding⁵,
Peter Hennigar², Stephen Jones¹, John Machell², Judith Pederson⁶, William Robinson⁷,
John Sowles⁸, Darrell Taylor⁹

1 University of New Hampshire

2 Environment Canada

3 New Brunswick Department of Fisheries and Aquaculture

4 Nova Scotia Department of Fisheries

5 Department of Fisheries and Oceans, Canada

6 Massachusetts Coastal Program

7 University of Massachusetts/Boston

8 Maine Department of Environmental Protection

9 Nova Scotia Department of the Environment

TABLE OF CONTENTS

INTRODUCTION.....	4
Rational	4
Gulfwatch Objectives	5
METHODS	7
1994 Sampling Locations	7
Field Procedures	7
Laboratory Procedures	10
Analytical Procedures	11
metals	11
organic contaminants	11
Quality Assurance / Quality Control	13
Statistical Methods	15
RESULTS AND DISCUSSION	16
Field operations and logistics	16
Metal contaminants	16
Spatial variation in metal concentration	16
Silver	19
Lead	19
Chromium	21
Zinc	21
Nickel	23
Mercury	23
Cadmium	23
Copper	25
Iron and Aluminum	25
Organic contaminants	27
Spatial variation in organic concentration	27
Polyaromatic hydrocarbons	30
Polychlorinated Biphenyl	32
Pesticides	32

Acceptable levels and standards of mussel contamination	34
Morphometric comparison.....	36
Shell morphology	36
Condition index	36
CONCLUSIONS	42
ACKNOWLEDGEMENTS	43
REFERENCES	43
APPENDIX A: Methods for mussel extraction and analysis of organic contaminants.....	48
APPENDIX B: Quality assurance / Quality control protocol.....	58
APPENDIX C: Tissue concentrations of heavy metals.....	64
APPENDIX D: Tissue concentrations of polyaromatic hydrocarbons.....	68
APPENDIX E: Tissue concentrations of polychlorinated biphenyls.....	83
APPENDIX F: Tissue concentrations of chlorinated pesticides.....	96

INTRODUCTION

Rational

The Gulf of Maine extends from Cape Sable, Nova Scotia, through New Brunswick, Maine, and New Hampshire to Cape Cod, Massachusetts and includes the Bay of Fundy, and Georges Bank. The combined primary productivity of seaweeds, salt marsh grasses and phytoplankton make the Gulf environment a highly productive system that supports a vast array of animal species, including many species of invertebrates, fish, seabirds and marine mammals, some of great commercial importance. Commercial fisheries and aquaculture are its principal income generating enterprises, although tourism is a very important source of income to many small coastal communities. As coastal populations around the Gulf and its watersheds have increased, agricultural lands have been converted to industrial and residential developments. Such changes in land use and increases in population have contributed to the deteriorating quality of sections of the coastal environment (GMCME, 1992; Dow and Braasch, 1996). Contaminants from non-point source and point source pollution are a significant threat to the near shore environment of the Gulf (GMCME, 1992; Dow and Braasch, 1996). Growth in industrial activity during the 20th century has resulted in a rapid increase in inputs from chemicals, either mobilized or synthesized by humans, into the estuarine and coastal environments. Many of these chemicals are bioaccumulated to concentrations significantly above ambient levels. Furthermore, some of these environmental contaminants may also be present at toxic levels, and thus induce adverse biological effects.

In order to protect water quality and commercial uses in the Gulf of Maine, the *Agreement on the Conservation of the Marine Environment of the Gulf of Maine* was signed in December, 1989 by the premiers of Nova Scotia and New Brunswick, and the governors of Maine, New Hampshire and Massachusetts, establishing the Gulf of Maine Council on the Marine Environment. The overarching mission of this council is to maintain and enhance the Gulfs' marine ecosystem, its natural resources and environmental quality.

To help meet the council's mission statement the Gulf of Maine Monitoring Committee was formed and charged with the development of the Gulf of Maine Environmental Monitoring Plan. The Monitoring Plan is based on a mission statement provided by the council:

It is the mission of the Gulf of Maine Environmental Quality Monitoring Program to provide environmental resource managers with information to support sustainable use of the Gulf and allow assessment and management of risk to public

and environmental health from current and potential threats.

Three monitoring goals were established to meet the mission statement:

- (1) To provide information on the status, trends, and sources of risk to the marine environment in the Gulf of Maine;
- (2) To provide information on the status, trends, and sources of marine based human health risks in the Gulf of Maine; and
- (3) To provide appropriate and timely information to environmental and resource managers that will allow both efficient and effective management action and evaluation of such action.

In support of the mission and to meet the desired goals a project named Gulfwatch was established, to measure chemical contamination throughout the Gulf.

Gulfwatch Objectives

Gulfwatch is presently a program in which the blue mussel, *Mytilus edulis*, is used as an indicator for habitat exposure to organic and inorganic contaminants. Bivalves, such as *M. edulis*, have been successfully used as indicator organisms in environmental monitoring programs throughout the world (see NAS, 1980; NOAA, 1991; Widdows and Donkin, 1992), to identify variation in chemical contaminants between sites, and contribute to the understanding of trends in coastal contamination (NOAA, 1991; O'Connor, 1992; O'Connor and Beliaeff, 1995; Widdows et al., 1995). The blue mussel was selected as the indicator organism for the Gulfwatch program for the following reasons:

- (1) mussels are abundant within and across each of the 5 jurisdictions of the Gulf Program and mussels are easy to collect and process;
- (2) much is known about mussel biology and physiology;
- (3) mussels are a commercially important food source and therefore a measurement of the extent of chemical contamination is of public health concern;
- (4) mussels are sedentary, thereby eliminating the complications in interpretation of results introduced by mobile species;
- (5) mussels are suspension-feeders that pump large volumes of water and concentrate many chemicals in their tissues; therefore the presence of trace contamination is easier to document; and the measurement of chemicals in bivalve tissue provides an assessment of biologically available contamination which is not apparent from measurement of

contamination in non-biological environmental compartments (water, sediment and suspended particles).

Gulfwatch has taken two approaches to using marine mussels as bioindicators of anthropogenic contamination. During the first two years of the program (1991-1992), both transplanted mussels and native mussels sampled from areas adjacent to the transplant sites were analyzed for organic and inorganic contaminants (GMCME, 1992). Transplanted mussels were initially collected from relatively pristine sites in each jurisdiction, moved to sites selected for monitoring, and held there for approximately 60 days. Because of the logistics and the analytical costs, only two sites per jurisdiction could be monitored each year using this transplant technique. The transplant experiments provided an assessment of the short-term exposure (on the order of weeks to months) to bioavailable contaminants throughout the region. In 1993, only indigenous mussels were sampled, although a greater number of sites were monitored compared to the years when mussels were transplanted (GMCME, 1996). Sampling of native mussels provided an assessment of long-term exposure to bioavailable contaminants (on the order of months to a year).

In addition to documenting the level of contaminants in mussel tissue, biological variables, including mussel shell growth and condition index, were measured as a means to determine the response of organisms to stress under different levels of contaminant burden. Growth is often one of the most sensitive measures of contaminant effects on an organism (Sheehan, 1984; Sheehan et al., 1984; Howells et al., 1990). Shell growth has often been used as a measure of environmental quality and pollution effects as it is a fundamental measure of physiological fitness / performance (Widdows and Donkin, 1992; Salazar and Salazar, 1995) and therefore, is a direct, integrative measure of the impairment of an organisms' physiology. Condition index (CI) was used as an indicator of the physiological status of the mussels. It relates the tissue wet weight to shell volume and is a measure traditionally used by shellfishery biologists (Widdows, 1985). Because gonadal weight is a significant contributor to total body weight just prior to spawning, CI also reflects differences in the reproductive state of sampled mussels.

The objective of the first two years (1991 and 1992) of the Gulfwatch program was to evaluate the feasibility of the project and the level of cooperation required through collecting comparative data from different locations in the Gulf of Maine. The sites that were selected fell into two categories; test sites that were suspected or known to be contaminated and reference sites that were free of any known contaminant source. After the success of the pilot studies in 1991 and 1992, it was recognized that there should be a broader distribution of mussel sampling. As such, in 1993 the sampling scheme was expanded. Native mussels in up to six new locations were sampled within each jurisdiction (state or province), where feasible, to increase the

geographic coverage. However, one location in each jurisdiction was chosen as a baseline station, to be resampled every year. This overall approach increased the chance of locating unforeseen environmental contamination. In the present account we report the results of the second year of the sampling design to extend the geographical coverage of the Gulf.

METHODS

1994 Sampling Locations

The 23 stations sampled in 1994 are shown in Figure 1 and Table 1. There were 5 sites in Massachusetts, 2 in New Hampshire, 8 in Maine, 3 in New Brunswick and 5 in Nova Scotia. Six sites were retained from previous years to enable trend analysis; Sandwich, MA, Clarke Cove, ME, Kennebec River, ME, Hospital Island, NB, Five Islands, NS, and Digby, NS.

Field Procedures

Details regarding the mussel collection, measurement and sample preparation are published (Sowles and Crawford, 1994). In some jurisdictions, measurements of nutrient and chlorophyll levels were also made but these data are not included in this report.

The mussels collected were intended to be *Mytilus edulis*, however, a similar species, *Mytilus trossulus*, was identified in some of the Bay of Fundy samples (GMCME, 1996). This species has a slower growth rate than *M. edulis* and attains a maximum size of approximately 50-60 mm compared to 70-80 mm for the blue mussel (Bayne, 1976). These physiological differences result in species-specific differences in shell allometric growth. Although an inter-species allometric gradient is present at sites inhabited by both species, *M. trossulus* can often be distinguished from *M. edulis* by its higher shell length:height ratio (Lobel et al., 1990; Freeman et al., 1992). A more precise distinction between the two species can be made using canonical discriminant analysis (Mucklow, 1996).

TABLE 1. Gulf of Maine, Gulfwatch study site locations sampled in 1994.

CODE	SAMPLE DATE	LOCATION	LATITUDE	LONGITUDE
MASN	October 24	Sandwich, MA	41°45.73'N	70°28.38'W
MADX	November 23	Duxbury, MA	42°02.01'N	70°40.03'W
MABI	October 14	Brewster Island, MA	42°20.55'N	70°52.68'W
MAWN	October 21	Winthrop, MA	42°21.89'N	70°57.85'W
MAIP	October 6	Ipswich, MA	42°42.04'N	70°47.44'W
NHRH	October 17	Rye Harbor, NH	43°00.00'N	70°14.42'W
NHDP	October 17	Dover Point, NH	43°07.09'N	70°49.39'W
MECC	October 26	Clarkes Cove, ME	43°45.95'N	70°10.75'W
MESA	October 25	Saco River, ME	43°26.52'N	70°21.08'W
MEPH	October 13	Portland Harbor, ME	43°38.75'N	70°15.50'W
MEPR	October 19	Presumpscot River, ME	43°41.60'N	70°15.00'W
MEKN	October 1	Kennebec River, ME	43°47.50'N	69°47.60'W
MEUR	October 14	Union River, ME	44°15.60'N	68°43.80'W
MEMR	November 3	Machias River, ME	44°41.20'N	67°23.50'W
MECK	October 26	Cobscook Bay, ME	44°54.28'N	67°03.25'W
NBNR	October 15	Niger Reef, NB	45°60.30'N	69°23.50'W
NBHI	October 11	Hospital Island, NB	45°07.30'N	67°00.20'W
NBLB	October 20	Limekiln Bay, NB	45°51.35'N	69°35.41'W
NSAR	October 10	Apple River, NS	45°27.60'N	64°51.80'W
NSFI	October 12	Five Islands, NS	45°39.50'N	64°06.70'W
NSDI	September 29	Digby, NS	44°38.10'N	65°44.70'W
NSSC	September 29	Spechts Cove, NS	44°32.30'N	65°52.20'W
NSBP	October 5	Barrington Passage, NS	43°31.00'N	65°38.00'W

All field sampling was conducted between September 29 and November 23, 1994. Collection times were set to avoid sampling during or shortly after periods when storm-water runoff and wave resuspension of bottom sediment result in unusual uptake and accumulation of sediment in the mussel gut which may result in elevated tissue concentrations of some metals (iron, aluminum and associated metals) (Lobel et al., 1991; Robinson et al., 1993). It is suspected that the presence of sediment in the mussel gut was the cause of the elevated concentrations of iron and aluminum observed in previous reports (GMCME, 1994, 1996).

Since mussel growth and mussel body burdens are affected by many different variables each site must meet certain minimum criteria to control variability:

- (1) Wherever possible mussels were collected from subtidal areas at each site. Mussel growth is known to be negatively affected by the duration of aerial exposure (Phillips, 1976). In the Nova Scotian sites, however, mussels were collected in the low intertidal zone because of the extreme tidal range in the Bay of Fundy. The reader is referred to the Gulfwatch report on standard procedures for field sampling, measurement and sample preparation manual for more detail (Sowles and Crawford, 1994).
- (2) Stations should be adjacent to the mainland to reflect anthropogenic contamination inputs. Water quality varies from offshore to near shore due to upwelling, terrigenous sources and current.
- (3) Natural indigenous subtidal mussels that are collected must be 50-60 mm shell length. Collecting mussels of a uniform size will minimize any differences that are directly associated with scaling effects (e.g. surface to volume ratios and to some degree metabolic rates).

Mussels were collected from 4 discrete areas within a segment of the shoreline that is representative of local water quality. Using a hand-held wooden gauge or a ruler, 45-50 mussels of a shell length of 50-60 mm were collected. Clean water from the collection site was used to remove of all sediment, epibiota, and other accretions from the mussels. They were then placed in clean glass containers and transported to the processing labs in coolers.

Laboratory Procedures

In the laboratory, individual mussel length, width and height (as defined by Seed, 1968) were determined to the nearest 0.1 mm using vernier calipers. Mussels were then shucked with either plastic or stainless steel wedges directly into appropriately prepared containers for metal and organic analysis, respectively (for details see Sowles and Crawford, 1994). Composite samples (20 mussels / composite; 4 composites / station) were capped, labelled and stored in a freezer at

15°C.

While a number of condition indices have been proposed over the years (Seed, 1968), the Gulfwatch Condition Index (CI) has been defined as:

$$CI = [\text{tissue wet wt (mg)}] / [\text{length (mm)} * \text{width (mm)} * \text{height (mm)}]$$

CI was determined for between 30 to 160 mussels at each sampling site, depending on the jurisdiction.

Analytical Procedures

Analytical procedures used followed those reported for the previous years (GMCME, 1994; GMCME, 1996). Table 2 contains a summary of the metal and organic compounds measured.

Metals

Inorganic contaminants were analyzed at the State of Maine Health and Environmental Testing Laboratory (Augusta, ME). Analyses for mercury were done on a subsample of 1 to 2 g of wet tissue and measured by cold vapor atomic absorption on a Perkin Elmer Model 503 atomic absorption spectrometer. Analyses for all other metals were conducted on 5 to 10 g of wet tissue dried at 100 °C. Zinc and iron were measured by flame atomic absorption using a Perkin Elmer Model 1100 atomic absorption spectrometer. All remaining metals (Ag, Al, Cd, Cu, Cr, Ni and Pb) were run using Zeeman background corrected graphite furnace atomic absorption on a Varian Spectra AA 400. The analytical detection limit for the various metals in µg / g dry weight are as follows; Ag, 0.1; Al, 3.0; Cd, 0.2; Cr, 0.3; Cu, 0.6; Fe, 6.0; Hg, 0.1; Ni, 1.2; Pb, 0.6; and Zn, 1.5.

Organic Contaminants

Organic contaminants in mussel samples were analyzed at the Environment Canada Laboratory in Dartmouth, N.S. The analytical detection limit for aromatic hydrocarbons was 10 ng / g (20-30 ng/g for some lower molecular weight aromatics) and generally <2 ng / g for PCB congeners.

TABLE 2. Inorganic and Organic contaminants analyzed in mussel tissues from the Gulf of Maine in 1994.

INORGANIC CONTAMINANTS

Metals

Ag, Al, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn

ORGANIC CONTAMINANTS

Aromatic Hydrocarbons

Naphthalene
 1-Methylnaphthalene
 2-Methynaphthalene
 Biphenyl
 2,6-Dimethylnaphthalene
 Acenaphthylene
 Acenaphthene
 2,3,5-Trimethylnaphthalene
 Fluorene
 Phenanthrene
 Anthracene
 1-Methylphenanthrene
 Flouranthene
 Pyrene
 Benzo [a] anthracene
 Chrysene
 Benzo [b] flouranthrene
 Benzo [k] flouranthrene
 Benzo [a] pyrene
 Benzo [e] pyrene
 Perylene
 Indeno [1,2,3-cd] pyrene
 Dibenzo [a,h] anthracene
 Benzo [g,h,i] perylene

Chlorinated Pesticides

Hexachlorobenzene (HCB)
 gamma-Benzenehexachloride (BHC)
 Heptachlor
 Heptachlor epoxide
 Aldrin
 Mirex
 cis-Chlordane
 trans-Nonachlor
 Dieldrin
 Alpha-Endosulfan
 beta-Endosulfan

DDT and Homologues

2,4'-DDE	4,4'-DDE
2,4'-DDD	4,4'-DDD
2,4'-DDT	4,4'-DDT

PCB Congeners

PCB 8, PCB 18, PCB 28, PCB 29, PCB 44,
 PCB 50, PCB 52, PCB 66, PCB 77,
 PCB 87, PCB 101, PCB 105, PCB 118,
 PCB 126, PCB 128, PCB 138, PCB 153,
 PCB 169, PCB 170, PCB 180, PCB 187,
 PCB 195, PCB 206, PCB 209

Eighteen of the PCB congeners identified and quantified are included in the National Oceanographic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program's designated congeners. Other organic compounds selected for analysis are consistent, for the most part, with NOAA Status and Trends mussel monitoring (NOAA, 1989).

The analyses of mussel tissue samples follow the diagram shown in Figure 2 and are summarized below. A description of the full analytical protocol and accompanying performance based QA/QC procedures are found in Appendix A and Appendix B.

