A Recommended Method for Monitoring Sediments to Detect Organic Enrichment from Mariculture in the Bay of Fundy

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ABSTRACT

Wildish, D. J., H. M. Akagi, N. Hamilton, and B. T. Hargrave. 1999. A recommended method for monitoring sediments to detect organic enrichment from mariculture in the Bay of Fundy. Can. Tech. Rep. Fish. Aquat. Sci. 2286: iii + 31 p.

Presented here are the details of two geochemical methods recommended for monitoring sediments to detect organic enrichment from particulate wastes from the Bay of Fundy salmon mariculture industry. Electrochemical methods were chosen because of their speed and simplicity that allowed analyses to be completed in the field. Redox potentials were measured with a combined reference and platinum electrode, while sulfides were determined with a silver/silver-sulfide electrode with a glass calomel as reference. Included are field sampling protocols for collecting undisturbed sediment by SCUBA divers and remotely by coring or grab device, subsampling and analytical details. For the latter, it is emphasized that determinations of redox status and sulfide concentrations in sediments be made as soon as possible after collecting core samples. It is recommended that redox probes be regularly cleaned and checked against Zobell's solution and results expressed relative to the normal hydrogen electrode. Sulfide concentrations are expressed as micromoles per litre (µM or $\mu M \bullet L^{-1}$), and a calibration procedure based on stock solutions of sodium sulfide is described. An empirical relationship for Bay of Fundy condions is used to translate the sediment geochemical results into four categories along a gradient of organic impact based on previously published microbial and macrofaunal effects. These categories, here referred to as oxic a, oxic b, hypoxic, and anoxic, can be used for mariculture management purposes and in general coastal zone management. A review concerning organic enrichment research in sediments and environmental monitoring relating to it is also presented.

RÉSUMÉ

Wildish, D. J., H. M. Akagi, N. Hamilton, and B. T. Hargrave. 1999. A recommended method for monitoring sediments to detect organic enrichment from mariculture in the Bay of Fundy. Can. Tech. Rep. Fish. Aquat. Sci. 2286: iii + 31 p.

Présenté ici sont les détails de deux techniques géochimiques du sédiment recommandées comme méthodes de surveillance environnementale pour l'industrie salmonicole de la Baie de Fundy en 1999. Les techniques électrochimiques ont été choisies car elles sont simples et rapides ce qui permet d'effectuer les analyses dans le terrain. Le potentiel rédox fût mesuré avec une électrode en platine et référence combinée. Les sulfures furent déterminés avec une électrode argent/argent - sulfure avec comme référence un calomel de verre. Inclus sont les protocoles d'échantillonnage sur le terrain pour la cueillette intact du sédiment par des plongeurs SCUBA et avec une carotteuse ou une benne aux endroits éloignés, le sous-échantillonnage et les détails analytiques. Pour ce dernier, l'emphase est mise sur la détermination du statut rédox et de la concentration de sulfure dans le sédiment aussitôt que possible après avoir recueilli les échantillons avec une carotteuse. Il est recommandé que l'électrode rédox soit nettoyée régulièrement, vérifiée contre la solution de Zobell et les résultats exprimés par rapport à l'électrode normale d'hydrogène. Les concentrations de sulfure sont exprimées en micromoles par litre (µM ou µM/L) et une procédure d'étalonnage basée sur une solution stock de sulfure de sodium est décrite. Une relation empirique pour les conditions de la Baie de Fundy est utilisée pour traduire les résultats géochimiques du sédiment en quatre catégories le long d'un gradient d'impact organique. Celles-ci sont basées sur des publications antécédentes d'effets microbiens et macrofaunals déterminées par autrui. Ces catégories sont désignées ici sous les noms de oxique a, oxique b, hypoxique, anoxique, et peuvent être utilisées à des fins de gestion de la mariculture et des zones côtières en générale. Une révision concernant la recherche de l'enrichissement organique dans le sédiment et la surveillance environnementale qui y est reliée est aussi présentée.

INTRODUCTION

Scientific methodology applicable to habitat questions of coastal zone management (CZM) recognized by Wildish and Strain (1994) are:

- environmental monitoring
- ecosystem simulation modelling to make predictions about alternative management options
- specific research to address particular management questions in the absence of sufficient prior knowledge

The first two in the list above require that there be prior intensive research results available which allow a general understanding of the environmental effect. Presented below is a brief review of organic matter enrichment studies to show that the knowledge required for environmental effects monitoring and basic research is sufficiently complete to adequately assess the magnitude of organic enrichment.

We focus here on practical environmental monitoring (that is #1 in the list of goals shown below) to determine the ecological effects of organic wastes, inclusive of: waste feed and faeces from Bay of Fundy salmon mariculture and Prince Edward Island (PEI) blue mussel culture. As a result of mariculture, organic wastes may accumulate and exceed the assimilation capacity limits of the coastal zone. They then build up on sediments, forming a mariculture sludge (near-field effect) or after mineralization, result in hypernutrification in seawater and consequent eutrophication (Wildish et al. 1990), or after seawater transport and deposition result in organic enrichment (far-field effects). In this presentation we concentrate on near-field effects of particulate wastes from mariculture which reach sediments in the near vicinity of sea cages or longlines. We employ two well established sediment geochemical techniques recently tested and compared with other available methods, with reference to the salmon mariculture industry, by Hargrave et al. (1997). Redox and sulfide were selected as the most cost-effective monitor of the sedimentary environment (Wildish et al., in prep.) to determine whether decreased levels of dissolved oxygen and increased levels of sulfide in pore water, contingent on changes from aerobic to anaerobic microbial functioning and caused by organic enrichment, had occurred. Thus, the sediment geochemistry changes could, after calibration, indicate characteristic microbial and macrofaunal structural changes.