Tissue samples were extracted by homogenization with an organic solvent and a drying agent. Solvent extracts were obtained by vacuum filtration, and biomatrix interferences were separated from target analytes in extracts by size exclusion chromatography. Purified extracts were subjected to silica gel liquid chromatography which provided a non-polar PCB/chlorinated pesticides fraction and a polar chlorinated pesticide fraction. PCB and /or pesticides in each fraction were analyzed by High Resolution dual column Gas Chromatography / Electron Capture Detection (HRGC/ECD). Following PCB and pesticide analysis, the two fractions were combined and the resulting extract was analyzed for aromatic hydrocarbons by High Resolution Gas Chromatography / Mass Spectrometry (HRGC/MS).

Quality Assurances / Quality Control

Standard laboratory procedures for metals incorporated method blanks, spiked matrix samples, duplicate samples, surrogate addition and standard oyster tissue (SRM 1566A). Ten method blanks were inserted: three at the beginning of the run, one at the end, and six at various intervals during the run. Duplicate samples and matrix spike recoveries were conducted on 15% of the samples.

The Dartmouth laboratory participated in the NIST Status and Trends Intercomparison Marine Sediment Exercise IV and Bivalve Homogenate Exercise V. Internal quality control and method performance specifications are described in the Environment Canada Shellfish Surveillance Protocol (Appendix B). The protocol includes mandatory QC measures with every sample batch including the analysis of method blanks, spiked matrix samples, duplicate samples, surrogate addition, and certified reference materials. The protocol specifies the performance criteria relevant to the method accuracy, precision and detection limits and the data reporting requirements for the analysis of organic contaminants in shellfish samples.

Changes made to the analytical method for organic contaminants since 1992 are listed in Appendix A. In 1994, the analytical method was modified slightly to provide for sequential

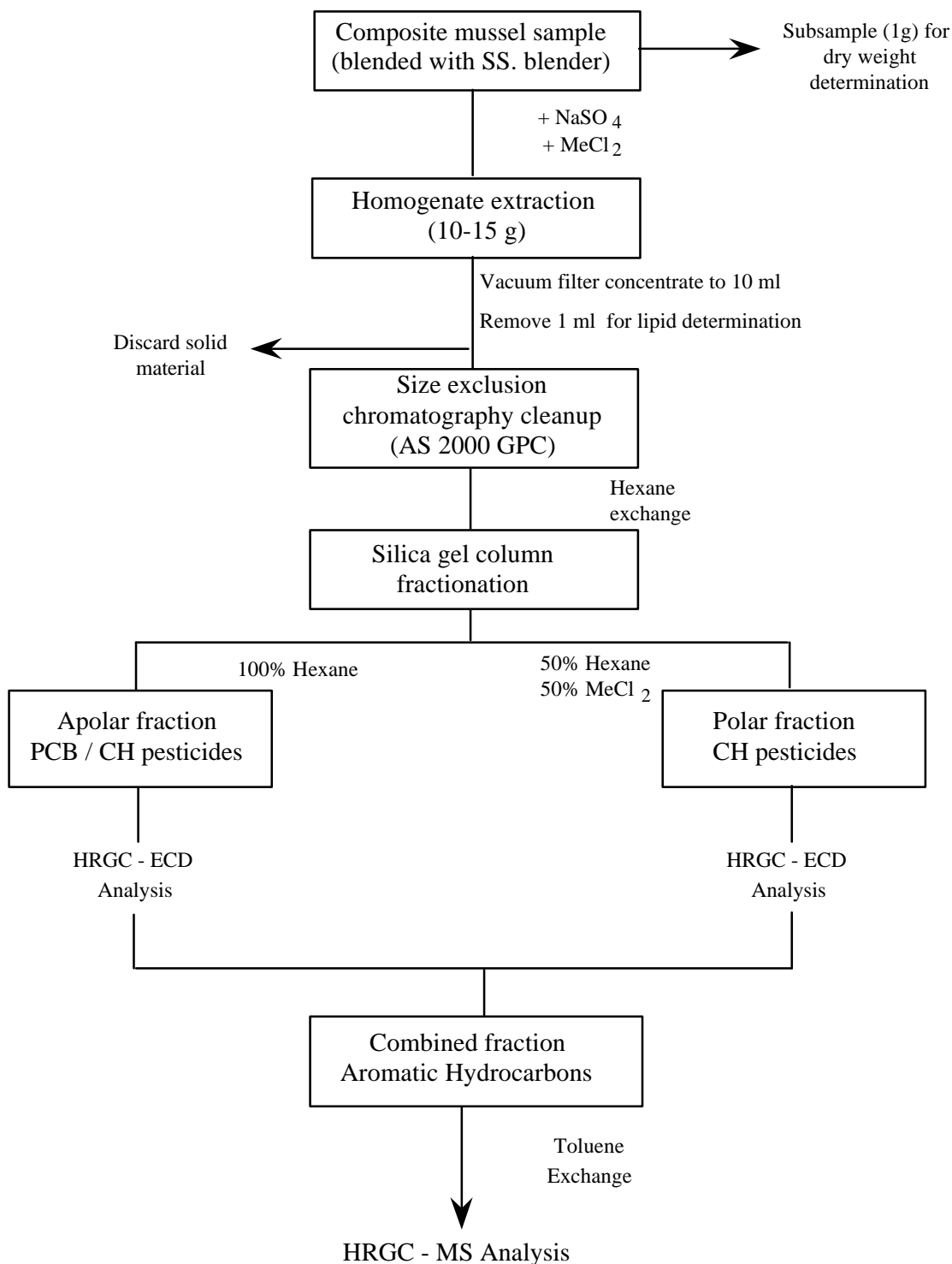


FIGURE 2. Analytical flow chart for organic analyte determination at the Environment Canada Laboratory in 1994. HRGC-MS, high resolution gas chromatography /massspectrometry; HRGC-ECD, high resolution dual column gas chromatography/electron capture detection; GPC, Gel permeation chromatography; SS., Stainless steel.

extraction of sample homogenates in order to provide better assurance of satisfactory analyte recovery.

Statistical Methods

All metal data were \log_{10} transformed to correct for heterogeneity of variances. In cases where there were ND (non detectable) values of data: if all 4 replicates from a given site showed ND concentrations, the contaminant concentration was recorded as ND; if at least one of the replicates was greater than the detection limit then the other replicates were recorded as 1/2 the detection limit. Arithmetic means were used to summarize the results of replicate samples and are presented in all subsequent tables and figures. In addition, geometric means were calculated to facilitate comparison with data from other reports (O'Connor, 1992). The standard deviation (s) around the geometric mean (s_g) was calculated as:

$$s_g = \text{antilog}(s) = 10^{s/2}$$

where s = standard deviation around the mean of the \log_{10} transformed data (Snedecor and Cochran, 1967).

Total PAH (ΣPAH_{24}), total PCB (ΣPCB_{24}), and total pesticides (ΣPest_{17}) values were created from the sum of all individual compounds or isomers with values greater than the detection limit for the compound. Total DDT (ΣDDT_6) is the sum of 2,4'-DDT, 4,4'-DDT and homologues (2,4'-DDE, 4,4'-DDE, 2,4'-DDD and 4,4'-DDD). Organic variables that were below the detection limit, were treated as zero. All data were $\log_{10}(x+1)$ transformed to correct for nonnormality. Arithmetic means were used to summarize the results of replicate samples and are presented in all subsequent tables and figures. In addition, geometric means were calculated for regional comparison. The standard deviation (s) around the geometric mean (s_g) of the organic data was calculated as above. Organic concentrations above the mean plus one standard deviation were considered high.

All data were analyzed using one-way analysis of variance (ANOVA), followed by Tukey-Kramer multiple comparison test of means. A probability of less than or equal to 0.05 was chosen as the level of significance.

RESULTS AND DISCUSSION

FIELD OPERATIONS AND LOGISTICS

Field collection proceeded as planned, with no sample loss in transit to the organic analysis laboratory at the Bedford Institute of Oceanography, Environment Canada Laboratory in Dartmouth, N.S., or to the metal analysis laboratory at the State of Maine Health and Environmental testing Laboratory in Augusta, ME.

METAL CONTAMINANTS

Table 3 contains the metal concentrations (arithmetic mean \pm SD, $\mu\text{g} / \text{g}$ dry weight) for indigenous mussels from all sites sampled in 1994. Metal concentrations for each of the composite samples (n=4) are provided in Appendix C. An overall, gulfwide concentration for each metal is given as a geometric mean so as to compare the Gulfwatch results to that of NOAA (O'Connor, 1992) National Status and Trends program (NS & T) concentrations for Gulf of Maine sites (n = 13) (Table 4). The geometric means of Ag, Al, Cu, Pb and Zn were below the mean concentration and the geometric means for Cd, Cr, Fe, Hg and Ni were above the mean concentrations measured for the Gulf of Maine in the NOAA (O'Connor, 1992) National Status and Trends program. Similar results were observed in previous reports (see GMCME, 1994; GMCME, 1996). In addition, the geometric means for Cd and Hg were above the calculated "high value" (geometric mean plus one standard deviation) for NOAA mussels. This is not surprising given that half of the Gulfwatch stations were chosen as potentially contaminated areas, whereas the NS & T stations were chosen to avoid acute human activity or known sources of contamination.

Spatial variation in metal concentrations

Figures 3 to 6 show the concentration of the metals measured in the tissue of *M. edulis* at the 1994 sampling stations presented from south to north. In addition, the mean tissue metal concentrations at each of the Gulfwatch sites are compared to two "benchmark" values for each metal previously reported by Sowles (1993) from 23 Maine reference sites: (1) the arithmetic mean for each metal concentration (Maine reference mean or ME-RM); and, (2) the arithmetic mean plus three standard deviations (Maine High Value or ME-HV; referred to by Sowles as the "anomalous value") (Table 5). These Maine reference stations are located in areas where anthropogenic contamination should be low. Mean mussel

TABLE 3. Tissue metal concentrations (arithmetic mean \pm SD, $\mu\text{g/g}$ dry wt.) for messels collected throughout the Gulf of Maine in 1994 and ANOVA of sites by jurisdiction. ND, non detect. The same letter indicates no significant difference among sites within each jurisdiction ($p > 0.05$). GM, geometric mean \pm 1 standard deviation (SD).

Station	Ag	Cd	Cr	Cu	Fe
MASN	1.05 ± 0.29^B	1.6 ± 0.2^B	1.10 ± 0.1^A	7.5 ± 0.5^A	265 ± 31^B
MADX	0.23 ± 0.05^A	1.1 ± 0.1^A	1.65 ± 0.1^B	9.3 ± 0.7^B	403 ± 33^C
MABI	0.13 ± 0.05^A	1.8 ± 0.1^B	1.73 ± 0.1^B	6.5 ± 0.7^A	228 ± 30^B
MAWN	0.25 ± 0.10^A	1.8 ± 0.2^B	2.80 ± 0.3^C	7.8 ± 1.0^{AB}	745 ± 30^D
MAIP	0.27 ± 0.12^A	1.2 ± 0.1^B	1.17 ± 0.1^A	7.6 ± 0.3^{AB}	170 ± 17^A
NHRH	ND	1.4 ± 0.1^A	1.48 ± 0.1^A	6.5 ± 0.6^A	280 ± 14^A
NHDP	0.08 ± 0.03	3.1 ± 0.3^B	3.13 ± 0.2^C	7.9 ± 0.9^A	455 ± 58^B
MECC	ND	1.5 ± 0.3^A	1.90 ± 0.1^B	7.5 ± 1.3^A	367 ± 67^B
MESA	0.08 ± 0.03^A	1.6 ± 0.3^A	1.63 ± 0.3^{CD}	6.2 ± 1.4^A	288 ± 50^B
MEPH	ND	1.4 ± 0.4^A	1.65 ± 0.4^D	8.1 ± 1.7^B	558 ± 149^C
MEPR	ND	1.1 ± 0.1^A	1.63 ± 0.2^{CD}	5.4 ± 0.9^A	400 ± 39^{BC}
MEKN	ND	1.4 ± 0.4^A	1.13 ± 0.2^{ABC}	6.6 ± 1.3^A	230 ± 47^{AB}
MEUR	0.11 ± 0.07^A	1.2 ± 0.2^A	0.80 ± 0.1^{AB}	6.5 ± 1.0^A	183 ± 19^A
MEMR	ND	1.4 ± 0.4^A	1.50 ± 0.3^{BC}	4.5 ± 0.5^A	557 ± 47^C
MECK	ND	1.2 ± 0.1^A	1.01 ± 0.1^{AB}	6.3 ± 1.4^A	406 ± 19^{BC}
NBNR	0.08 ± 0.03^A	1.6 ± 0.1^A	0.95 ± 0.1^A	6.3 ± 1.8^A	363 ± 22^A
NBHI	0.20 ± 0.00^B	1.9 ± 0.4^A	1.33 ± 0.3^{AB}	7.0 ± 0.6^{AB}	400 ± 56^A
NBLB	ND	1.5 ± 0.2^A	0.92 ± 0.1^{AB}	7.5 ± 0.5^B	330 ± 45^A
NSAR	ND	3.1 ± 0.5^D	1.53 ± 0.2^{BC}	6.6 ± 0.5^B	538 ± 120^B
NSFI	ND	2.1 ± 0.2^C	1.83 ± 0.1^C	5.3 ± 0.3^A	1033 ± 79^C
NSDI	ND	1.5 ± 0.1^A	1.43 ± 0.2^B	7.1 ± 0.3^B	573 ± 145^B
NSSC	ND	1.8 ± 0.1^B	1.58 ± 0.2^{BC}	6.3 ± 0.7^{AB}	700 ± 96^B
NSBP	0.06 ± 0.03	1.4 ± 0.1^A	0.98 ± 0.1^A	6.2 ± 0.7^{AB}	190 ± 14^A
GM(SD)	0.08 ± 2.24	1.6 ± 1.4	1.4 ± 1.4	6.8 ± 1.2	380 ± 2

TABLE 3. Continued

Station	Hg	Ni	Pb	Zn	Al
MASN	0.51 ± 0.1^A	1.05 ± 0.06^B	2.9 ± 0.4^B	103 ± 9^A	84 ± 18^A
MADX	0.62 ± 0.0^A	1.23 ± 0.05^B	3.9 ± 0.6^C	88 ± 4^A	188 ± 29^C
MABI	0.72 ± 0.1^B	1.08 ± 0.10^B	6.1 ± 0.9^D	153 ± 21^B	79 ± 24^A
MAWN	0.64 ± 0.1^A	1.98 ± 0.22^C	4.8 ± 0.7^{CD}	115 ± 14^{BC}	368 ± 29^B
MAIP	0.49 ± 0.1^A	0.70 ± 0.10^A	1.6 ± 0.1^A	$90 \pm 9^A^C$	72 ± 17^A
NHRH	0.61 ± 0.1^A	1.43 ± 0.13^A	2.1 ± 0.2^A	90 ± 18^A	125 ± 10^A
NHDP	0.83 ± 0.0^B	1.65 ± 0.19^A	3.4 ± 0.3^B	145 ± 21^B	238 ± 28^C
MECC	0.58 ± 0.1^A	1.30 ± 0.35^A	4.6 ± 0.6^C	95 ± 7^A	157 ± 15^B
MESA	0.56 ± 0.1^B	1.13 ± 0.22^B	2.5 ± 0.1^B	86 ± 14^A	103 ± 23^B
MEPH	1.31 ± 0.3^{CB}	1.13 ± 0.17^B	8.3 ± 1.4^D	146 ± 49^B	340 ± 100^C
MEPR	0.55 ± 0.5^B	1.08 ± 0.17^B	3.9 ± 0.7^C	77 ± 12^A	240 ± 39^C
MEKN	0.80 ± 0.1^{BC}	0.68 ± 0.13^A	1.4 ± 0.3^A	60 ± 11^A	84 ± 13^B
MEUR	0.57 ± 0.1^{BC}	0.78 ± 0.10^{AB}	1.3 ± 0.2^A	68 ± 10^A	66 ± 7^{AB}
MEMR	0.15 ± 0.0^A	1.43 ± 0.21^B	1.4 ± 0.4^A	54 ± 9^A	333 ± 23^C
MECK	0.11 ± 0.0^A	0.91 ± 0.09^{AB}	1.4 ± 0.2^A	72 ± 11^A	225 ± 13^C
NBNR	0.52 ± 0.1^A	0.93 ± 0.05^A	1.0 ± 0.1^A	95 ± 6^A	223 ± 17^A
NBHI	0.48 ± 0.1^A	1.18 ± 0.13^B	1.5 ± 0.4^B	99 ± 21^A	213 ± 22^A
NBLB	0.69 ± 0.1^B	1.02 ± 0.17^B	1.9 ± 0.5^C	80 ± 21^A	192 ± 22^A
NSAR	0.46 ± 0.1^A	2.00 ± 0.45^B	1.6 ± 0.3^A	75 ± 5^A	305 ± 70^B
NSFI	0.44 ± 0.1^A	1.90 ± 0.14^B	1.3 ± 0.1^A	71 ± 10^A	688 ± 31^C
NSDI	0.44 ± 0.1^A	1.33 ± 0.13^A	3.3 ± 0.3^{BC}	83 ± 7^A	325 ± 84^B
NSSC	0.49 ± 0.0^A	1.40 ± 0.14^A	2.6 ± 0.5^B	79 ± 8^A	303 ± 53^B
NSBP	0.53 ± 0.1^A	1.33 ± 0.10^A	3.9 ± 0.3^C	114 ± 15^B	49 ± 9^A
GM(SD)	0.52 ± 1.7	1.2 ± 1.4	2.5 ± 1.8	90 ± 1	177 ± 2

TABLE 4 . NOAA, National Status and Trends Mussel Watch summary
the Gulf of Maine mussel samples collected in $\mu\text{g/g}$ dry weight), $n = 13$ sites
(O'Connor, 1992).