Other methods that could have been used to monitor organic enrichment, such as total organic matter (measured as loss in weight on ignition), organic carbon or nitrogen in sediments were discarded on the basis of increased cost over Eh and sulfide determinations. Hargrave et al. (1995, 1997) compared many of the possible ways to monitor organic enrichment in sediments in studies directly under farm sites and at reference locations 50 m away. The results also suggested that Eh and sulfide were more sensitive than measures of organic carbon and nitrogen to detect organic enrichment.

The accumulation of organic matter in sediments is a dynamic process affected by the rate of supply, decomposition processes and physical loss/additions by resuspension and lateral transport by water movements (e.g. tidal currents and wind-wave activity). Measures such as total organic matter or organic carbon may not reflect the availability of carbon as a substrate for microbial decomposition as do Eh and sulfide. The latter measures are directly related to microbial activity, notably sulfate reduction, although the pool of reduced sulfur products is affected by the specific local conditions of sediment diffusion and oxidation potential.

The detection of organic enrichment by environmental monitoring actually encompasses four distinct goals:

1. practical, determining the general magnitude of effect;
2. comparison of enriched and reference locations;
3. temporal, determining before:after status of sediments; and
4. spatial, determining the geographical limits of the enrichment effect.

In this report, only the first of these goals, practical monitoring, is considered, and the others are left for later reports. A satisfactory method for the second goal, also using redox and sulfide measures, is presented in Wildish et al. (in prep.).

The aim here is to present useful information to those interested in the details of measuring redox and sulfide as a practical measure to determine the magnitude of organic enrichment of sediments in Atlantic Canadian conditions.

REVIEW: PRIOR RESEARCH ON ORGANIC ENRICHMENT AND ENVIRONMENTAL MONITORING

This review is not intended to be comprehensive, because the published research on organic matter enrichment in sediments is such a large and diffuse body of work. Instead, we have tried to pick out the highlights of the subject, where it directly bears on the aim of this presentation.

Basic research on organic matter degradation in sediments

Organic matter decay and mineralization are fundamentally important processes in both terrestrial and aquatic environments, inclusive of freshwater, estuarine and marine ecosystems. This importance led to their early study, e.g. Darwin (1881), who showed that the macrofauna was an important factor in promoting the decay of leaf litter in terrestrial soils.

Three main groups of research workers have studied organic matter degradation in the aquatic environment from quite different perspectives. They include: sedimentary geochemists concerned with nutrient cycling inclusive of carbon, plant nutrients and non-essential elements; benthic macro-faunal ecologists interested in the role that macrofauna have in organic matter mineralization (e.g. Hargrave 1976; Poole and Wildish 1979), as well as differences caused by the structural components of macrofaunal communities throughout their geographic range; and microbial ecologists concerned with sediment metabolism, as well as the characterization of the causative microorganisms (e.g. Zobell 1938; Martens and Berner 1974; Jørgensen 1977; Poole et al. 1977).

The 1960s and 1970s was a period in which important basic research in aquatic sediments was achieved. Thus, Fenchel and Riedl (1970) described the universally present sulfide system characteristic of all estuarine/marine soft sediments. The upper boundary of the sulfide biome was named the redox potential discontinuity (RPD). Within it sulfate-reducing bacteria utilized sulfate present in seawater as an electron acceptor, and whose byproducts caused the reducing conditions. The bacterial and meiofaunal populations of sediments were found to be regulated by sulfide and oxygen conditions (Fenchel 1969). Sulfate-reducing bacteria activity was also influenced by the redox conditions (Brown et al. 1973). Martens and Berner (1974) showed how sulfate reduction and methanogenesis were mutually exclusive processes and that the latter only occurred where sulfate had been depleted, either deep within the sediment or in microniches free of sulfate. Jørgensen (1977) showed that sulfate reduction could occur in anoxic microniches present within an overall oxic soft sediment. Sediment cores from marine/estuarine conditions typically have four dominant zones, equivalent to microbial communities, distributed with depth as shown in Fig. 1. The redox potentials represent maxima and, because of the presence of microniches within sediments, cannot be used reliably to indicate the types of microbial respiration present.

In soft sediments, Hargrave (1972) investigated redox conditions and oxygen uptake potential of freshwater sediments with depth in the core and found that these variables were inversely related. This suggested that redox measurements could indicate both "stagnation" in sediments (Whitfield 1969), that is, the degree to which they were anaerobic, and the combined oxygen uptake due to chemical and biological causes.