	Ag	Al	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Geometric mean	0.22	203	1.10	1.39	10.3	312	0.13	1.18	2.97	92
"high value"*	0.51	387	1.52	2.78	11.6	482	0.31	1.72	6.75	113

* Logarithmic mean (geometric) plus one standard deviation (O'Connor, 1992)

TABLE 5. Summary statistics for mussels collected at twenty-three Maine
stations ($\mu\text{g/g}$ dry weight) (Sowles, 1993). ME-RM = Arithmetic,
mean; ME-HV = Maine high value = Arithmetic mean plus three times
standard

	Ag	Al	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
ME-RM	0.12	-	1.75	1.53	6.9	-	0.12	1.80	2.60	89
SD	0.09	-	0.46	0.66	1.28	-	0.12	0.38	1.13	15.5
ME-HV	0.40	-	3.14	3.51	10.7	-	0.48	2.90	6.00	136

metal concentrations (ME-RM values) should therefore be lower than that observed at several of the Gulfwatch stations, and should be comparable to the NS&T Gulf of Maine sites (O'Connor, 1992).

Sites were grouped by jurisdiction and ANOVA and Tukey Kramer tests were employed to examine difference among sites within a jurisdiction in 1994 (Table 3). Differences among all sites (23 stations throughout 5 jurisdictions) were not examined statistically. MECC is discussed as being a New Hampshire site because it is located in the Great Bay / Piscataqua River watershed, and therefore most comparable to other sites in New Hampshire.

Silver (Ag)

Elevated silver exposure concentrations have been shown to coincide with regions receiving municipal sewage (Sanudo-Wilhelmy and Flegal, 1992; Bucholtz ten Brink et al., 1996). Mussel tissue concentrations of Ag ranged from non-detect (ND) at 13 stations to $1.05 \pm 0.29 \mu\text{g} / \text{g}$ dry weight at MASN (Table 3). As in previous reports (see GMCME, 1994; GMCME, 1996) the concentration of Ag in mussel tissue increases in concentration from north to south (Figure 3). Ag concentrations at MASN were significantly higher than all other sites in 1994 and exceed the Maine high value (ME-HV) of $0.40 \mu\text{g} / \text{g}$ dry weight for the Maine reference stations. The exceptionally high silver concentrations at MASN were also observed in the 1993 Gulfwatch samples from this site, but were much lower in the 1992 Gulfwatch collections (GMCME, 1994, 1996). However, even the mean silver concentrations measured in the 1992 samples ($0.44 \pm 0.13 \mu\text{g} / \text{g}$ dry weight) were higher than values obtained for the other Gulfwatch stations in 1995. These high Ag concentrations are unusual since there are no POTW outfalls or industrial effluent in the area. Ag concentrations at MADX, MABI, MAWN, MAIP and NBHI exceed the Maine reference mean (ME-RM) of $0.12 \mu\text{g} / \text{g}$ dry weight. All other sites examined in 1994 were below the Maine reference mean. Analysis of mussel tissue burdens within jurisdictions (Table 3) showed that for Massachusetts, other than MASN, there was no significant difference between sites. In Maine, there was no significant difference between MEUR and MESA. In New Brunswick, NBHI was significantly higher than NBNR.

Lead (Pb)

The concentration of lead ranged from a value of $1.0 \pm 0.1 \mu\text{g} / \text{g}$ dry weight (NBNR) to $8.3 \pm 1.4 \mu\text{g} / \text{g}$ dry weight (MEPH) (Table 3, Figure 3). The high lead concentrations (greater

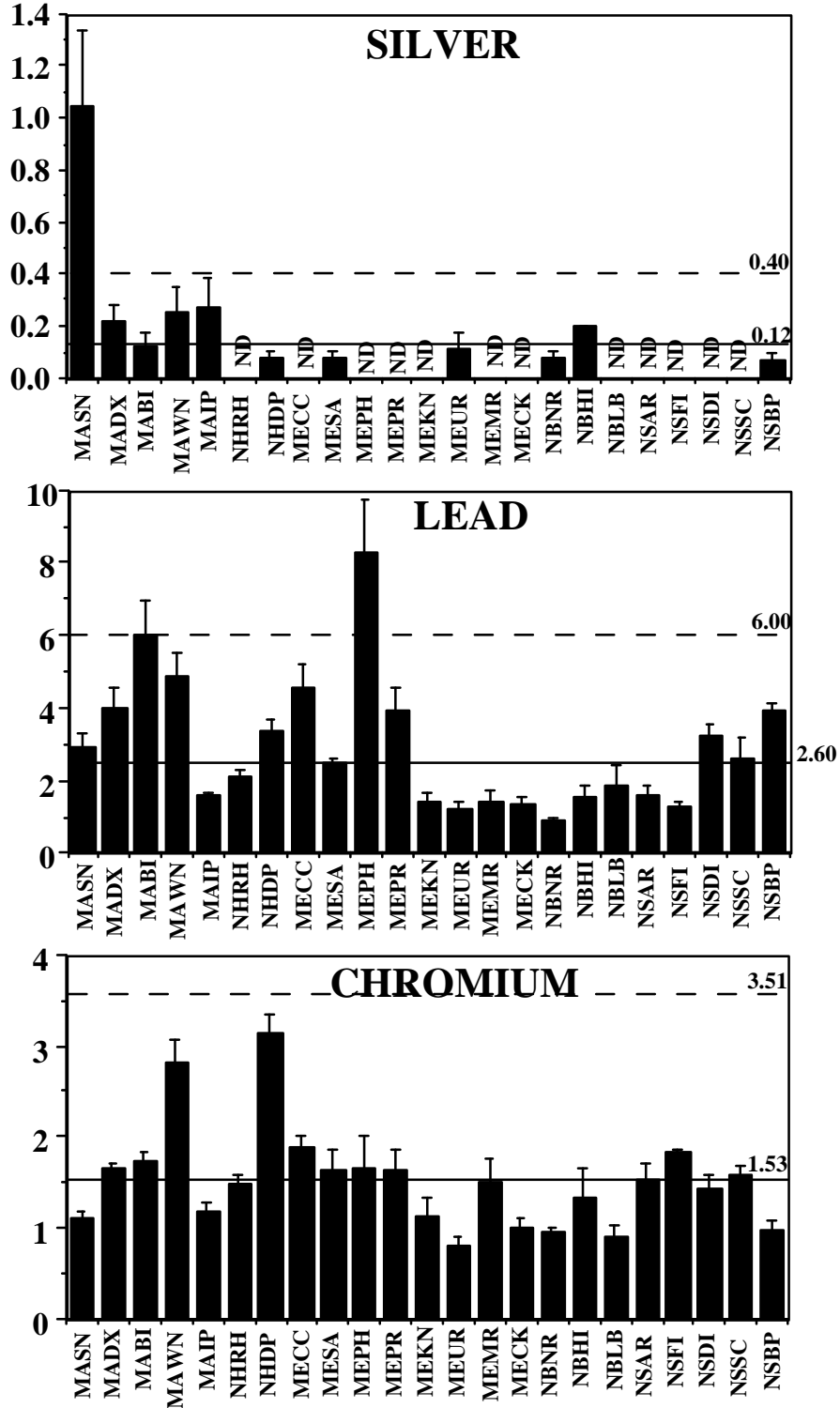


Figure 3. Distribution of silver, lead, and chromium tissue concentrations (arithmetic mean \pm SD, μ g/g dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. The reference mean, ME-RM (straight line) and the high value, ME-HV (dashed line) from the Maine reference data (Sowles, 1993) are shown for comparison. ND = non-detect.

than the Maine reference values) were recorded at MASN, MADX, MABI, MAWN, NHDP, MECC, MEPH, MEPR, NSDI, and NSBP. Of these only, MABI and MEPH exceed the ME-HV concentration (6.00 µg / g dry weight). Both sites are located near highly populated and industrialized regions, and may be subject to elevated non-point source discharges (e.g. direct regional atmospheric input, and runoff from streets and parking lots). The site at MABI is located on Brewster Island, at the mouth of Boston Harbor. As such it is also impacted by contaminants from the inner portion of Boston Harbor and from a major municipal waste-water outfall which serves 43 communities and towns around Boston. MEPH is in Portland Harbor where there are similar influences. Elevated Pb concentrations at MECC reflect known present and historical municipal, industrial and military sources.

Analysis of the concentrations of Pb in mussel tissue within each jurisdiction (Table 3) showed that the concentration of Pb varied. There were significant differences among sites within all jurisdictions. There is a trend for higher concentrations in population centres such as in Massachusetts, New Hampshire and Portland Harbor.

Chromium (Cr)

The concentration of chromium exceeded the Maine reference mean (1.53 µg / g dry weight) in sites in Massachusetts, New Hampshire, Maine, and Nova Scotia. No sites exceed the ME-HV (3.51 µg / g dry weight). The highest concentration was at NHDP (3.13 ± 0.22 µg / g dry weight) and the lowest at MEUR (0.80 ± 0.12 µg / g dry weight) (Table 3, Figure 3). NHDP is located in the Piscataqua River a few miles downstream from where tannery wastes were historically discharged (Jones et al., 1992).

Analysis of the mussel tissue concentrations of Cr within each jurisdiction (Table 3) revealed that there were significant difference between sites in all jurisdictions. The Cr concentration at NSF1 was significantly higher than at all other sites in Nova Scotia. However, because of elevated Al and Fe, the elevated Cr concentrations may reflect ingested contaminant sediments or natural particles (Robinson et al., 1993).

Zinc (Zn)

Zinc concentrations generally reflect human activity associated with tire wear, galvanized materials and industrial discharges. In each jurisdiction there was at least one site that had concentrations greater than the Maine reference mean (89 µg / g dry weight) with MABI, NHDP

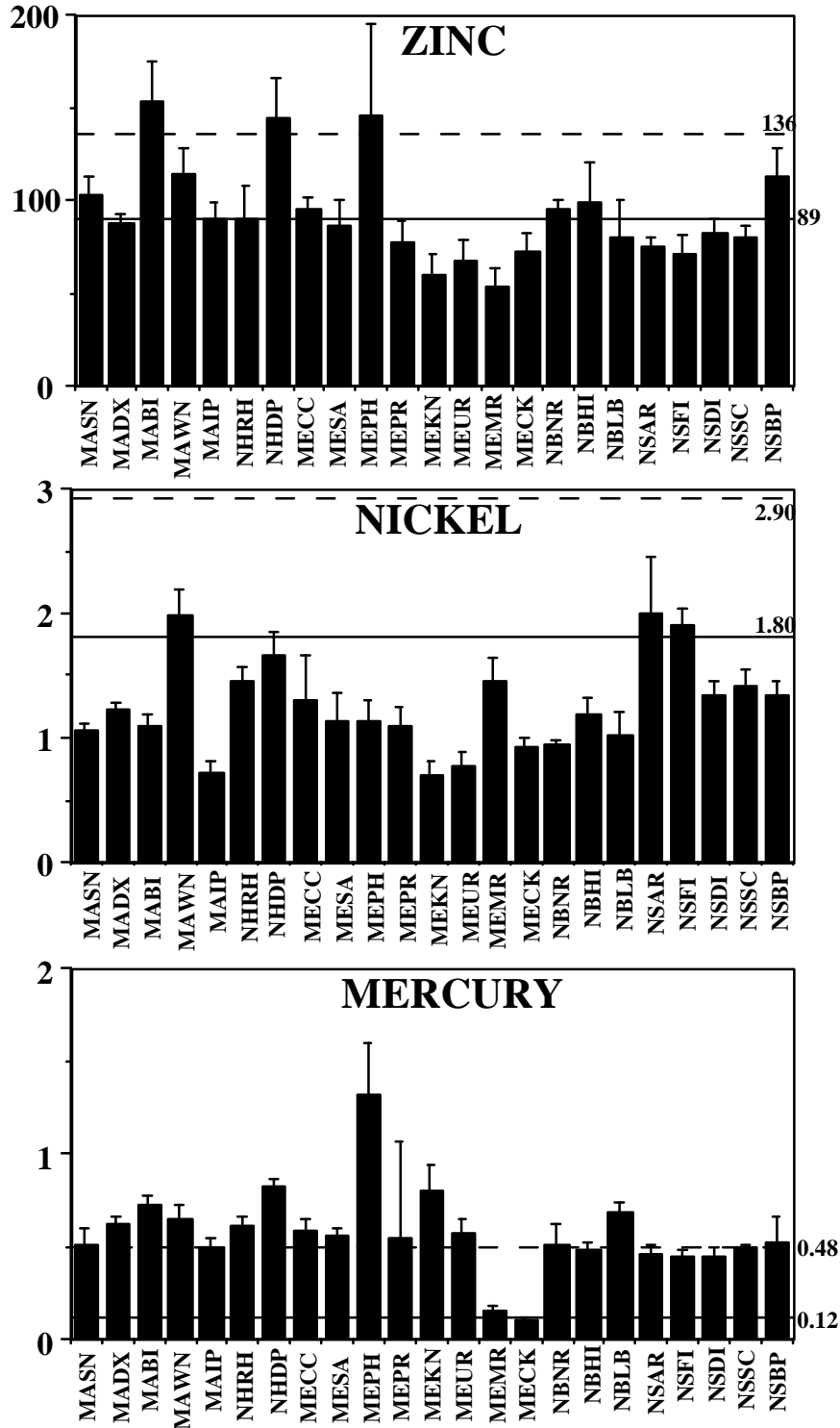


Figure 4. Distribution of zinc, nickle, and mercury tissue concentrations (arithmetic mean \pm SD_{μ} g/g dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. The reference mean, ME-RM (straight line) and the high value, ME-HV (dashed line) from the Maine reference data (Sowles, 1993) are shown for comparison.

and MEPH having concentrations greater than the Maine high value ($136 \mu\text{g} / \text{g}$ dry weight) (Table 3, Figure 4). The lowest concentration of Zn measured was at NBNR ($54 \pm 9 \mu\text{g} / \text{g}$ dry weight) and the highest was at MABI ($153 \pm 21 \mu\text{g} / \text{g}$ dry weight). Analysis of the mussel tissue concentrations of Zn within each jurisdiction revealed that only New Brunswick had consistent concentrations of Zn among sites (Table 3).

Nickel (Ni)

The concentration of nickel ranged from a value of $0.68 \pm 0.13 \mu\text{g} / \text{g}$ dry weight at MEKN to $2.00 \pm 0.45 \mu\text{g} / \text{g}$ dry weight at NSAR (Table 3, Figure 4). Only 3 sites, MAWN, NSAR and NSFI were higher than the Maine reference mean of $1.8 \mu\text{g} / \text{g}$ dry weight.

Analysis of the mussel tissue concentrations of Ni within each jurisdiction (Table 3) revealed that the concentration of Ni varied greatly within jurisdictions. Only in New Hampshire was the concentration of Ni consistent among sites.

Mercury (Hg)

The concentration of mercury in mussel tissue ranged from a value of $0.11 \pm 0.01 \mu\text{g} / \text{g}$ dry weight at MECK to $1.31 \pm 0.28 \mu\text{g} / \text{g}$ dry weight at MEPH (Table 3, Figure 4). Mercury at all sites except MECK exceeded the Maine reference mean of $0.12 \mu\text{g} / \text{g}$ dry weight. Of those sites that exceeded the Maine reference mean, only MEMR, MECK, NBHI, NSAR, NSFI, and NSDI did not exceed the Maine high value of $0.48 \mu\text{g} / \text{g}$ dry weight.

Cadmium (Cd)

Cadmium is widely used in industry for batteries, plating, stabilizers, and as a neutron absorber in nuclear reactors. The concentration of cadmium in mussel tissue ranged from $1.1 \pm 0.1 \mu\text{g} / \text{g}$ dry weight at MEPR and MADX to $3.1 \pm 0.3 \mu\text{g} / \text{g}$ dry weight at NHDP and NSAR (Table 3, Figure 5). In addition to being downstream from tannery discharges, NHDP is within close proximity to numerous municipal discharges and other industrial sources. NSAR had mean tissue concentrations that were the same as NHDP. Unlike NHDP, however, NSAR is not located near any known source of toxic compound discharge (B. Crawford, personal communication). Most values were below the Maine reference mean of $1.75 \mu\text{g} / \text{g}$ dry weight with the exception of MABI, MAWN, NHDP, NBHI, NSAR, NSFI, and NSSC. No values exceeded the Maine high

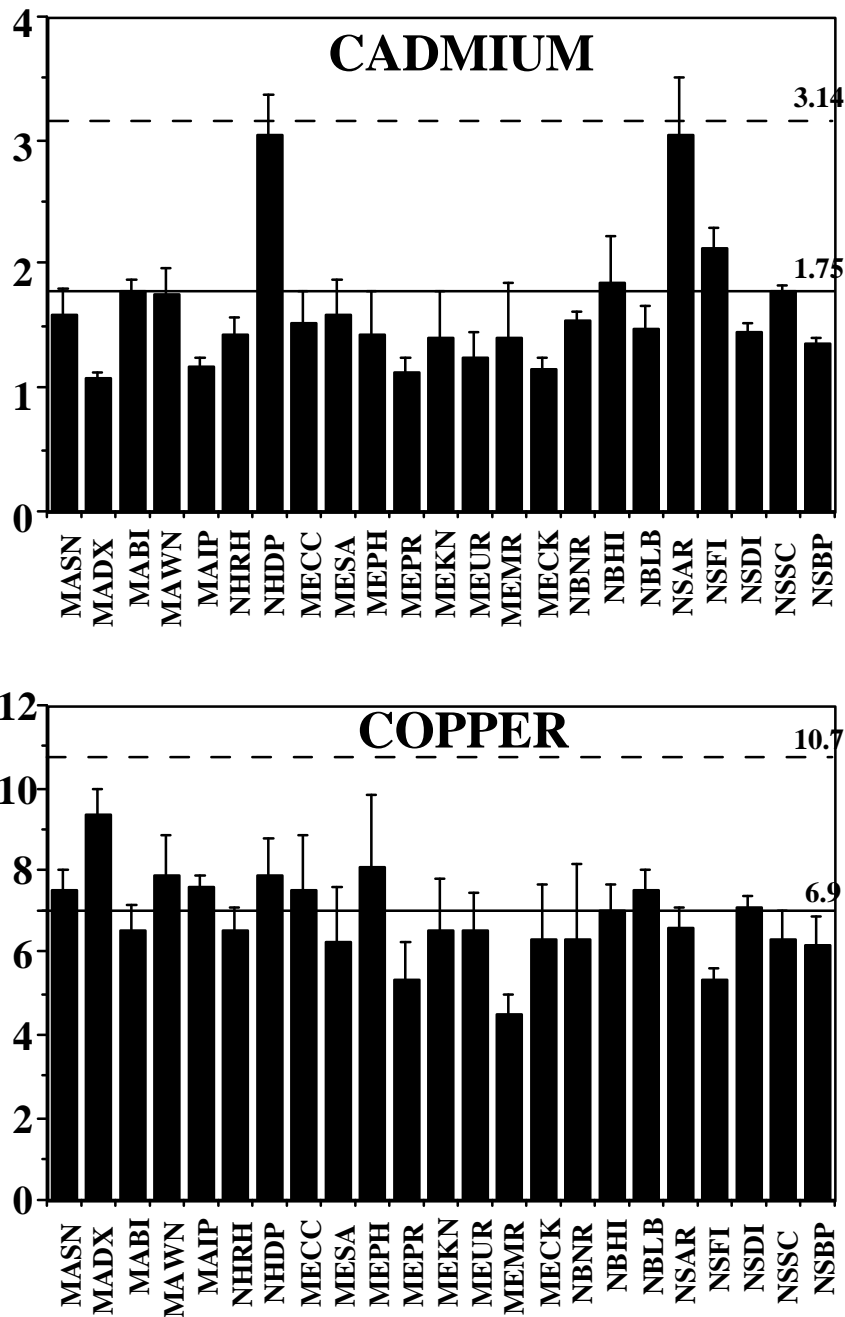


Figure 5 Distribution of cadmium, and copper tissue concentrations (arithmetic mean \pm SD, $\mu\text{g/g}$ dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. The reference mean, ME-RM (straight line) and the high value, ME-HV(dashed line) from the Maine reference data (Sowles, 1993) are shown for comparison.

value ($3.14 \mu\text{g} / \text{g}$ dry weight).

Within the jurisdictions the concentration of Cd varied. There were significant differences between sites in each jurisdiction with the exception of Maine and New Brunswick (Table 3).

Copper (Cu)

The concentration of copper in mussel tissue ranged from $4.5 \pm 0.5 \mu\text{g} / \text{g}$ dry weight at MEMR to $9.3 \pm 0.7 \mu\text{g} / \text{g}$ dry weight at MADX (Table 3, Figure 5). Approximately half of the sites had copper concentrations that exceeded the Maine reference (ME-RM) of $6.9 \mu\text{g} / \text{g}$ dry weight. No sites were above the ME-HV ($10.7 \mu\text{g} / \text{g}$ dry weight). Analysis of the mussel tissue concentration of Cu within each jurisdiction showed that the concentration of Cu was fairly consistent (Table 3).

Iron (Fe) and Aluminum (Al)

The concentration of iron in mussel tissue ranged from $170 \pm 17 \mu\text{g} / \text{g}$ dry weight at MAIP to $1033 \pm 79 \mu\text{g} / \text{g}$ dry weight at NSFI (Table 3, Figure 6). While there were no reference values for Fe from Maine stations with which to compare our data, Fe concentrations at the Gulf of Maine NS&T sites can be used for comparison (Figure 6). Tissue Fe concentrations at MADX, MAWN, NHDP, MEPH, MEPR, MEMR, MECK, NBHI, NSAR, NSFI, NSDI, and NSSC exceeded the mean concentration of Fe from mussels analyzed in the Gulf of Maine by the NS&T program (O'Connor, 1992). Concentrations at three sites, MAWN, NSFI, and NSSC, exceeded the high value (mean plus one standard deviation). Analysis of the mussel tissue concentrations of Fe within jurisdictions (Table 3) showed that there were no significant differences between sites in New Brunswick but there were significant differences between sites in Massachusetts, Maine, New Hampshire, and Nova Scotia.

The concentration of aluminum in mussel tissue ranged from $49 \pm 9 \mu\text{g} / \text{g}$ dry weight at NSBP to $688 \pm 31 \mu\text{g} / \text{g}$ dry weight at NSFI (Table 3, Figure 6). While there were no reference values for Fe from Maine stations with which to compare our data, Fe concentrations at the Gulf of Maine NS&T sites can be used for comparison (Figure 6). Tissue concentrations of Al at MAWN, MEPH, MEMR, NSAR, NSDI, NSFI, and NSSC exceeded the mean concentration of Al from mussels analyzed in the Gulf of Maine by the NS&T program (O'Connor, 1992). NSFI was the only site at which the tissue concentrations of Al exceeded the high value. Analysis of the concentration of Al in mussel tissue within jurisdictions showed that it was not consistent in any

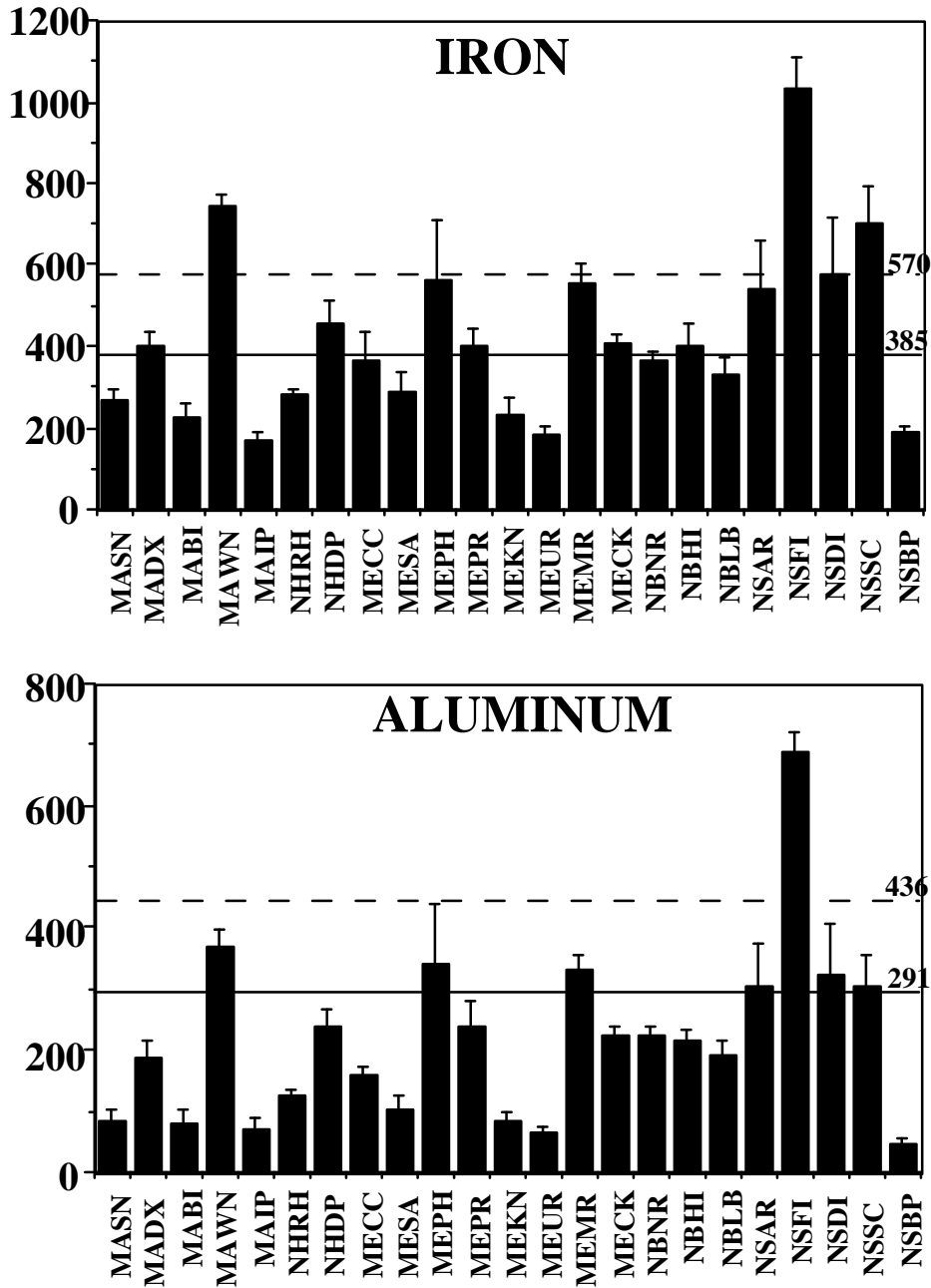


Figure 6 Distribution of cadmium, and copper tissue concentrations (arithmetic mean \pm SD, $\mu\text{g/g}$ dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. The mean (straight line) and the high value (mean plus one standard deviation, dashed line from the NS&T data (O'Connor, 1992) are shown for comparison.

jurisdiction, with the exception of New Brunswick (Table 6).

The trends for Fe and Al concentrations were quite similar (Figure 6). As in previous reports (GMCME, 1994, 1996), data from 1994 continue to suggest that the eastern stations generally contain higher concentrations of Al and Fe than most in the western stations (Figure 6). Higher concentrations tend to be consistent with elevated concentrations of suspended sediments at sites. Differences in Al:Fe ratios may reflect local sediment geochemistry. Composition of the organic and inorganic fractions of the resuspended material must be considered in interpreting metal concentrations. The elevated concentrations of Al and Fe at NSFI, however, may be unacceptable. Perhaps NSFI should be eliminated from future analysis or a method developed that enables us to account for sediment contributions of contaminants.

ORGANIC CONTAMINANTS

The total concentration of polynuclear aromatic hydrocarbons (PAH's), polychlorinated biphenyls (PCB's) and organochlorine pesticides (OCs) measured in mussel tissue samples of indigenous mussels are presented in Table 6. Individual analyte concentrations of each compound class are provided in Appendices D, E and F.

Spatial variation in organic contaminants

Figures 7 and 8 show the concentration of Σ PAH₂₄ (Figure 7), Σ PCB₂₄ (Figure 7), Σ DDT₆ (Figure 8), and Σ PEST₁₇ (Figure 8) measured in tissue of *M. edulis* in the 1994 sampling stations presented from south to north. Sites were grouped by jurisdiction and the organic contaminant concentrations of mussel tissue were compared using ANOVA and Tukey Kramer tests to examine differences among sites. The results of this analysis are shown in Table 6. The concentration of contaminants were plotted on a log scale and the geometric mean \pm 1 SD has been added for comparison purposes. Concentrations above the geometric mean + 1 SD are considered high. Table 7 contains a summary of the geometric means for each jurisdiction as well as an overall Gulf of Maine estimate based on all sites. Geometric means of the Σ PAH₂₄ concentrations range from ND (non-detected), in New Brunswick, to 108 ng / g dry weight in Maine. All sites except NHRH, MEUR, NBNR, NBHI, NBLB, NSAR, NSFI and NSSC exceed the geometric mean + 1 SD (Figure 7). The geometric mean of Σ PCB₂₄ ranges from 1 ng/g dry weight in New Brunswick, to 50 ng/g dry weight in Massachusetts. All sites in Massachusetts,

TABLE 6. Tissue organic contaminant concentrations (arithmetic mean \pm SD, ng/g dry wt.) from mussels collected throughout the Gulf of Maine, 1994 and ANOVA of concentrations by jurisdiction. Same letter indicates no significant difference among sites within each jurisdiction. ND, nondetected.

LOCATION	Σ PAH ₂₄	Σ PCB ₂₄	Σ DDT ₆	Other Pesticides	Σ PEST ₁₇
MASN	42.38 \pm 9.81 ^A	28.63 \pm 6.92 ^A	14.10 \pm 1.58 ^A	6.15 \pm 3.51 ^{AB}	20.25 \pm 5.06 ^A
MADX	91.00 \pm 6.38 ^B	69.00 \pm 6.78 ^C	29.08 \pm 1.76 ^C	6.68 \pm 2.81 ^{AB}	35.75 \pm 3.59 ^B
MABI	135.00 \pm 31.33 ^B	80.25 \pm 7.93 ^C	21.75 \pm 4.81 ^B	12.75 \pm 2.93 ^B	34.50 \pm 6.14 ^B
MAWN	89.50 \pm 10.47 ^B	46.25 \pm 5.74 ^B	15.70 \pm 2.63 ^A	10.30 \pm 2.63 ^{AB}	26.00 \pm 4.97 ^{AB}
MAIP	108.75 \pm 24.36 ^B	39.25 \pm 1.50 ^B	14.63 \pm 0.47 ^A	4.13 \pm 1.95 ^A	18.75 \pm 2.06 ^A
NHRH	23.00 \pm 7.35 ^A	5.30 \pm 0.80 ^A	3.48 \pm 0.26 ^A	ND	3.48 \pm 0.26 ^A
NHDP	187.00 \pm 16.51 ^C	26.00 \pm 6.33 ^B	7.78 \pm 1.37 ^B	2.63 \pm 1.12	10.40 \pm 2.45 ^B
MECC	136.75 \pm 9.54 ^B	66.75 \pm 4.79 ^B	12.50 \pm 1.29 ^B	ND	12.50 \pm 1.29 ^B
MESA	48.50 \pm 17.06 ^B	13.20 \pm 6.90 ^A	5.48 \pm 2.96 ^A	ND	5.48 \pm 2.96 ^A
MEPH	1098.50 \pm 359.57 ^C	90.75 \pm 34.74 ^B	24.35 \pm 5.88 ^C	11.58 \pm 1.57 ^D	35.75 \pm 7.18 ^C
MEPR	225.75 \pm 54.76 ^B	11.25 \pm 5.57 ^A	15.00 \pm 1.93 ^{BC}	4.75 \pm 2.22 ^B	19.75 \pm 3.86 ^B
MEKN	102.75 \pm 15.20 ^B	42.50 \pm 3.70 ^B	10.68 \pm 3.93 ^B	7.58 \pm 1.31 ^C	18.25 \pm 4.43 ^B
MEUR	12.50 \pm 14.46 ^A	ND	3.10 \pm 1.08 ^A	2.33 \pm 0.26 ^A	5.43 \pm 1.27 ^A
MEMR	136.50 \pm 45.99 ^B	5.45 \pm 0.37 ^A	14.50 \pm 1.29 ^B	ND	14.50 \pm 1.29 ^B
MECK	183.50 \pm 58.79 ^B	5.15 \pm 0.58 ^A	9.88 \pm 0.90 ^B	6.88 \pm 0.13 ^C	16.75 \pm 0.96 ^B
NBNR	ND	ND	3.48 \pm 0.29 ^A	ND	3.48 \pm 0.29 ^A
NBHI	ND	ND	3.43 \pm 0.10 ^A	ND	3.43 \pm 0.10 ^A
NBLB	ND	3.20 \pm 3.67	3.97 \pm 0.35 ^A	ND	3.97 \pm 0.35 ^A
NSAR	ND	1.38 \pm 2.757 ^A	2.85 \pm 0.13 ^A	2.68 \pm 0.15 ^A	5.53 \pm 0.26 ^B
NSFI	ND	ND	3.08 \pm 0.47 ^A	ND	3.08 \pm 0.47 ^{AB}
NSDI	70.50 \pm 8.66 ^B	1.18 \pm 1.36 ^A	1.70 \pm 1.14 ^A	ND	1.70 \pm 1.14 ^A
NSSC	ND	3.73 \pm 2.75 ^A	2.58 \pm 0.56 ^A	ND	2.58 \pm 0.56 ^{AB}
NSBP	27.25 \pm 3.59 ^A	3.85 \pm 2.64 ^A	12.70 \pm 2.09 ^B	2.80 \pm 0.12 ^A	15.50 \pm 2.08 ^C

TABLE 7. Geometric mean (\pm SD) of tissue organic contaminants for mussels within each jurisdiction and for all the Gulf of Maine, 1994 stations.

JURISDICTION	Σ PAH ₂₄	Σ PCB ₂₄	Σ DDT ₆	OTHER PESTICIDES	Σ PEST ₁₇
Massachusetts	87.2 \pm 1.5 ¹	49.9 \pm 1.5	19.2 \pm 1.3	8.0 \pm 1.7	26.9 \pm 1.4
New Hampshire	84.0 \pm 2.7	22.4 \pm 2.8	8.1 \pm 1.6	1.5 \pm 1.9	8.8 \pm 1.7
Maine	104.5 \pm 5.4	12.7 \pm 4.0	10.9 \pm 1.9	3.9 \pm 2.7	14.7 \pm 1.9
New Brunswick	ND	1.4 \pm 2.0	4.6 \pm 2.0	ND	4.6 \pm 2.0
Nova Scotia	4.6 \pm 6.9	2.2 \pm 2.2	4.5 \pm 1.9	1.7 \pm 1.9	5.2 \pm 2.1
Gulf of Maine ²	28.0 \pm 9.1	9.2 \pm 5.0	8.8 \pm 2.1	2.9 \pm 2.7	10.8 \pm 2.3

¹Geometric mean (\pm SD)

²All sites

ND, nondetected

plus NHDP, MECC, MESA, MEPH, MEPR and MEKN exceed the geometric mean + 1 SD (Figure 7). ΣDDT_6 geometric mean range from 4.5 ng/g dry weight in Nova Scotia to 19 ng/g dry weight in Massachusetts. All sites in Massachusetts, and MECC, MEPH, MEPR, MEKN, MECK, and NSBP exceed the geometric mean + 1SD (Figure 7). Nine sites examined in 1994 (MASN, MADX, MABI, MAWN, MAIP, MECC, MEPH, MEPR, and MEKN) exceed the geometric mean + 1SD in each of ΣPAH_{24} , ΣPCB_{24} and ΣDDT_6 .