Sediment geochemical methods for measuring organic enrichment by electrochemistry

Electrochemical methods borrowed from analytical chemistry (see Clark 1960) were adapted for field use in sediments (e.g. Scerbina 1939; Zobell 1946). Improvements in redox probe design introduced by Whitfield (1969, 1971) allowed Eh measurement to be used as a semi-quantitative measure of "stagnation" in the sediments. Whitfield (1969) discussed the problems of redox measurement including: that during core sampling sediment disturbance may occur which changes its redox status, that the platinum electrode may be influenced by sedimentary conditions to give spurious readings (e.g. two probes sampling the same sediment may vary by 10-30 mV), and that the uneven thermodynamic nature of the sediment, or patchiness, can lead to variability in the results obtained.

Despite these problems, redox measures have been significant in making advances in the basic research described above. A comparison of the two sets of environmental data obtained by separate redox measurement systems at the same 17 stations in Baltic and Gulf of Bothinia sediments was made by Bågander and Niemistö (1978). Their field results with 107 bivariate measurements were significantly correlated (r=0.98), showing that redox can be measured with acceptable reproducibility.

An electrochemical method to measure sulfide in sediments was introduced by Berner (1963)

and see also in Adams et al. (1972). The use of a silver/silver-sulfide membrane electrode and double-junction reference electrode permits the method to be completed in the field if necessary. Berner (1963) demonstrated a linear relation between the log of the sulfide ion concentration and observed electromotive potentials. Sulfide measurements made in field conditions (Adams et al. 1972) were reproducible and highly correlated (r=0.99) with the standard colorimetric method (Cline 1969) utilizing methylene blue.

Applied research in pulp mill and sewage impacts in the marine/estuarine environment

At the same time that basic research on organic matter assimilation in sediments was active (1960s and 1970s), so was applied research based on organic inputs from pulp mills and municipal sewage. This work was summarized in two reviews, both published in 1978.

The much-cited review of Pearson and Rosenberg (1978) considers the response of benthic macrofauna to organic enrichment. They found a consistent pattern among the large number of field macrofauna surveys reviewed along a spatial gradient of organic input (Fig. 2). The four zones of response by macrofauna/sediment structural changes correspond to four zones of response noted in the independent review of Poole et al. (1978): anoxic, hypoxic, oxic and normal (Fig. 3). The latter were defined by microbial/macrofaunal functioning in sediments as follows:

> Anoxic - presence of anaerobic bacteria, absence of autotrophs and macrofauna;
> Hypoxic - facultative anaerobic and aerobic microorganisms, low biomass of autotrophic and macrobenthic organisms; and
> Oxic - with facultative anaerobic and aerobic microorganisms often with an enhanced aerobic, heterotrophic, prokaryotic and eukaryotic productivity.

Both reviews emphasized the importance of water movement, concentrations and amount of organic input in determining the sedimentary responses along the organic enrichment gradient. Both also emphasize that the enrichment gradient responses may either be on spatial or temporal scales. They differ in that one relies only on macrofaunal structure, while the other depends on both macrofaunal structure and microbial functioning in sediments.

Investigators in this field of research also used electrochemical measures; for example, Poole et al. (1976) measured Eh and sulfide levels, and Pearson and Stanley (1979) Eh, to aid in characterizing sedimentary responses to pulp mill pollution.

METHODS

The following details of field sampling, subsampling and redox/sulfide measurement apply to eastern Canadian conditions and, specifically, to the Bay of Fundy salmon culture industry in New Brunswick. Readers should be aware that local conditions that differ from those of the Bay of Fundy might cause small differences in methodology, and our recommendations apply only to goal #1 of the four shown on page 1. We expect that changes in monitoring protocol will be reviewed regularly, and this to lead to changes, as new research indicates improvements.

FIELD SAMPLING AT LESS THAN 30 M DEPTH

Establishing a transect

In order to guide the SCUBA diver where to take samples at similar relative positions under salmon cages, we recommend the laying of a temporary leadline transect. The positioning of the transect is decided by determining which are the cages with the highest biomass of fish. The transect is set up under one of these cages to pass through its midpoint and in the same direction as the major tidal flow direction at the site. The transect is a 10-m leadline placed on the seabed through the diver-determined, visually most impacted part of it.

The number of transects used, and hence number of core samples obtained, will depend on the likely effects of organic enrichment at a particular site. This will depend on the biomass of fish being fed, as well as the water movement patterns characteristic of the site as indicated by sedimentary grain size distribution. Initially, we propose that the transects deployed at each site is one per 100,000 fish, so that a 300,000-fish site will need three transects.

Taking samples

Samples of the sediment are taken in a plastic core tube (50 cm long by 5 cm diameter) which is drilled at 2-cm intervals in a spiral pattern. Each hole is just big enough to take a 5-cc, cut-off

syringe and is sealed with duct tape. At the surface the diver fills the core tube with seawater and caps both ends so that it is watertight. At the bottom the diver removes each cap and pushes the tube into the sediment to a depth of 10-20 cm if possible. The lower cap is put in place while still in the sediment, followed by the upper one. During ascent, no leaking from the core must be present and, if this does occur, the sample must be discarded and repeated. Cores must be kept upright and, during ascent, can be placed in a tray or basket for safer transport. Highly organically enriched sediments with an excessive organic matter loading may have a "fluffy" interface due to the high water content (>80%) near the surface. Sediment sampling in these conditions requires considerable skill in taking undisturbed cores and requires the diver to keep feet and other parts of the body away from the easily disturbed, fluffy sediments while sampling. In the absence of *Beggiatoa* sp. mats in such locations, it is probable that the redox discontinuity layer is present within the lower benthic boundary layer. Satisfactory cores are those in which the water above the core is relatively undisturbed.