In 1994, as in the previous year, there is a general southward trend toward higher organic contaminant concentrations. Although New Hampshire stations displayed concentrations of organic contaminants that were intermediate between the more contaminated Maine sites and the Massachusetts sites. This north-to-south increase in contaminant concentrations can be attributed to the increasing population density and industrialization in the watersheds in the south. This trend is most evident in the PCB and DDT data sets (Figure 7 and 8), which probably reflects the historical use and deposition of these contaminants in sediments.

Polyaromatic Hydrocarbons

Total PAH concentration (ΣPAH_{24}) in indigenous mussels ranged from ND (non-detected) to 1099 ± 360 ng / g dry weight at MEPH (Table 6, Figure 7). Some mean concentrations of ΣPAH_{24} were as high as those reported from areas influenced by oil spills and municipal sewage outfalls (148 ng / g in Rainio et al., 1986; 63-1060 ng / g in Kveseth et al., 1982), however, concentrations were not as high as in industrialized areas affected by coking operations in Sydney Harbor NS (1400-16000 ng / g, Environment Canada, 1986) or by smelting operations in Saudafjord, Norway (5111-225163 ng / g, Bjorseth et al., 1979).

The highest mean concentration of ΣPAH_{24} was measured at MEPH (1098 ng / g dry weight). This value is the highest concentration reported for any Gulf of Maine site since 1992 (Nut Island, MA, 721 ± 53 ng / g dry weight). MEPH, Portland Harbor is an oil handling facility and also receives significant urban runoff. The concentration of PAH at MEPH, although somewhat lower, is comparable to results reported previously by NOAA for sites in Boston Harbor (Dorchester Bay, 1865 ng / g; Deer Island, 2226 ng / g; O'Connor, 1992). High concentrations were also observed at NHDP (187 ± 17 ng / g) MEPR (226 ± 55), and MECK (184 ± 59 ng/g). PAH's were not detected in New Brunswick samples in 1994.

The concentration of measurable ΣPAH_{24} was significantly different in all jurisdictions (Table 6). In Massachusetts, MASN was significantly lower than all other sites. MASN is a Gulfwatch reference site and expected to have contaminant concentrations lower than other Massachusetts sites. Sites in New Hampshire, Maine and Nova Scotia NHDP, MEPH and NSDI, respectively, had concentrations that were significantly higher than all other sites.

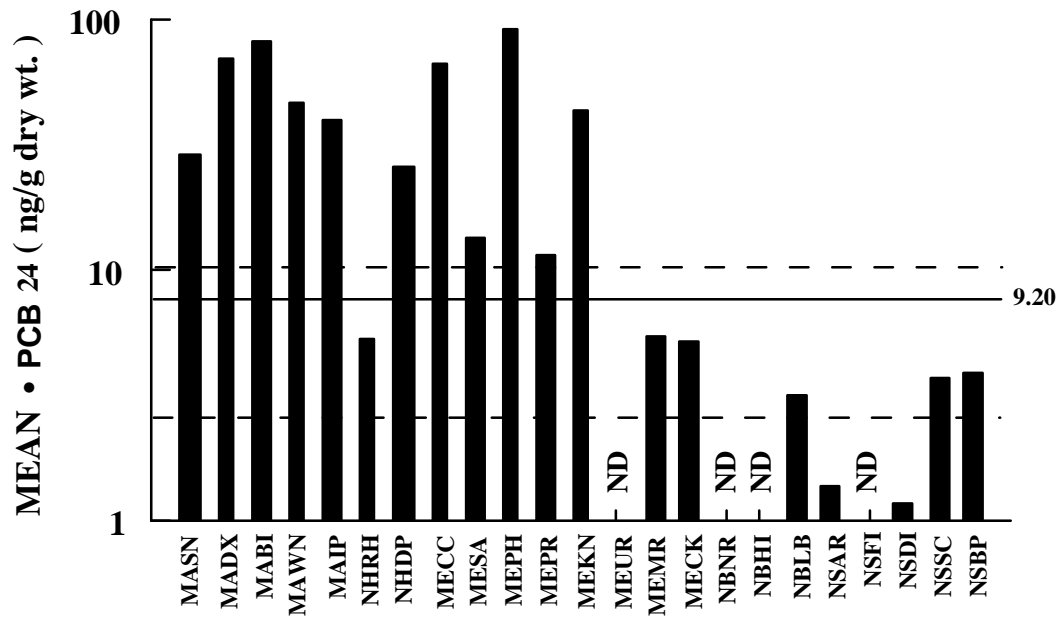
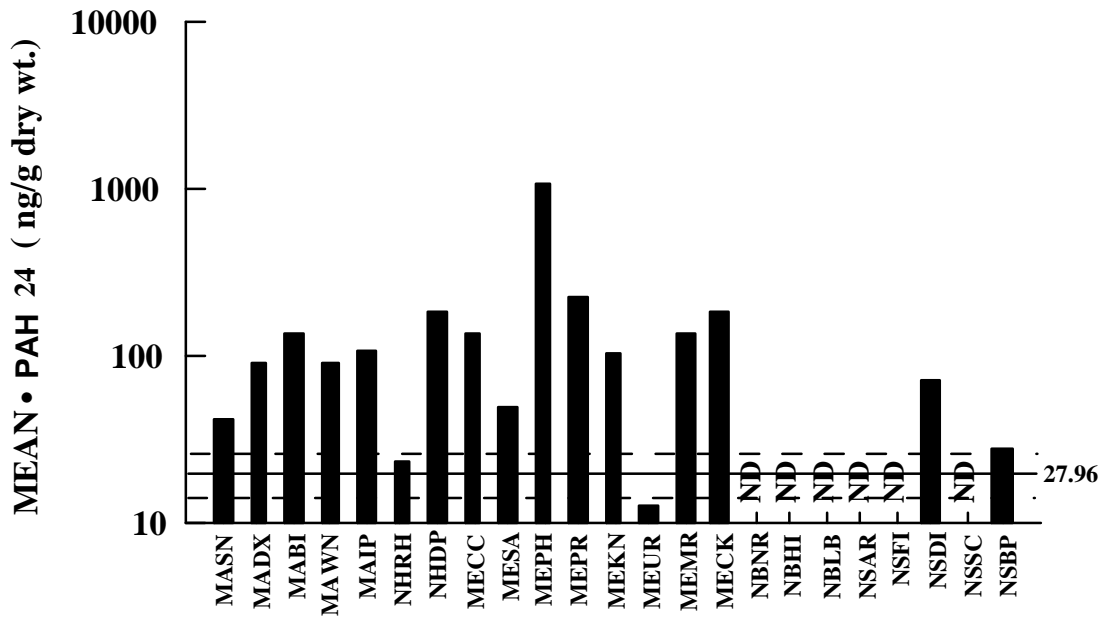


Figure 7. Log distribution of PAH 24 and PCB 24 tissue concentrations (arithmetic mean ng/g dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. Geometric mean (straight line) and \pm one standard deviation (dashed line) of all Gulf of Maine stations. ND, non detected.

Polychlorinated Biphenyls

The mean total PCB (ΣPCB_{24}) concentration in indigenous mussels ranged from undetected to 91 ± 35 ng / g dry weight at MEPH (Table 6, Figure 7). Analysis by jurisdiction (Table 6) showed no significant difference between sites in New Brunswick and Nova Scotia. In Massachusetts, concentrations above the mean ± 1 SD were observed at all sites, although concentrations at MADX, MABI, MAWN and MAIP were significantly higher than MASN. In New Hampshire MECC and NHDP were significantly higher than NHRH, and in Maine, MEKN and MEPH were significantly higher than all other sites.

Pesticides

The total pesticide concentration (ΣPEST_{17}) in indigenous mussels ranged from 1.7 ± 1.1 ng / g dry weight at NSDI to 35.8 ± 7.2 ng / g dry weight at MEPH and MADX (Table 6, Figure 8). In 1994, as in previous reports (GMCME, 1994; GMCME, 1996), DDT and its degenerative metabolites were the main contributors to total detectable pesticides. The range of ΣDDT_6 was 1.7 ± 1.1 ng / g dry weight at NSDI to 29.1 ± 1.8 ng / g dry weight at MADX (Table 6 and Figure 8).

Analysis of ΣPEST_{17} and ΣDDT_6 concentrations showed that New Brunswick was the only jurisdiction where there were no significant differences between sites (Table 6).

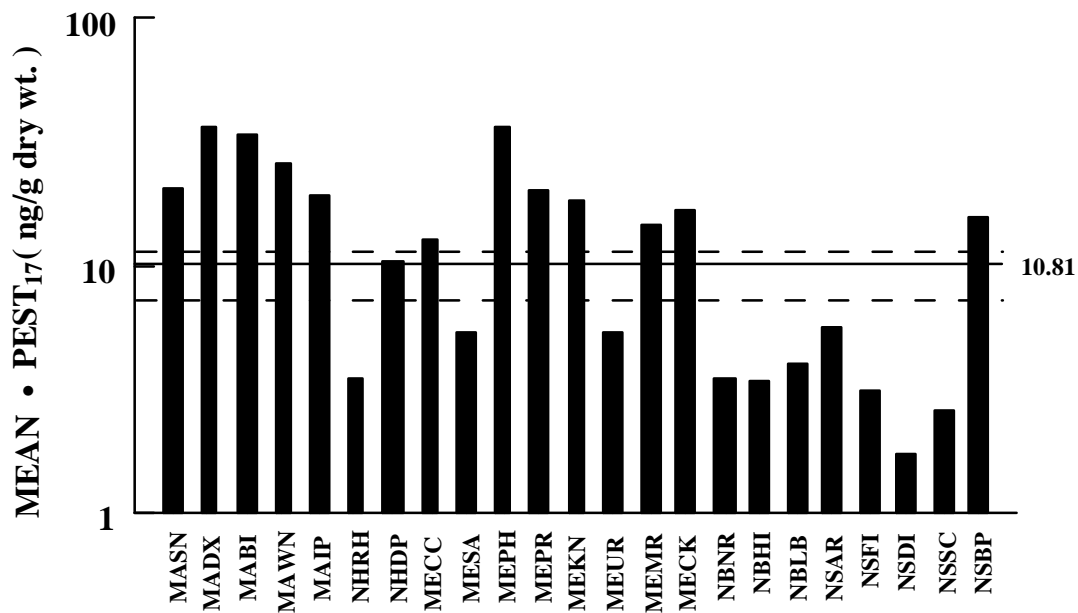
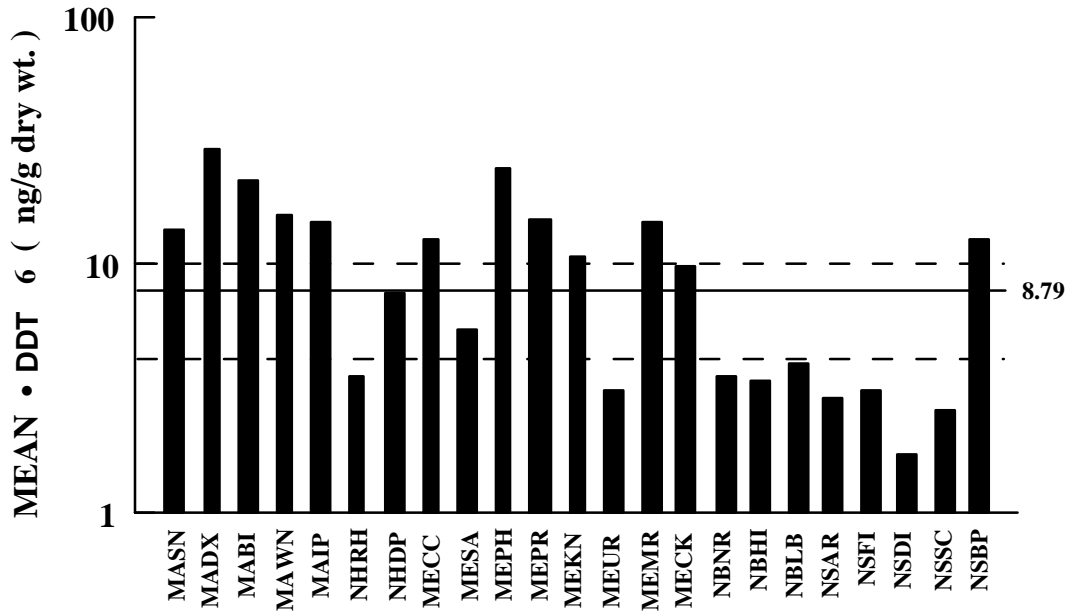


Figure 8. Log distribution of •DDT 6 and •PEST 17 tissue concentrations (arithmetic mean; ng/g dry weight) in indigenous mussels at the Gulf of Maine stations in 1994. Geometric mean (straight line) and \pm one standard deviation (dashed line) of all Gulf of Maine stations.

ACCEPTABLE LEVELS AND STANDARDS OF MUSSEL CONTAMINATION

Limited information is available for human health effects. Published tolerance or action levels for PAHs in commercial marine species are not available in Canada or in the United States. In marine areas where PAH contamination may be a human health concern, closure of commercial fisheries as a result of high contamination levels has been dealt with on a case by case basis. In general, most levels reported in the literature are on a wet weight basis in contrast to Gulfwatch dry weight values. To facilitate general comparisons with Gulfwatch values, an average moisture content of 85% has been applied to wet weight health values to derive dry weight equivalents. The reported organic concentrations are within acceptable levels for those compounds which have established Federal Drug Administration (FDA) Action Limits in fish and shellfish. Total PCB concentrations found (Appendix E) are less than the action level of 13 ppm dry weight or 2 ppm wet weight (USFDA, 1990; CSSP, 1992). MEPH had the highest levels of PCBs in mussels during the 1994 survey, with 0.09 ± 0.03 ppm dry weight. The action level for the pesticides dieldrin, aldrin, chlordane, heptachlor and heptachlor epoxide is 2.0 ppm dry weight or 0.3 ppm wet weight (USFDA, 1990). Canadian limits for agricultural chemicals exclusive of DDT are 0.67 ppm dry weight or 0.1 ppm wet weight (CSSP, 1992). All of the pesticides were below detection levels in the 1994 mussel survey. The total DDT levels found are several orders-of-magnitude below the action level of 33 ppm dry weight or 5 ppm wet weight (USFDA, 1990; CSSP, 1992). Duxbury, MA (MADX) had the highest level in 1994 of 0.03 ± 0.02 ppm dry weight.

Admissible levels of methyl mercury, expressed as mercury, are less than 6.7 ppm dry weight or 1 ppm wet weight in the United States (USFDA, 1990) and less than 3.3 ppm dry weight or 0.5 ppm wet weight in Canada (CSSP, 1992). If it is assumed that measured mercury was present at all sites as methyl mercury, then the highest concentration of mercury found in the 1994 Gulfwatch Project data was 1.31 ± 0.28 $\mu\text{g/g}$ dry weight, at Portland Harbor, Maine, which was below the two federal action levels.

Recently, a series of FDA "Guidance Documents" (USFDA, 1993) for cadmium, chromium, lead and nickel have been released in the United States to complement the FDA Mercury Action Level. These "alert levels", however, are guidelines and by themselves do not warrant the issuance of health advisories. In Table 8, guidance concentrations are reported on a wet weight basis and dry weight equivalent and compared to the highest observed concentration in any single replicate analyzed in the 1994 Gulfwatch Project. All metal levels were below the guidelines. Lead concentrations at MEPH were close to the limit of 11.5 $\mu\text{g/g}$ dry weight with a value of 8.3 $\mu\text{g/g}$ dry weight. Although, this area of the coast is closed to the harvest of shellfish

and poses no threat to humans, it would be prudent to resample Portland Harbor, ME in the near future.

TABLE 8. A comparison of United States Food and Drug Administration (USFDA) guidelines for various metals with the Gulfwatch results.

Metal	Guideline (wet weight)	Guideline (dry weight)	Highest Observed 1994 Gulfwatch value (dry weight)	Location
Cadmium	3.7 µg/g	25 µg/g	3.1 µg/g	Dover Point, NH
Chromium	13 µg/g	87 µg/g	3.1 µg/g	Dover Point, NH
Lead	1.7 µg/g	11.5 µg/g	8.3 µg/g	Portland Harbor, ME
Nickel	80 µg/g	533 µg/g	2.0 µg/g	Apple River, NS

The United States Environmental Protection Agency (EPA) has promulgated a series of “screening values” for three metals (Cd, Hg, Se), 11 organochlorines, 6 organophosphate compounds, one chlorophenoxy herbicide, total PCBs and Dioxins/dibenzofurans (EPA, 1993) which were derived using human health risk assessment procedures. The promulgated values are based on several exposure assumptions (70 kg man, an average consumption rate of 6.5 g/d), and either the most current Reference Dose (RfD) values for non-carcinogens or the most recent Slope Factor (SF) plus an acceptable lifetime cancer risk of 1×10^{-5} for the carcinogenic compounds listed. Exceedences of any of the screening values is meant to trigger a more in-depth assessment of actual human health risk. Applying these screening values to the Gulfwatch data set provides yet another index of possible human health concern.

Mean concentrations of Cd, Hg, and ΣDDT_6 at all Gulfwatch stations are well below the EPA screening values (EPA, 1993). The screening value for the ΣPCB_{24} is exceedingly low (0.01 µg/g wet weight or approximately 0.07 µg/g dry weight; EPA, 1993). Mean ΣPCB_{24} concentrations at two Gulfwatch sites (MABI and MEPH) exceed this value. Individual composite samples from MABI and MEPH were as much as 129 and 181 times higher than the EPA Screening Value, respectively. These stations should therefore be examined in much more detail in order to adequately assess potential human health risk to PCBs.

MORPHOMETRIC COMPARISON

Shell morphology

Table 9 contains a summary of the morphological measurements [length (mm), height (mm), width (mm), wet weight (g) and condition index (CI)] for indigenous mussels collected at each site in 1994. The field protocol recommended the collection of mussels within the length range of 50 - 60 mm. The gulfwide mean length (\pm SD) at the 23 sites was 55.2 ± 3.7 mm (Table 9, Figure 9). ANOVA on the mean length at all sites was significant ($p < 0.05$). The significant difference is mainly attributed to the Maine station, MEMR, where the mussels were significantly smaller than all other sites (48.1 ± 4.8 mm) and the New Brunswick station, NBHI where the mussels were significantly larger than all other sites (63.1 ± 4.1 mm). This size difference, however, reflects mussel availability at the sites and not a contamination effect. For the majority of sites, the mean length of mussels collected fell within the range of 50 - 60 mm.

Differences in shell length, height and width were also determined for sites within each jurisdiction (Table 9). New Hampshire was the only jurisdiction in which the shell morphology (length, height and width) of the mussels was consistent among sites, i.e. no significant differences were observed for any measurement.

Condition index

Condition index (CI) of indigenous mussels collected in 1994 are shown in Table 9 and Figure 10. The average CI (\pm SD) for all sites throughout the Gulf of Maine was 0.191 ± 0.046 . ANOVA on the mean CI of all indigenous mussels was significant ($p < 0.05$). The highest CI of mussels was at MECK, with a value of 0.292 ± 0.037 and the lowest CI was at NSAR, with a value of 0.121 ± 0.017 . In a previous report (GMCME, 1996) a north-south gradient was observed in condition index, which may reflect differing seasonal stages of gonad maturity and growth around the Gulf of Maine. In 1994 there was no gradient present but there was much variation in CI. Most of the variation was across jurisdictions, while within jurisdictions the CIs were similar, although significant differences in CI among sites within a jurisdiction were observed (Table 9). Greater variability among jurisdictions likely reflects the different sampling schedules adopted by each jurisdiction, and whether or not sampling was conducted before or after spawning. This should be taken into consideration for future sampling efforts if CI is to continue to be used as a measurement of biological response to contaminant levels throughout the Gulf of Maine.

TABLE 9. Morphometric characteristics (mean \pm SD) of mussels collected at Gulf of Maine, 1994 Stations and ANOVA of measurements by jurisdiction. Same letter indicates no significant difference among sites within each jurisdiction. Overall mean for all stations given below. Wet wt. (adj) = wet weight (g) adjusted for significant covariates (ANCOVA, $p < 0.001$).

STATION	N	LENGTH (mm)	HEIGHT (mm)	WIDTH (mm)	WET WEIGHT (g)	WET WT. (ADJ) (g)	CONDITION INDEX (CI)
MASN	30	54.8 (3.7)B	28.2 (1.5)B	25.7 (6.5)B	7.72 (1.40)	6.87 (1.17)BC	0.195 (0.030)BC
MADX	30	54.3 (3.6)B	27.5 (1.4)B	23.0 (2.0)A	7.10 (2.09)	7.00 (2.04)AC	0.205 (0.056)BC
MABI	30	50.8 (3.5)A	26.2 (2.5)A	21.5 (2.2)A	5.28 (1.71)	6.26 (2.22)AB	0.178 (0.033)AB
MAWN	30	53.4 (2.5)B	27.6 (1.8)B	22.4 (1.4)A	5.58 (1.24)	5.64 (1.25)A	0.167 (0.037)A
MAIP	30	55.1 (2.8)B	28.4 (1.9)B	22.3 (2.5)A	7.92 (2.25)	7.60 (2.13)C	0.222 (0.031)C
NHRH	40	56.2 (4.0)A	29.5 (2.6)A	22.8 (2.0)A	6.48 (1.49)	6.40 (1.38)B	0.165 (0.019)B
NHDP	40	58.3 (3.9)A	29.5 (1.7)A	22.9 (1.9)A	4.73 (1.49)	4.78 (1.04)A	0.124 (0.019)A
MECC	40	56.8 (4.0)A	30.4 (2.1)A	23.5 (2.2)A	6.94 (1.91)	6.29 (1.29)B	0.157 (0.015)B
MESA	40	55.0 (3.5)B	27.3 (1.5)A	21.6 (1.5)B	5.91 (1.19)	6.06 (0.93)A	0.181 (0.017)A
MEPH	40	55.2 (2.6)B	29.2 (1.7)B	23.6 (2.3)C	7.24 (2.34)	6.20 (2.34)A	0.187 (0.045)A
MEPR	40	55.4 (3.5)B	29.2 (1.8)B	22.0 (2.2)B	9.36 (2.17)	8.78 (2.17)BC	0.267 (0.058)C
MEKN	40	55.2 (3.4)B	27.3 (1.6)A	22.1 (1.3)B	7.81 (1.85)	7.84 (1.85)B	0.239 (0.071)B
MEUR	40	56.4 (2.7)B	30.5 (2.1)B	21.9 (1.2)B	9.97 (2.03)	8.89 (2.81)BC	0.267 (0.056)C
MEMR	40	48.1 (4.8)A	28.1	18.5 (2.3)A	7.00 (2.40)	9.27 (2.40)BC	0.260 (0.022)C
MECK	40	54.5 (2.6)B	27.7 (2.8)A	21.9 (2.1)B	9.56 (1.93)	9.71 (1.93)C	0.292 (0.037)C
NBNR	30	56.8 (5.4)A	27.8 (2.6)A	24.7 (3.5)B	6.50 (1.78)	6.80 (1.90)A	0.165 (0.021)A
NBHI	30	63.1 (4.1)B	30.7 (4.3)B	24.6 (1.9)B	7.53 (2.05)	6.38 (1.60)A	0.157 (0.032)A
NBLB	30	56.2 (4.7)A	27.5 (4.0)A	22.5 (3.0)A	6.40 (1.71)	7.22 (2.06)A	0.184 (0.028)B
NSAR	90	54.0 (2.7)A	26.9 (3.9)A	21.0 (1.6)B	3.68 (0.68)	4.22 (0.88)A	0.121 (0.017)A
NSFI	160	54.6 (2.5)A	28.3 (1.6)B	22.5 (1.5)C	5.84 (1.51)	5.77 (1.48)BC	0.167 (0.034)BC
NSDI	160	54.1 (2.9)A	29.5 (1.9)C	22.8 (1.6)C	6.51 (1.59)	6.14 (1.45)C	0.177 (0.033)C
NSSC	160	56.2 (2.7)B	28.6 (1.7)B	22.9 (1.6)C	5.85 (1.56)	5.47 (1.40)B	0.158 (0.035)B
NSBP	160	54.7 (2.6)A	29.7 (1.8)C	20.4 (1.5)A	5.30 (1.43)	5.68 (1.59)B	0.159 (0.034)B
MEAN		55.2 (2.7)	28.5 (1.5)	22.5 (1.5)	6.83 (1.49)		0.191 (0.046)

Analysis of covariance (ANCOVA) on wet weight, using length, height and width as covariates, was performed among sites within each jurisdiction to determine the cause of differences in CI. ANCOVA revealed that for most sites length, height and width were significant covariates, i.e. the wet weight of mussels at a given site depended on the length, width and height of the mussels collected at each site. The only exception was New Hampshire where only length and width were significant covariates. As a result, the wet weight among sites within each jurisdiction was adjusted for the covariates and then analyzed by ANOVA and Tukey Kramer test. Figure 11 and Table 9 show the adjusted mean weights for stations sampled in 1994. There was a significant relationship between the adjusted wet weight and the CI of mussels at a given site ($r^2=0.90$, $p<0.05$).

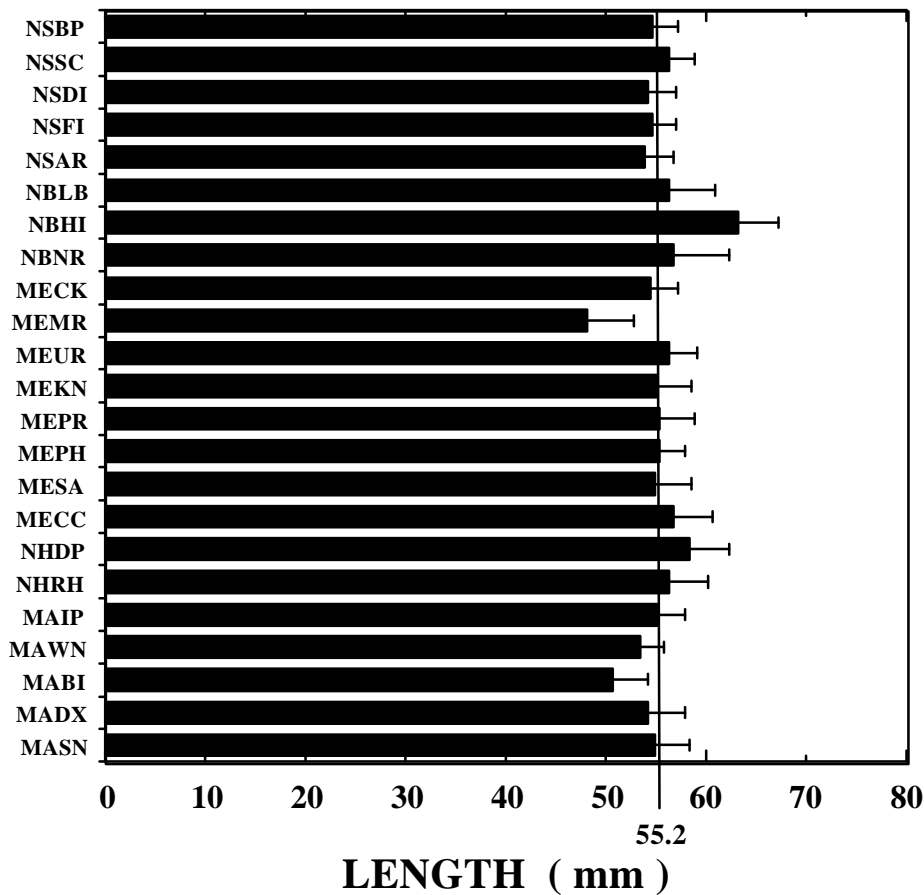


Figure 9. Mean length (\pm SD, mm) of mussels collected at Gulf of Maine, 1994 organized clockwise from south to north. Mean length of mussels from all sites indicated by the straight line

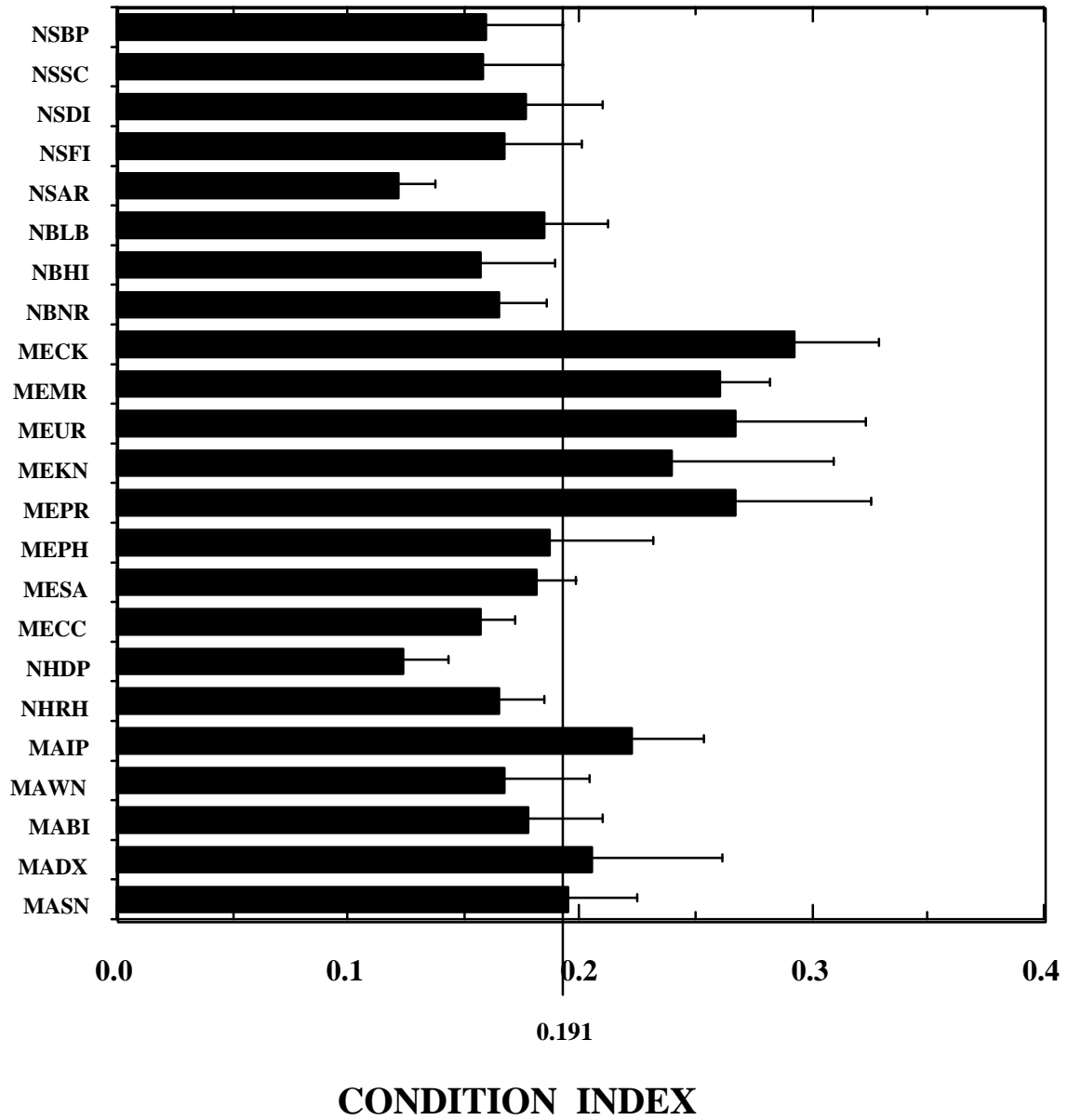


Figure 10. Mean condition index (CI) (\pm SD) of mussels collected at Gulf of Maine, 1994 stations organized clockwise from south to north. Mean condition index of mussels from all sites indicated by the straight line

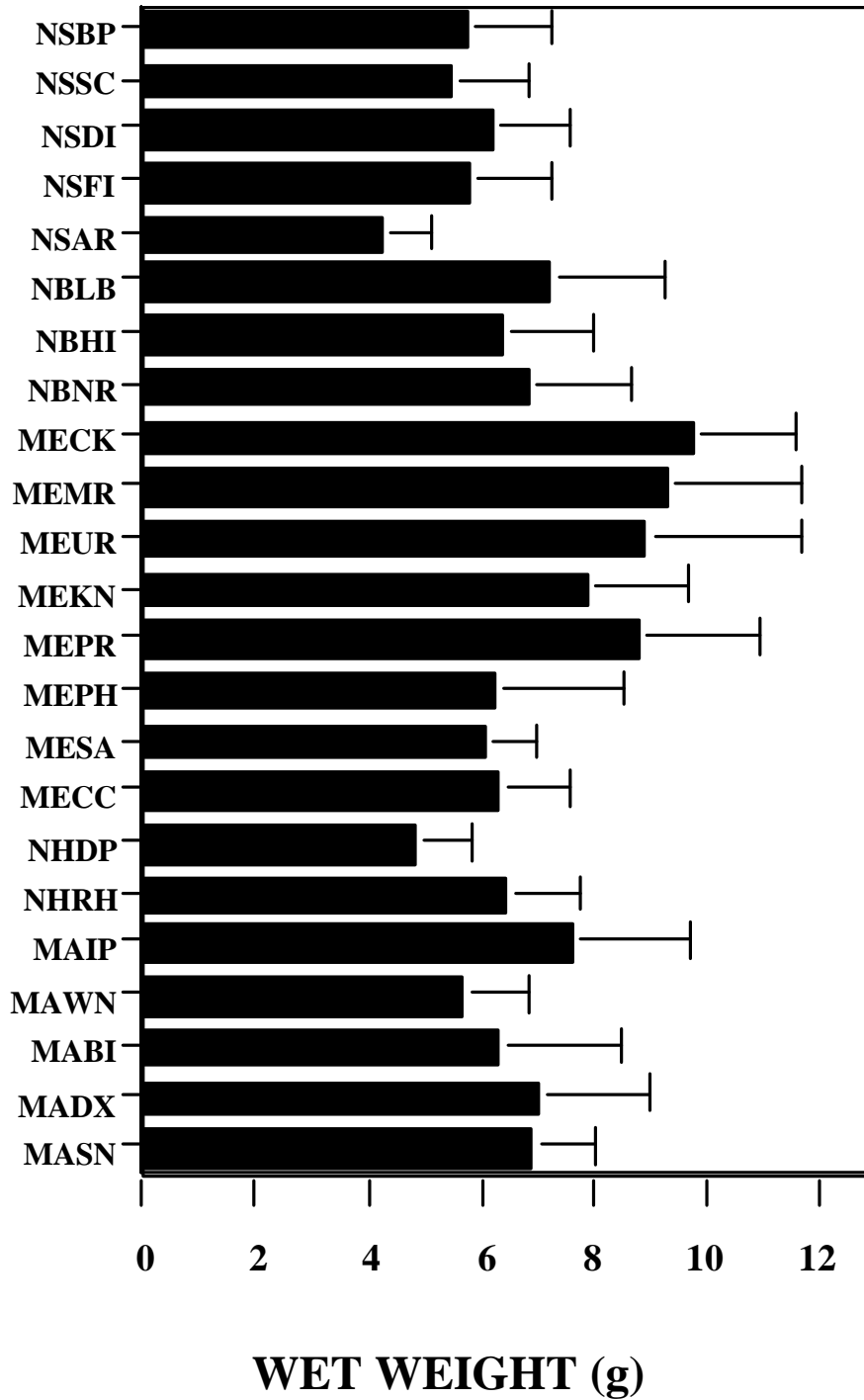


Figure 11. Mean adjusted weight (g) (\pm SD) of mussels collected at the Gulf of Maine, 1994 stations organized clockwise from south to north.