For some harder sediments, e.g., sand and gravel, the core tube is not a satisfactory way of sampling, and here it may be necessary to scoop the sediment directly into a cut-off syringe with a spatula. Samples collected in this way must be marked to indicate non-standard sampling.

Three core tube samples are taken along each transect as close to the leadline as possible, and at random points along it.

FIELD SAMPLING AT GREATER THAN 30 M DEPTH

Safety

Because of SCUBA diving safety considerations and regulations under the NB Health and Safety Act (Anon. 1998), any site which has depths in excess of 30 m should be sampled by remote corer or grab.

Taking samples

For the following reasons, remote sampling with corer or grab is less satisfactory than by SCUBA diver:

- it is much harder to obtain an intact sediment-water interface;
- because the gear is operated from a vessel, it is not possible to locate the sample area in the middle of a cage - only near it. Hence, samples taken in this way are not comparable to those taken by a diver who has free access underneath salmon pens; and
- one sampler will not be optimal for all sediments; thus, a gravity corer will only operate in silt/clay sediments and a grab sampler is required for harder sediments.

It is recommended that a gravity corer, weighted to at least 20 kg, be used for silt/clay sediments and a heavy grab for all other sediments. The deployment of this gear requires the use of a sturdy winch and an experienced winchman to operate it. There is considerable skill required in operating the winch to obtain a good sample. Any cores or grabs which leak must be discarded, as are any samples where an intact sediment-water interface is absent.

The Kajak gravity corer, also referred to as a KB heavy model core sampler, is available from Wildco (contact Hoskin Scientific, 4210 Morris Drive, Burlington, ON, L7L 5L6). The core tube must be fitted with a plastic egg catcher to prevent sediment falling out during retrieval. Heavy grabs such as the Hunter-Simpson or Van Veen are not available locally, but could be fabricated by a competent local machine shop by copying working models at St. Andrews Biological Station (SABS).

Number of cores/grabs

Three per 100,000 fish.

SUBSAMPLING

Core samples either from the SCUBA diver or the Kajak corer are placed so that the sediment-water interface is uppermost. The Kajak corer also uses a 50 x 5-cm core tube, prepared with duct-tape-covered holes, as in the diver-held corer. The upper cap of each core tube is removed and excess seawater slowly drained off by removing part of the duct tape. The duct tape is then fully peeled back from the hole over the top 2 cm of sediment (the sediment-water interface) and the redox probe placed there. After allowing up to 5 min for the reading to come to equilibrium, during which time the probe is moved gently in and out (not up and down), a reading is taken and the probe removed. When longer times to equilibrium are required, this indicates poorly poised oxidation-reduction reactions in the sediments. These

may result from steep redox gradients at the point sampled, or the presence of microniches where different redox conditions occur. We suggest that the equilibrium point is reached when drift is <2 mV/min. A cut-off, 5-cc plastic syringe is then pushed through the same hole and a 5-mL sample obtained by slowly pulling on the plunger. The subsample is expressed into a plastic vial, capped and placed on ice and in the dark for storage (≤3 h). If longer storage times than 3 h are required, it is best to place the whole core on ice and in the dark before beginning sampling to determine sulfide. It is preferable to complete both redox and sulfide determinations as soon as possible after obtaining the sample, i.e. on deck. The whole depth of the core may be examined vertically at 2-cm intervals down the core. Frequently, at impacted sites, vertical changes of Eh and sulfide are small, as indicated by a uniform black color throughout the core.

REDOX POTENTIAL MEASUREMENT

Materials

- Accumet portable meter AP25 (see Anon. 1997)
- Orion platinum redox electrode model 96-78-00 (see Anon. 1983), connected to channel B
- 2, 50-mL volumetric flasks
- 2, 150-mL beakers
- Distilled water
- Potassium ferrocyanide ($K_4Fe(CN)_6 * 3H_2O$)
- Potassium ferricyanide ($K_3Fe(CN)_6$
- Potassium fluoride ($KF * 2H_2O$)
- 1 core tube with holes at 2-cm intervals
- Corer
- Duct tape

Preparation of standard, Zobell solutions

Standard A is prepared by weighing 2.11 g of $K_4Fe(CN)_6 * 3H_2O$ and 0.825 g of $K_3Fe(CN)_6$ into a 50-mL volumetric flask. Approximately 25 mL of distilled water is added, then stirred to dissolve the solids. The solution is then diluted to volume.

Standard B is prepared by weighing 0.21 g of $K_4Fe(CN)_6 * 3H_2O$, 0.825 g of $K_3Fe(CN)_6$, and 1.695 g of $KF * 2H_2O$ into a 50-mL volumetric flask. Approximately 25 mL of distilled water is added to dissolve the solids. The solution is then diluted to volume.

Calibration of the redox electrode

Dry platinum electrodes, after storage, must be activated by adding 0.2 M KCl filling solution 24 h before use, and standardized against Zobell's solutions as shown below:

- Press channel on the meter and make sure it is selected for channel B.
- Press mode and select option 2 for mV.
- Pour each standard into a beaker and stir the solution with the redox electrode. Wait a couple of minutes for the reading to stabilize.
- Standard A should read +234 ± 9 mV and Standard B should be +300 ± 9 mV. The millivolt readings for calibration may vary if a different electrode is being used. Consult the instruction manual (Anon. 1983).
- Between readings, rinse the electrode with distilled water and store temporarily in distilled water.
- The standards should be at room temperature.

Redox readings

When the core tube comes to the surface, take the reading at the sediment-water interface. Place the electrode in the hole closest to the interface and gently move in a lateral motion to maximize the surface that comes in contact with the electrode. It takes a couple of minutes or more for the reading to stabilize. After a day's use, the platinum probe tip may be cleaned with detergent and an abrasive pad, followed by rinsing with distilled water. For storage longer than a week, the probe solution should be removed and the probe stored dry.

To express the mV readings as relative to the normal hydrogen electrode (NHE), use:

$$E_{NHE} = E_0 + C$$

where E_0 = mV of unknown and C = mV of reference relative to NHE shown in Table 1.

SULFIDE MEASUREMENT

Materials

- Accumet portable ion meter AP25 (see Anon. 1997)
- Orion silver/sulfide half-cell electrode model 9416 (see Anon. 1996) connected to channel B
- Orion reference electrode 90-01 (see Anon. 1970) connected to "ref" channel

- Distilled water
- 2, 150 mL beakers
- 1 volumetric pipette
- 1 graduated pipette
- 2 graduated cylinders
- 2, 5-mL volumetric flasks
- 1, 100-mL volumetric flask
- 1, 250-mL volumetric flask
- Solution of 3% $Na_2S * 9H_2O$ or reagent grade $Na_2S * 9H_2O$ crystals
- SAOB (sulfide anti-oxidant buffer solution) or NaOH and EDTA ($Na_2C_{10}H_{14}O_8N_2 * 2H_2O$)
- L-ascorbic-acid
- 5-cc syringe
- 1 core tube with holes at 2-cm intervals
- Corer
- 37-mm x 71-mm plastic vials
- Kimwipes
- Duct tape
- 5-mL macropipette
- Pipette tips

Preparation of sodium sulfide stock solution

A solution of 3% $Na_2S * 9H_2O$ can be purchased from chemical suppliers and is used as stock. If this is not available, a 0.01-M solution of Na_2S can be prepared by weighing 0.2402 g of $Na_2S * 9H_2O$ in a 100-mL volumetric flask and diluting to volume with distilled water. The stock solutions are not stable and oxidize in aerobic conditions. The 0.01-M stock solution of sodium sulfide is valid for 48 h if kept in the dark.

Sodium sulfide should be handled under a fume hood and gloves should be worn at all times.

Preparation of SAOB (sulfide anti-oxidant buffer solution)

A solution of SAOB can be purchased, or it can be prepared by weighing 20.0 g of NaOH and 17.9 g of EDTA in a 250-mL volumetric flask and diluting it to volume with distilled water. This solution must be stored in a refrigerator until used. Just before the SAOB is added to the sediment sample, add 8.75 g of L-ascorbic acid for every 250 mL of solution.

Once the L-ascorbic acid is mixed with the SAOB, the solution is only stable for a maximum of 3 h. It is therefore recommended that you only mix the two just before taking the readings with the meter.

Calibration of the sulfide probe

The reference electrode should be filled with Orion 90-00-01 filling solution 24 h before use. Prepare a standard solution by pipetting 0.4 mL of the $Na_2S * 9H_2O$ 3% stock solution (or 5 mL of the 0.01 M Na_2S solution) and place immediately (as it is unstable) in a 50-mL volumetric flask and diluting to volume with distilled water to give a concentration of 0.001 M (1000 µM). Pipette 5 mL of the 0.001 M standard solution in another 50-mL volumetric flask and dilute to volume with distilled water to give a concentration of 0.0001 M (100 µM). A minimum of two points is needed to make a calibration curve.

Pour 25 mL of the standard solution into a beaker. Mix the L-ascorbic acid with the SAOB and add 25 mL in the beaker. (The amount does not have to be 25 mL, as long as equal amounts of standard and SAOB are added.)

- On the Accumet portable meter AP25, press the channel button and make sure it is on channel B to be able to take sulfide readings. The reference electrode should be in the pin outlet "ref" next to channel B.
- Press the mode button and select option 3, ISE.
- Press the std button and select number 2 and follow the instructions on the screen to clear all previous standards.
- Press std again and select number 1.
- Then select the ion name by pressing 6 for sulfide, then enter.
- Press 8 to select the unit that is used for the standard concentrations, moles/L (M).
- Insert the silver/sulfide half-cell electrode (model 9416) and the reference electrode in the solution and follow the prompts.
- Enter the concentration of your standards; for 0.001 enter 1000, and for 0.0001 enter 100, then press enter.
- When the reading is stable, the meter accepts the value and you can repeat the procedure for the other standard.
- It is best to calibrate with the most diluted standard first.