CONCLUSIONS

The field season of 1994 represented the second year of the first of three, three-year rotations of the overall ten year plan in the Gulfwatch program. Such a sampling design will ensure that there will be sufficient spatial and temporal replication of sites to allow for analysis at the end of the study, in the year 2001. The results build on observations made in the pilot stages of the program in providing information on present and recent contamination conditions at sites.

Monitoring of indigenous mussels revealed that the sites with the highest level of metal and / or organic contaminants (MABI, NHDP, MEPH, MEPR) were generally sites with high human population densities and known sources of contaminant input. MABI is located on Brewster Island, MA at the mouth of Boston Harbor. This site is impacted by contaminants from the northern portion of Boston Harbor, over 20 combined sewer overflows, outfall from the Deer Island POTW (370 MGD), non-point source runoff, and contaminant loadings from Charles River, Mystic River and Chelsea Rivers (W. Robinson and J. Pederson, pers. comm.). NHDP is located where the Piscataqua River and Little Bay meet within the Great Bay Estuary of New Hampshire. As such, it is located just a few miles downstream of numerous historical tanneries, petroleum processing facilities, and other industries, mostly located on the Cocheco River in Dover. This site is probably also impacted by the eight POTW discharges in the estuary, two military installations with numerous Superfund sites, and occasional oil spills. The two Maine sites, MEPR and MEPH are located in or close to Portland Harbor, where a long history of discharges of toxic contaminant discharges have also occurred. Industrial and POTW discharges, and occasional oil spills in the harbor and urban runoff pose potential sources of present day contaminants.

The biological response (CI) of mussels within a jurisdiction appeared to be related to the total level of metal and organic contaminants present, although differences in reproductive state cannot be discounted even for sites in close proximity. This pattern was not evident from an examination of all sites throughout the Gulf of Maine because of the different sampling schedules, which have probably resulted in the collection of mussels at different stages of maturity and reproductive state. However, within a jurisdiction the sites with the lowest levels of total metals and total organic contaminants (MAIP in Massachusetts; NHRH in New Hampshire; MECK in Maine; NBLB in New Brunswick; and NSDI in Nova Scotia) typically had the highest CI. Interestingly, at MESA, a site with a low level of metal and organic contaminants, mussels had a low CI for that jurisdiction. Condition indices in *Mytilus* sp. vary according to body size, level of parasitic infection, gonadal maturation, and with local environmental conditions, especially the availability of food and the degree of aerial exposure (see Widdows and Donkin, 1992). The role

of these additional environmental factors will be taken into account for the report on the five year review of the Gulfwatch program. The results of that report should enable us to gain an insight into the factors important in predicting chemical accumulation in *M. edulis*.

Coastal monitoring programs such as Gulfwatch provide a valuable measure of the current state of the coastal environment, for identifying future problems that may be prevented by early action, for determining trends in contamination over space and time, and for identifying potential sources of contamination. Gulfwatch results provide a geographically comprehensive, region specific perspective on relative contaminant concentrations in both contaminated and pristine areas. As such, it is unique and an invaluable basis for making management decisions on issues relating to toxic contaminants. Continuation of the Gulfwatch program according to the ten year plan will provide the temporal perspective necessary to determine trends and impacts of remediation efforts.

ACKNOWLEDGEMENTS

The authors are grateful to the following individuals: Zhihong Gao for his dedicated analytical effort; Don Walter, Andy Bagnell, Richard Langan, Deb Lamson, Noel Carlson, Charles Elvin, Tina Nims, John Nims, and Irma Simon for their assistance in field collection and sample preparation and laboratory analyses. Robert Bailey and Michael Topping from the University of Western Ontario for statistical advice. This study was made possible through the diligent field work of teams in Massachusetts, New Hampshire, Maine, New Brunswick, and Nova Scotia. The study team gratefully acknowledges financial support from Environment Canada, Atlantic Region and the office of Ocean and Coastal Resources Management (OCRM) of the U.S. National Oceanic and Atmospheric Administration. The metal analyses were partially supported by the U.S. Environmental Protection Agency.

REFERENCES

- Bayne, B.L., 1976. Marine Mussels. Their Ecology and Physiology. International Biological Programme 10, Cambridge University Press, Cambridge UK. 506 pp.
- Bjorseth, A., J. Knutzen, and Skei, 1979. Determination of polycyclic aromatic hydrocarbons in sediments and mussels from Saudafjord, W. Norway, by gas capillary chromatography. *Sci. Total Environ.* 13: 71-86.
- Buchholtz ten Brink, M.R., F.T. Manheim and M.H. Bothner, 1996. Contaminants in the Gulf of

- Maine: What's here and should we worry? In: The Health of the Gulf of Maine Ecosystem: Cumulative Impacts of Multiple Stressors. D. Dow and E. Braasch, eds. Regional Association for Research on the Gulf of Maine (RARGOM) Report 96-1. April 30, 1996. pp 91-115.
- CSSP (Canadian Shellfish Sanitation Program), 1992. Action levels and tolerances and other values for poisonous or deleterious substances in seafood. Appendix III. Manual of Operations. Fisheries and Oceans and Environment Canada.
- Dow, D. and E. Braasch, 1996. The Health of the Gulf of Maine Ecosystem: Cumulative Impacts of Multiple Stressors. Regional Association for Research on the Gulf of Maine (RARGOM) Report 96-1. April 30, 1996. 181 pp. plus appendices.
- Environment Canada, 1986. Polynuclear aromatic hydrocarbons and heterocyclic aromatic compounds in Sydney Harbour, Nova Scotia. A 1986 survey. Surveill. Rep. EPS-5-AR-88-7, Atlantic Region: 41p.
- EPA (Environment Protection Agency), 1993. Guidance for assessing Chemical Contaminant Data for Use in Fish Advisories. Vol. 1. Fish Sampling and Analysis. EPA 823-R-93-002.
- Freeman, K.R., K.L. Perry, and T.G. BiBacco, 1992. Morphology, condition and reproduction in two co-occurring species of *Mytilus* at a Nova Scotia mussel farm. Bull. Aquacult. Assoc. Can., 93-3: 1-3.
- GMCME (Gulf of Maine Council on the Marine Environment), 1992. Gulfwatch Project, standard procedures for field sampling, measurement and sample preparation. Gulfwatch pilot project period 1991-1992. 11pp.
- GMCME (Gulf of Maine Council on the Marine Environment), 1994. Evaluation of Gulfwatch 1992: second year of the Gulf of Maine Environmental Monitoring Plan. The Gulf of Maine Council on the Marine Environment, State Planning Office, Augusta Maine. 135pp.
- GMCME (Gulf of Maine Council on the Marine Environment), 1996. Evaluation of Gulfwatch 1993: third year of the Gulf of Maine Environmental Monitoring Plan. The Gulf of Maine Council on the Marine Environment, State Planning Office, Augusta Maine. 128pp.
- Howells, G, D. Calamari, J. Gray and P.G. Wells, 1990. An analytical approach to assessment of long-term effects of low levels of contaminants in the marine environment. Mar. Pollut. Bull., 21: 371-375.
- Jones. S.H., F.T. Short and M. Webster, 1992. Pollution, pp. 50-84. In: An estuarine profile and bibliography of Great Bay, New Hampshire. Short, F.T. (ed.) Great Bay National Estuarine Reserve/ NOAA. Durham, NH.
- Kveseth, K., B. Sortland and T. Bokn, 1982. Polycyclic aromatic hydrocarbons in sewage, mussels, and tap water. Chemosphere 11: 623-639.
- Lobel, P.B., S.P. Belkhole, S.E. Jackson and H.P. Longerich, 1990. Recent taxonomic

- discoveries concerning the mussel *Mytilus*: Implications for biomonitoring. *Arch. Environ. Contam. Toxicol.*, 19: 508-512.
- Lobel, P.B., S.P. Belkhole, S.E. Jackson and H.P. Longerich, 1991. Sediment in the intestinal tract: A potentially serious source of error in aquatic biological monitoring programs. *Mar. Environ. Res.*, 31: 163-174.
- Mucklow, L.C., 1996. Effects of season and species on physiological condition and contaminant burdens in mussels (*Mytilus edulis* L. and *Mytilus trossulus* G.): Implications for the Gulfwatch program.. The Gulf of Maine Council on the Marine Environment, State Planning Office, Augusta Maine.
- NAS (National Academy of Sciences), 1980. The International Mussel Watch. National Academy of Sciences, Washington D.C. 248 pp.
- NOAA (National Oceanic and Atmospheric Administration), 1989. A summary of data on tissue contamination from the first three years (1986-1988) of the mussel watch project. National Status and Trends Program for Marine Environmental Quality Progress Report. NOAA Technical Memorandum NOS OMA 49.
- NOAA (National Oceanic and Atmospheric Administration), 1991. Mussel Watch Worldwide Literature Survey - 1991. NOAA Technical Memorandum NOS ORCA 63. Rockville MD. 143 pp.
- O'Connor, T.P., 1992. Recent Trends in Coastal Environmental Quality: Results from the first five years of the NOAA Mussel Watch Project. NOAA/NOS. 46 pp.
- O'Connor, T.P. and B. Beliaeff, 1995. Recent Trends in Coastal Environmental Quality: Results from the Mussel Watch Project. NOAA/NOS. 40 pp.
- Phillips, D.J.H., 1976. The common mussel *Mytilus edulis* as an indicator of pollution by zinc, cadmium, lead, and copper. I. Effects of environmental variables on uptake of metals. *Mar. Biol.*, 38: 59-69.
- Rainio, K., R.R. Linko, and L. Ruotsila, 1986. Polycyclic aromatic hydrocarbons in mussels and fish from the Finnish Archipelago Sea. *Bull. Environ. Contam. Toxicol.*, 37: 337-343.
- Robinson, W.E., D.K. Ryan and G.T. Wallace, 1993. Gut contents: A significant contaminant of *Mytilus edulis* whole body metal concentrations. *Arch. Environ. Contam. Toxicol.*, 25: 415-421.
- Salazar, M.H. and S. M. Salazar, 1995. In situ bioassays using transplanted mussels: I. Estimating chemical exposure and bioeffects with bioaccumulation and growth. In: *Environmental Toxicology and Risk Assessment. Vol. 3. American Society for Testing and Materials (ASTM STP 1218) Philadelphia.* pp 216-241.
- Sanudo-Wilhelmy, S.A. and A.R. Flegal, 1992. Anthropogenic silver in the Southern California Bight: A new tracer of sewage in coastal waters. *Environ. Sci. Technol.*, 26: 2147-2151.

- Seed, R., 1968. Factors influencing shell shape in the mussel *Mytilus edulis*. J. Mar. Biol. Ass. U.K., 48: 561-584.
- Sheehan, P.J., 1984. Effects on individuals and populations. Chapter 4. In: Effects of pollutants at the ecosystem level. John Wiley and sons, Chichester, U.K. pp. 23-50.
- Sheehan, P.J., D.R. Miller, G.C. Butler and P. Bourdeau, 1984. Effects of pollutants at the ecosystem level. John Wiley and sons, N.Y.
- Snedecor, G.W. and W.G. Cochran, 1967. Statistical Methods. 6th ed. Iowa State University Press, Ames IO. 593 pp.
- Sowles, J., 1993. Maine mussel watch heavy metal baseline survey in blue mussels 1988 - 1992. Maine Department of Environmental Protection Tech. Report, Augusta, Maine. 12pp.
- Sowles, J. and R. Crawford, 1994. Gulfwatch project standard procedures for field sampling, measurement and sample preparation - Gulfwatch implementation period 1993 - 2001. Gulf of Maine Council on the Marine Environment, Augusta Maine. 16 pp.
- USFDA (United States Food and Drug Administration), 1990. U.S. Food and Drug Administration Shellfish Sanitation Branch, Washington, D.C.
- USFDA (United States Food and Drug Administration), 1993. National Shellfish Sanitation Manual of Operations. Part I, Appendix D, U.S. Department of Health and Human Services.
- Widdows, J., 1985. Physiological measurements. In: Bayne, B.L., D.A. Brown, K. Burns, D.R. Dixon, A. Ivanovici, D.R. Livingstone, D.M. Lowe, M.N. Moore, A.R.D. Stebbing and J. Widdows (ed.). The effects of stress and pollution on marine animals. New York: Praeger Publishers. pp 3-39.
- Widdows, J. and P. Donkin, 1992. Mussels and environmental contaminants: Bioaccumulation and physiological aspects. In: Gosling, E. (ed.). The mussel *Mytilus*: Ecology, physiology, genetics and culture. New York: Elsevier Science Publishers. pp. 383-424.
- Widdows, J., P. Donkin, M.D. Brinsley, S.V. Evans, P.N. Salkeld, A. Franklin, R.J. Law and M.J. Waldock, 1995. Scope for growth and contaminant levels in North Sea mussels *Mytilus edulis*. Mar. Ecol. Prog. Ser., 127: 131-148.

APPENDIX A. METHODS FOR MUSSEL EXTRACTION AND ANALYSIS OF ORGANIC CONTAMINANTS

Compounds for organic analysis were selected to be consistent with NOAA status and trends mussel monitoring. All samples were analyzed at the environment Canada Atlantic Regional Laboratory in Dartmouth, N.S.

Analytical Methods

Modifications to the methods for organic contaminants have been made since the 1991 Gulf of Maine Mussel Watch Effort (GMCME 1992a and b). The major changes include: (1) lowering target analyte detection limits to 10 ng/g for most aromatic hydrocarbons (20-30 ng/g for some of the lower molecular weight aromatic); (2) the addition of 17 chlorinated pesticides to the variable list including alpha and beta endosulfan; (3) identification and quantification of PCB by congener analysis which include 18 NOAA designated congeners and 6 other congeners including some coplanar PCBs. The specific compounds and their detection limits are listed in Tables A1 and A2.

Some modifications were made in the analysis of the 1993 samples in order to improve the analytical quality control. These include the addition of two PCB recovery surrogates (CB-103 and CB-198) and an organochlorine pesticide recovery surrogate (γ -chlordene) to sample homogenates prior to extraction. The PCB and pesticide surrogates replace 3,4,5-trichlorobiphenyl-d5 which was used previously to assess method performance of both PCBs and pesticides.

Methods Description

Sample preparation and extraction

Composite samples of shucked mussels meats from various coastal locations were provided to the laboratory in solvent cleaned glass sample jars and stored at -20 °C until samples were processed.

Prior to analyzing mussel tissue samples, the laboratory verified that all glassware, chemical reagents, and solvents used in the analysis of tissue samples were free of contamination which could interfere with the identification and quantification of target analytes.

A frozen composite sample (5-200 g) was thawed and homogenized in a Waring blender at high speed for 3 minutes (for details on sample homogenization refer to Shrimpton, 1988). Ten grams of homogenate were transferred to a 300 ml Berzelius beaker and 50 ml of methyl chloride

added. Two grams of homogenate were put aside for dry weight determination.

One hundred microliters of surrogate solution containing five deuterated aromatic hydrocarbon recovery standards (Table A1) and 100 μ l of surrogate solution containing one pesticide and two PCB congener recovery standards (Table A2) were added to the homogenate. Anhydrous sodium sulphate (7 g/g of homogenate) was added and the contents blended for 2 minutes at high speed with a Polytron tissumizer. The solvent was decanted, saved and the solid material extracted twice more with 50 ml methylene chloride. The combined solvent extract along with the solid material from the last extraction step were vacuum filtered with rinsings through a Whatman GF/C glass microfiber filter. The filtered solvent was concentrated to 10 ml and a 1 ml aliquot removed for lipid determination. The remaining extract was concentrated to about 3 ml, transferred to a 10 ml glass syringe, and forced through a 0.5 μ m Millex SR filter unit into a 15 ml ABC AS2000 System GPC-autovap loading tube. The final volume of extract was made exactly to 8.0 ml with methylene chloride.

TABLE A1. Aromatic hydrocarbons.

Compound	Quantitation ion	Confirmatory ion	Spike * concentration (ng/g)
Naphthalene	128	127[15]	40
2-Methylnaphthalene	142	141[90]	“
1-methylnaphthalene	142	141[90]	“
Biphenyl	154	152[35]	“
2,6-Dimethylnaphthalene	156	155[30]	“
Acenaphthylene	152	151[20]	“
Acenaphthene	153	154[90]	“
2,3,5-trimethylnaphthalene	170	169[90]	“
Fluorene	166	165[90]	“
Phenanthrene	178	176[20]	“
Anthracene	178	176[20]	“
1-Methylphenanthrene	192	191[50]	“
Fluoranthene	202	200[20]	“
Pyrene	202	200[20]	“
Benzo(a)anthracene	228	226[20]	“
Chrysene	228	226[20]	“
Benzo(b)fluoranthene	252	250[20]	“
Benzo(k)fluoranthene	252	250[20]	“
Benzo(e)pyrene	252	250[20]	“
Benzo(a)pyrene	252	250[20]	“
Perylene	252	250[25]	“
Indeno(123cd)pyrene	276	277[25]	“
Dibenzo(ah)anthracene	278	279[25]	“
Benzo(ghi)perylene	276	277[25]	“

* Spike Matrix samples

[] % % of base peak

TABLE A1. Cont...

SURROGATES :			Amount *
			(ng)
Naphthalene-d8	136	137	120
Acenaphthene-d10	164	162	120
Chrysene-d12	240	241	60
Benzo(a)pyrene-d12	264	265	60
Benzo(ghi)perylene-d12	288	289	60

* Added to sample homogenate

Compound	Quantitation	Confirmatory	
Concentration*	ion	ion	(pg/μl)

INTERNAL STANDARDS

Fluorene-d10	176	174	350
Pyrene-d12	212	210	350
Perylene-d12	264	260	350

* In calibration curve

TABLE A2. Polychlorinated biphenyls.