Rinse the probe with distilled water after every reading, blot dry and store temporarily in distilled water. For longer storage, the probes may be stored dry (Orion 9416 simply by capping the electrode - no filling solution required, and for Orion 90-01, after emptying the filling solution). Other probe models may be gel filled, dry or require filling

solutions, so you should check the model used and the appropriate instruction sheet.

The meter should be recalibrated before each batch of sample analyses are run.

Sulfide concentration of sediments

Add 5 mL of SAOB - L-ascorbic acid to the 5-mL sediment sample and shake the vial to mix thoroughly. Place the electrodes in the vial and mix so that all of the surface comes in contact with the sediment. It takes about 1 min for the reading to stabilize. Rinse the probe with distilled water after every reading and blot dry with a Kimwipe.

RESULTS

SAMPLE TREATMENT

The removal of a sediment core from its natural place on the sea floor initiates changes (Whitfield 1969) so that it becomes progressively less representative of the natural sediment with time due to changes in temperature, oxidation/reduction and light. Because of this, the best strategy is to make redox measurements and take subsamples for sulfide determination as soon as possible after the core samples are obtained.

Because of logistical constraints, there is frequently pressure to delay subsampling or store samples before the analysis is completed. To investigate various ways of doing this to determine sulfide, we compared the following treatments:

(1) - sediment + SAOB
- sediment alone

(2) - sediment in a 50-mL plastic vial
- sediment in covered plastic syringe

to see the effect of storage time on results.

For (1) we homogenized sediments in a Waring blender for 2 min, followed by withdrawal of 5 mL of sediment in a cut-off syringe. Subsamples were treated either by adding 5 mL of SAOB solution to each subsample or by extruding the 5-mL sediment subsample into a clean plastic vial and capping. All of these numbered samples were stored on ice in a freezer chest until analysis. Five mL of SAOB was added to untreated subsamples just before analysis. Shown in Table 2 are the elapsed times used and sulfide concentrations measured on three independent subsamples of well mixed sediment. Note that the internal variability of replicates at each time is reasonable, e.g. at time 0, sediment + SAOB, $\overline{x} = 357 \pm 15$ and sediment only, $\overline{x} = 390 \pm 56$ mM (mean ± standard error). The results of Table 2 clearly show that sediment + SAOB is an unsatisfactory way of storing sediments for sulfide analysis (range 0.22-6200 µM). For sediment only samples, after 24 h over half of the sulfide content had been lost. After 49 h, all of the ice had melted in the freezer chest and the rise in sulfide concentration for both treatments at 72 h may be linked to the temperature rise. Following storage of each subsample, the solutions were allowed to approach lab temperature (range 14.1-24.6°C) before analysis.

In a similar experiment with mixed Tongue Shoal sediments stored at 5°C in a refrigerator, we tested the effect of holding time after adding SAOB initially or at the time of analysis. The results (Table 3) are consistent with mixed Reserve Cove sediments and support the conclusion that sediments must be stored without the addition of SAOB. At the time of analysis, temperatures were 15.3-24.3°C.

For (2), we used an unmixed sediment (the top 10 cm) obtained by digging silt/clay mud from the intertidal region at Brandy Cove. We tested the effect of holding sediment in either a capped plastic vial (as recommended for standard use) or in a plastic syringe with the open end covered with aluminum foil. The results are shown in Table 4 and Fig. 4, and suggest that if the vial and syringe results are compared by Mann-Whitney U-test at each storage time, the H_0 cannot be rejected at $p < 0.05$ and thus both sets of results have the same variation and median values. However, if the comparison is made between initial and the 3 h stored sample within vials or syringes, by the same test, there is suggestion of an increase in sulfide within 3 h. Thus, for vials, $U = 0.0$, $n_1 = 5$, $n_2 = 5$ and for syringes, $U = 3.5$, $n_1 = 5$, $n_2 = 5$. Since U must be <2 (Table 14 in Elliot 1977) for vials at $p > 0.05$, we can reject the null hypothesis, although not for syringes where the data are less homogenous (range 1200-3100 µM sulfide/L).

BAY OF FUNDY SALMON MARICULTURE INDUSTRY RESULTS IN 1998

During the 1998 season Dominator Diving Services completed field sampling and analyses for Eh and brought sediment subsamples to the Biological Station for analyses of sulfides as outlined in this report. These analyses were additions to the regular environmental monitoring as described in Anon. (1995), and the results were not used in making recommendations for the 1998 summer growth season.

Dominator Diving Services were responsible for the field work under the salmon net-pens, in making the redox determinations and bringing subsamples back to SABS where fresh SAOB solution was added and sulfide levels determined. The delay between sampling and analysis varied from a few to 12 h. Thus, the delay in analyzing for sulfide could have influenced the results obtained.

The results from 65 different sites throughout the Fundy Isles area for sediment geochemical measurements are shown in Appendix 1.

The data are plotted in Fig. 5, with Eh versus sulfide on a logarithmic scale. Also shown in Fig. 5 are the earlier results of Hargrave et al. (1997) which includes reference stations as well as fish farm sites in 1994-95. The similar slopes (not significantly different at $p<0.05$) of the inverse relationship between Eh and log sulfide concentration, and high R^2 values, both support the view that the sediment geochemistry data for 1998 presented here were valid and useful for resource management purposes.