IUPAC	Congener	Spike concentration * (ng/g)
8/5	2,4'-dichloro	20
18/15	2,2',5-trichloro	"
28/31	2,4,4'-trichloro	"
29	2,4,5-trichloro	"
44	2,2',3,5-tetrachloro	"
50	2,2',4,6-tetrachloro	"
52	2,2',5,5'-tetrachloro	"
66/95	2,3',4,4',-tetrachloro	"
77/110	3,3',4,4',-tetrachloro	"
87	2,2',3,4,5-pentachloro	"
101/90	2',2,4,5,5',-pentachloro	"
104	2,2',4,6,6',-pentachloro	"
105	2,3,3',4,4',-pentachloro	"
118	2,3',4,4',5-pentachloro	"
126/178	3,3',4,4',5-pentachloro	"
128	2,2',3,3',4,4'-hexachloro	"
138/163/164	2,2',3,4,4',5'-hexachloro	"
153/132	2,2',4,4',5,5',-hexachloro	"
169	2,2',4,4',5,6',-hexachloro	"
170/190	2,2',3,3',4,4',5-heptachloro	"
180	2,2',3,4,4',5,5'-.heptachloro	"
187	2,2',3,4',5,5',6-heptachloro	"
188	2,2',3,4',5,6,6',-heptachloro	"
195/208	2,2',3,3',4,4',5,6-octachloro	"
200	2,2',3,3',4,5',6,6'-octachloro	"
206	2,2',3,3',4,4',5,5',6-octachloro	"
209	decachloro	"

* Spike matrix samples
/coeluting congeners

TABLE A2 Cont....

SURROGATE :	Amount * (ng)
CB-103	25
CB-198	25

* In all samples

INTERNAL STANDARDS :	Concentration * (pg/μl)
4,4'-dibromooctafluorobiphenyl	10
octachloronaphthalene (ref time only)	10

* In calibration curve

Extract Clean-up and Fractionation

Gel permeation chromatography

Lipids, elemental sulphur, and other larger molecular-size compounds derived from the biomatrix were removed by gel permeation using an Autovap AS2000 GPC Sample Processing System (Analytical Bio-Chemistry Laboratories). The system included a low-pressure GPC column packed with methylene chloride preswollen SX-3 envirobeads and was run in dual GPC/auto-evaporation mode with an end-of-run hexane solvent exchange. A sample matrix effect helped reduce analyte losses during the evaporation stage; and a keeper, therefore, was not used.

Silica column chromatography

PCB congeners and apolar pesticides were fractionated from more polar pesticides on 1 cm X 10 cm silica gel columns. Columns were prepared by sandwiching a pentane slurry of 7% deactivated silica gel (Davidson 923, mesh 100/200) between two 1 cm layers of anhydrous sodium sulphate.

A column was pre-rinsed with 30 ml of pentane, and 1 ml of concentrated sample extract in pentane was placed on top of the column bed. Twenty millilitres of pentane was passed through the column which eluted most PCB congeners and apolar pesticides. This was followed by 20 ml of pentane/methylene chloride (1:1) which eluted the more polar pesticides.

Each fraction was collected separately and concentrated to 0.5 ml. Ten microliters of PCB/pesticide internal standard solution (Tables A2 and A3) were added to each fraction prior to analysis by high-resolution gas chromatography-ECD.

After completion of the PCB/pesticide GC-ECD analysis, the two fractions were combined and concentrated to 0.5 ml in toluene. Ten microliters of internal standard solution containing five deuterated aromatic compounds (Table A1) were added to the extract and reanalyzed by GC-MS for aromatic hydrocarbons.

TABLE A3. Pesticides.

Compound	Concentration * (ng/g)
Hexachlorobenzene	20
Heptachlor	“
Aldrin	“
4,4’-DDE	“
Mirex	“
Lindane	“
Heptachlor Epoxide	“
cis-Chlordane	“
trans-Nonachlor	“
Dieldrin	“
2,4’-DDE	“
2,4’-DDD	“
4,4’-DDD	“
2,4’-DDT	“
4,4’-DDT	“
alpha-Endosulfan	“
beta-endosulfan	“

* Spike matrix samples ABCDEFGHIJKLMNOP

SURROGATES :	Amount * (ng)
y-chlordene	40

* Added to sample homogenate

INTERNAL STANDARDS :	Concentration * (pg/μl)
4,4’-dibromooctafluorobiphenyl	10
Octachloronaphthalene (ref time only)	10

* In calibration curve

Instrumental Analysis

Polychlorinated biphenyls and pesticides

PCB congeners and pesticides in mussel tissue extracts were analyzed by high resolution gas chromatography-electron capture detection. A four-point calibration curve was constructed covering the concentration range 2 to 500 pg/ μ l for these analyses.

Apolar PCB congeners and pesticides contained in fraction one and the more polar compounds contained in fraction two were analyzed on two different fused silica capillary columns. Column 1 contained a 5% phenylmethyl polysiloxane stationary phase while column 2 contained a 50% phenylmethyl polysiloxane stationary phase. PCB congeners analyzed on column 1 were identified and quantified individually or as co-eluting pair (Table A2). Pesticides detected on column 1 were confirmed on Column 2. PCB congeners and pesticides which co-eluted on Column 1 were resolved on Column 2 for identification and quantification.

Gas chromatography-electron capture detector operating conditions

Gas chromatograph :	HP 5890 Series 11
Column 1 :	DB-5, 30 m x 0.20 mm fused silica, 0.33 μ film
Injection :	Splitless
Temperature program:	90 °C for 0 minutes, to 175 °C at 10 °C/minute, to 280 °C at 2.5 °C/minute, and hold for 5 minutes
Carrier gas :	Helium

Secondary analysis

Gas chromatograph :	HP 5880
Column 2 :	HP-17, 25 m x 0.32 fused silica, 0.26 μ film
Injection :	Splitless
Temperature program :	As above
Carrier gas :	Helium

Polyaromatic Hydrocarbons

Analysis of aromatic hydrocarbons was conducted by high-resolution capillary gas chromatography and low-resolution quadruple mass spectrometry in selective ion mode. A five-point calibration curve was constructed for analysis covering the concentration range 10 to 100 pg/ μ l.

Gas chromatograph and mass spectrometer operating conditions

Gas chromatograph :	HP 5890 Series 11
Column :	DB-5, 30 m x 0.25 mm fused silica, 0.25 μ film or equivalent
Injection :	Cool on column
Temperature program :	70 °C for 1 minute, to 250 °C at 10 °C/minute, to 290 °C at 20 °C/minute, and hold 12 minutes
Carrier gas :	Helium,
Mass spectrometer :	HP 5971A MSD
Ionization mode :	Electron impact 70 ev
Ion dwell time :	150-250 msec (optimized for maximum sensitivity)
Scan speed :	1 cps

REFERENCES

- GMCME (Gulf of Maine Council on the Marine Environment), 1992a. Evaluation of Gulfwatch 1991 pilot project of the Gulf of Maine Environmental Monitoring Plan. October. 39 p + Appendices A-D.
- GMCME (Gulf of Maine Council on the Marine Environment), 1992b. Gulfwatch Project, standard procedures for field sampling, measurement and sample preparation. Gulfwatch Piolet project period 1991-1992. 11p.
- Shrimpton J., 1988. Contaminants Control-Toxic Chemicals Program Technical Resources Manual, 1988. Environ. Can., Conservation and Protection, Pacific and Yukon Region., p. 14-17.

APPENDIX B. QUALITY ASSURANCE / QUALITY CONTROL PROTOCOL

1.0 INTRODUCTION

The quality assurance provisions of this performance-based standard are intended as a guide for the generation of acceptable analytical data for use in Canadian shellfish contaminants monitoring. The standard permits flexibility in the selection of an analytical method for the generation of chemical data, provided the laboratory institutes the quality control measures identified and the method can attain the minimum performance stated.

2.0 SPECIFIED VARIABLES

Essential target analytes required for reporting are listed in the following tables:
Polyaromatic Hydrocarbons (Table A1 and Appendix D)
PCB Congeners and Chlorinated Pesticides (Tables A2 and A3 and Appendices E and F)
Metals (Appendix C)

3.0 EXTERNAL CHECK SAMPLE PROGRAM PARTICIPATION

A laboratory providing analytical data for use in shellfish contaminants monitoring is required to demonstrate proficiency in contaminant analysis through yearly participation in a reference interlaboratory check sample program if available. Exercise results are provided to the regional project coordinator for review. Deficiencies in check sample performance must be discussed with the project coordinator and corrective action taken where necessary.

The check sample program must be relevant to the analysis of organic and inorganic contaminants at trace concentrations in marine shellfish matrices. The National Institute of Standards and Technology (NIST) (Gaithersburg, Md.) conducts a QA intercomparison exercise program for both government and private laboratories engaged in the measurement of organic and inorganic contaminants in marine sediment, fish and shellfish samples.

4.0 INTRALABORATORY QUALITY CONTROL: INSTRUMENT OPERATING REQUIREMENTS AND PERFORMANCE CRITERIA

4.1 Aromatic Hydrocarbon Analysis

Gas chromatography-mass spectrometry : Aromatic hydrocarbons in mussel tissue extracts are analyzed on a GC-mass spectrometer in selective ion mode. The gas chromatograph must be capable of ramp temperature programming up to 290 °C and accommodating a 25 m or

longer DB-5 capillary column or equivalent. It is recommended that on-column injection is used in order to avoid mass discrimination of higher molecular weight aromatic hydrocarbons which can occur with flash vaporization injection. It also is advisable that deactivated retention gaps are used and routinely replaced in order to maintain column performance.

4.1.1 Initial Set-up

MS Tuning : The mass spectrometer is tuned to standard specifications with perfluorotributylamine (PFTBA). Periodic retuning after initial set-up should be performed to ensure MS calibration consistency. Recalibration of the calibration curve is necessary after each retuning.

Following PFTBA tuning, it may be necessary to manually tune the mass spectrometer, maximizing sensitivity in the low- to mid-mass range (e.g., maximizing the absolute abundance of mass 264) in order to achieve analyte target detection.

Calibration curve : A five-point calibration curve is constructed for every target and surrogate analyte. The concentration range covered is 10 to 1000 pg/ μ l. The curve should not be forced through the origin. Linearity is verified when the relative standard deviation of response factors for each analyte is less than 30%.

Detection limits : Laboratories must verify that the method and instruments achieve target method detection limits of 30 ng/g (dry weight) or lower for low molecular weight aromatic hydrocarbons (two-ring compounds) and 10 ng/g or lower for higher molecular weight aromatic compounds.

Analyte Identification : Positive identification is assumed when relative to an internal standard, the analyte retention time is within ± 0.05 minutes of the corresponding standard retention time; the ratio of quantitation ion and confirmatory ion (Table A1) is within $\pm 20\%$ of the calculated theoretical value except when the abundance of the confirmation ion is too low to permit detection; and the peak maxima for quantification and qualifier ions coincide within 3 seconds. Identified analytes which fail to meet these criteria should be flagged.

Quantitation : An internal standard method is recommended for the quantification of sample data. A minimum of three internal standards should be spiked into sample extracts prior to GC-MS analysis. Suggested internal standards and spiking concentrations are given in Table A1.

Analyses are conducted within the range of the standard calibration curve. Sample extracts with concentrations of analytes greater than the highest calibration standard must be diluted to bring analyte concentrations within the calibration range.

4.1.2 Method Performance Test

Prior to processing any samples, a laboratory must demonstrate that its method and instrument operating conditions will provide acceptable recoveries of surrogate and target analytes. Three replicate uncontaminated tissue homogenate samples are spiked with surrogates and target analytes and analyzed by the full procedure. Recovery of target analytes and surrogates must meet the performance criteria stated in Section 4.1.2 under “Matrix Spike Sample” and “Surrogate Spikes”. Method precision (RSD) for each analyte should be greater than 25%.

4.1.3 Daily Performance Checks

Calibration Curve Check : At least one calibration standard is run prior to each batch analysis. The calculated amount for each analyte must be within $\pm 15\%$ on average and not exceed $\pm 25\%$ for any one analyte.

Chromatographic Column Performance : Chromatographic resolution is verified on a daily basis. Adequate resolution is demonstrated if for the highest peak there is no more than 1% valley between the phenanthrene/anthracene peaks and less than a 25% valley between the Benzo(a)anthracene / chrysene peaks. If these performance criteria are not met, column resolution must be restored before any further sample analyses can proceed.

4.1.4 Batch Analysis

A laboratory is required to analyze tissue samples for organic contaminants in batches of no more than 15 samples including quality control samples. The following quality control measures are required for each batch of sample analyses:

Method Blank (1) : The method blank must be free of contamination at or above the method detection limit. If contamination is greater than the MDL a correction may be made by subtracting the average amount in the blanks from the amount in samples when the blank contamination can be shown to be constant over a number of batch runs. If blank contamination is greater than two times the MDL, corrective action must be taken to eliminate the source of contamination.

Duplicate Samples (1 set) : The relative percent difference between the analytical results for duplicate samples should be no more than 25% for measured values greater than five times the MDL.

The percent difference is calculated by dividing the absolute difference of the duplicate values by

their average value.

Spiked Matrix Sample (1) : A matrix spike is prepared for all the analytes of interest (Table 1A). If possible, spike matrix concentrations should be in the same proximity as sample concentrations. Otherwise, the addition of 75 ng of each analyte to matrix homogenate is usually sufficient. Spike recoveries must fall into the range of 40-120% for 80% of analytes. If more than 20% of recoveries are outside the range, instrumental response, sample chromatographs and surrogate recoveries for each sample in the batch are checked to ensure that batch analysis is in control. Failing performance criteria will result in individual samples or the entire batch being reanalyzed.

Standard Reference Material : Ideally, one mussel tissue SRM should be included with each batch of sample analyses. Availability and cost of bivalve reference material, however, may preclude a SRM in every batch. As a minimum at least one SRMs is analyzed with every two or three batches. For projects with higher numbers of samples, a SRM is run at the beginning, mid-point, and end of the analytical project. Marine bivalve certified reference material (SRM 1974) can be obtained from NIST (United States Department of Commerce, Gaithersberg Md.).

On average, laboratory results (corrected for surrogate recoveries) should be within $\pm 30\%$ of the certified value's confidence range for all analytes and may not exceed $\pm 35\%$ for more than 30% of individual analytes.

Surrogate spikes : Deuterated surrogate analytes (Table A1), representative of each aromatic hydrocarbon group of the same ring number, are spiked into each sample homogenate and method blank prior to extraction. Surrogate recoveries must be in the acceptable range of 30-150%. Samples with surrogate recoveries outside the range are reanalyzed.

4.2 PCB CONGENER AND CHLORINATED PESTICIDES ANALYSIS

The following QC and performance standards are intended for the analysis of PCB congeners and chlorinated pesticides by high-resolution gas chromatography and electron capture detection. Requirements for the gas chromatograph are the same as described in section 4.2. If flash vaporization injection is used, care should be exercised in selecting the injection port temperature in order to minimize degradation of thermally labile compounds such as 4,4'-DDT.

Gas chromatographic analysis is performed on a 30 m or longer 5% phenylmethyl polysiloxane column (DB-5 or equivalent).

It is highly recommended that a laboratory include in its analytical method provision for the absorptive column fractionation of apolar PCB congeners and chlorinated pesticides from more polar pesticides. The laboratory must verify the PCB and pesticide column elution pattern for every new batch of absorptive material used. Correction of analytical results based on the distribution of some analytes in the two fractions may be required.

4.2.1 Initial Set-up

Calibration Curve : For every target analyte a five point calibration curve is constructed which covers the concentration range 2 to 500 pg/μl. Calibration curve lineally is verified when the relative standard deviation of response factors for each analyte is less than 30%.

Detection Limit : The laboratory must verify that methods and instrument operating conditions can achieve target method detection limits of 2 ng/g for individual PCB congeners and chlorinated pesticides.

Chromatographic Column Performance : Chromatograms of standard analytes are checked regularly to ensure that analyte peak shape, resolution, and sensitivity have not degraded with time.

Analyte Identification : PCBs in mussel tissue are analyzed as selected congeners (Table A2). Co-eluting congeners are identified in data reports.

Analysis with a second capillary column possessing a stationary phase different from DB-5 type columns such as 50% phenylmethyl polysiloxane (DB-17 or equivalent) is required in order to resolve and accurately identify and quantify PCB congeners and pesticides which co-elute on DB-5 type columns.

The positive identification of a PCB congener or pesticide is assumed when relative to an internal standard, the analyte retention time is within ± 0.05 minutes of the corresponding standard retention time.

Quantitation : An internal standard method is recommended for the quantitation of sample data. Suggested internal standards and concentrations for the GC-ECD analysis of PCB congeners are given in Tables A2 and A3.

4.2.2 Method Performance Test

The same as per section 4.1.2.

4.2.3 Batch Analysis

Laboratories are required to analyze tissue samples in batches of 15 individuals or less. The following quality control measures are required with each batch:

Method Blank (1) : See section 4.1.4.

Duplicate Samples (1 set) : Performance criteria as in Section 4.1.4.

Spiked Matrix Sample (1) : A matrix spike is analyzed for all PCB and pesticide target analytes

(Table 3A). Performance criteria are the same as in Section 4.1.4.

Standard Reference Material : See Section 4.1.4

Surrogate Spikes : PCB congener and pesticide surrogates (Table A2) are spiked into each sample homogenate prior to extraction. Performance criteria as in Section 4.1.4.

4.4 REPORTING

Analytical results are reported individually on a dry weight basis. All surrogate recoveries and results of duplicate analysis must be reported with the relevant sample data. Data corrected for surrogate recoveries (done in agreement with the project coordinator) must be identified as such.

The results of check sample exercises are reported and discussed with project coordinators.

The results of all performance tests, matrix spike samples, and surrogate spiked method blanks are tabulated and provided at the request of the project coordinator.

A laboratory should be prepared to provide a copy of the analytical method including handling, storage, and any modifications required to accommodate problems encountered (example matrix interferences). A laboratory also should maintain on file all relevant sample, standard, and blank chromatographic and related QC data as well as tables of all calibration standard and surrogate solution concentrations for possible future examination.