PRINCE EDWARD ISLAND (PEI) SEDIMENTS UNDER OR NEAR BLUE MUSSEL CULTURE LONGLINES

In August 1998, one of us (NH) accompanied Dr. Shawn Robinson to make sediment geological observations in Tracadie Bay, PEI. In shallow, depositional sediments it was not surprising to find reducing conditions with negative Eh and high levels of sulfide in the 0-2 cm sediment surface layer at 18 stations sampled by SCUBA divers with a hand-held core tube drilled for sampling at 2-cm intervals.

The results are given in Appendix 2. Shown in Fig. 6 are the Eh and sulfide levels plotted with 1994-95 data from Hargrave et al. (1997). The PEI data fall within the earlier results, despite the different locations and types of mariculture. The sulfide levels in some PEI sediments are very high and correspond to highly negative redox values.

We compared the "reference" and impacted sites under mussel longlines. Of 21 reference samples from seven different locations, 13 Eh_{NHE} (that is, Eh <-100 mV) and 10 sulfide (that is >6000 μM) measurements classify as anoxic (see Wildish et. al., in prep.). For impacted sites, 28 of 33 samples at 11 locations were anoxic with Eh_{NHE}, and 22 of 33 were anoxic with sulfide concentration. Because we expected contagious distribution of enrichment within sediments and therefore non-normality, we could not use a parametric test on un-transformed data. Because of these considerations, we used a non-parametric statistical test that makes no assumptions about the distribution of variance. We compared the reference and impacted stations with replicate samples from Tracadie Bay, shown in Appendix 2. The results (Table 5) of a Mann-Whitney U-test (Elliot 1977) suggest that the null hypothesis is accepted. That is, that the two independent groups of samples are drawn from the same population with the same form of variance distribution and median values with respect to Eh and sulfide concentrations in these sediments.

ORGANIC ENRICHMENT GRADIENT ZONES

As discussed in the review section of the introduction to this report, two previous groups of workers have proposed four enrichment gradient zones based on microbial (Poole et al. 1978) and macrofaunal (Pearson and Rosenberg 1978) criteria. Wildish et al. (in prep.) have attempted to place sediment geochemical boundaries applicable, particularly, to Bay of Fundy conditions for the four groups shown in Table 6. We have also adopted the less emotive etymology of Wildish et al. (in prep) so that it now is: oxic a (for normal), oxic b (for oxic), hypoxic and anoxic. It should be understood that the groups do not imply, necessarily, that all sediments within the given one are uniform (due to the prevalence of microniches); rather that they are generalizations that most of the biological grouping of animals/microbes will be of this kind.

Wildish et al. (in prep.) used the data shown in Appendix 1 to help devise the Eh and sulfide limits shown in Table 6. Using this classification and average numbers from Appendix 1, 11 sites are anoxic (based on sulfide >6000 μM) and four sites (on the basis of Eh < -100 mV). As a percentage, ~17% of 65 sites visited in 1998 could be described as, or close to, anoxic.

DISCUSSION

The sediment geochemical methods described in detail in this report meet all of the substantive criteria for environmental monitoring developed by Wildish (in prep.). That is, that the method is scientifically defensible, can provide a means of statistical comparison and provides relevant management decision points. In addition, we have already shown (Wildish et al. in prep.) that the sediment geochemical method presented here is more cost-effective than the traditional benthic macrofaunal species/density one.

In this report we have used the sediment geochemical limits for the organic enrichment gradient based on redox and sulfide levels proposed in Wildish et al. (in prep.). We point out that these limits are tentative and need further verification within Bay of Fundy environmental conditions to show that the sediment geochemical limits do correspond to the macrofaunal and microbial characteristics as outlined in Fig. 2, 3 and Table 6. A further goal would be to determine whether the sediment geochemical limits proposed for Bay of Fundy conditions apply universally in soft sediment environments.

Although for this presentation we have stressed the application to mariculture, we point out that the method can be used successfully for environmental monitoring purposes by any industry or municipality that produces particulate organic wastes. Besides mariculture, these industries would include pulp and paper mill effluents, fish processing plant wastes and domestic or municipal wastes. Thus, the sediment geochemical methods outlined here are of general use for CZM purposes, if the source of the particulate organic waste can be inferred. If this is not the case and two or more sources are available locally, a special chemical method must be researched to identify the source of the organic matter in sediments - if this is required for a particular reason.

As stated in the Introduction, the sediment geochemical methods described have been applied only as a practical method of determining the general magnitude of organic enrichment effects due to mariculture wastes. This is frequently the most important requirement of an environmental monitoring method for both the farmer and regulator. For the special requirement of comparing reference with mariculture-exposed sites, where litigation may be involved, it is cost effective to use the sediment geochemical measures given here (see Wildish et al., in prep.). However, it is necessary to take more replicate samples to achieve a satisfactory statistical confidence level. For the more demanding aims of temporal and spatial monitoring of organic enrichment, a different strategy needs to be considered. A basic problem with the sediment geochemical methods described herein for the two latter purposes is that they rely on point source samples of limited spatial coverage in what is usually a heterogenous and contagious (patchy) sedimentary environment. The patchy benthic environment results from deposition and accumulation of particulate organic matter proximate to netpens which are characteristically non-uniform. One possible alternative for future research is to use the synoptic power of acoustics to determine spatial and temporal differences at mariculture sites.

The quantitative sediment geochemical methods described here in detail have been prepared to aid in replacing the qualitative one presently used (Anon. 1995). The criteria currently in use (Table 7) rely on semi-quantitative field observations to which quality control cannot be applied. The proposed redox and sulfide measurements and use of the enrichment index proposed herein (oxic a, oxic b, hypoxic, anoxic) should lead to better site management and a general CZM picture better than hitherto. It is emphasized that attention to the requirements of redox and sulfide monitoring, including frequent probe cleaning and calibration, will be amply repaid in a developing data base of current and future use for the mariculture industry and CZ managers. Future quality control assurance tests should be centered on redox and sulfide determinations.

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Table 1. Reference electrode potential, mV, relative to NHE (C) at different temperatures and probe filling solution concentrations (Anon. 1983).

Temperature °C	Orion #900001 1.5 M KCl	Orion #900011 Saturated KCl
5	254	219
10	251	214
15	249	209
20	244	204
25	241	199
30	238	194
35	235	189

Table 2. The effect of storage time on a mixed sediment sample from Reserve Cove 3-6/07/98.

Time h	Sediment + SAOB S^{2-}, µM	$\bar{x}$	SE	Sediment only S^{2-}, µM	$\bar{x}$	SE
0	380, 360, 330	357	15	430, 460, 280	390	56
3	2600, 2100, 1600	2100	289	360, 370, 350	360	6
24	1300, 1600, 840	1247	221	180, 110, 110	133	23
49	0.22, 0.24, 0.67	0.37	0.15	35, 39, 29	34	3
72	6200, 4700, 4300	5067	578	450, 400, 430	427	15

Table 3. Effect of storage times on a well-mixed sample from Tongue Shoal, 22-25/07/98.

Time h	Sediment + SAOB S^{2-}, µM	$\bar{x}$	SE	Sediment only S^{2-}, µM	$\bar{x}$	SE
0	900, 870, 940	903	20	520, 510, 630	553	38
4	2300, 1300, 2100	1900	306	270, 260, 270	267	3
25	3100, 3800, 240	2380	1089	280, 210, 170	220	32
48	3600, 2700, 2700	3000	300	140, 120, 180	147	18
71	1200, 1400, 1200	1267	67	390, 300, 120	270	79

Table 4. Effect of storage time on an unmixed sediment obtained from Brandy Cove on 9-12/11/98. Sediment subsamples stored at 5°C before analysis in either plastic snap-cap vials or plastic syringes sealed with aluminum foil.

Time h	Sediment in syringes sulfide, µM	$\bar{x}$	SE	Sediment in vials sulfide, µM	$\bar{x}$	SE
0	1000, 1300, 1300, 1400, 1200	1240	68	1300, 1400, 1300, 1300, 1400	1340	24
3	1200, 1800, 1700, 3100, 1800	1920	315	2000, 2100, 2300, 2100, 1900	2080	66
7	1800, 3500, 1900, 1600, 2000	2100	354	1700, 1800, 2200, 2100, 1900	1940	93
24	1500, 1700, 2000, 1600, 1700	1700	84	1500, 1900, 1800, 2400, 1800	1880	146
72	1600, 1800, 2300, 1500, 1900	1820	139	1700, 1700, 1700, 2000, 1700	1760	60

Table 5. Mann-Whitney U-tests for impacted and reference sediment samples from Tracadie Bay, PEI, based on calculation of the normal deviate, d.

Unpaired groups	N	Eh			Sulfide		
		U	d	P	U	d	P
Impacted	33	270	1.36	ND	289	1.02	ND
Reference	21						

H_0 rejected if d > 1.96 (at P=0.05).

Table 6. Organic enrichment gradient zones based on three types of environmental monitoring measure.

Type of Measure	Group				Reference
Microbial	Normal	Oxic	Hypoxic	Anoxic	Poole et al. (1978)
Macrofaunal	Normal	Transitory	Polluted	Grossly polluted	Pearson and Rosenberg (1978)
Geochemical	Oxic a	Oxic b	Hypoxic	Anoxic	
Eh, mV_{NHE}	>+100	0-100	-100-0	<-100	Wildish et al. (in prep.)
$S^{=}$, µM	<300	1300-300	6000-1300	>6000	

Table 7. Current qualitative criteria used for assessing low (A), moderate (B) and high (C) organic enrichment effects from the Bay of Fundy salmon mariculture industry (Anon. 1995).

Degree of effect	Observed conditions
High	Depositional sea floor, with a high percent of fines in sediment samples (silt/clay >90%). Bacterial coverage gray or absent under depositional conditions. Gas bubbles freely released from sediments. No epibenthic macrofauna, or benthic infauna.
Moderate	Moderately depositional sea floor (silt/clay ranging between 25 and 90%). Bacterial coverage 25-100%. No gas bubbles released from the sediment. Less diversity, but higher biomass than control sites. Occurrence of low-oxygen-tolerant species, but absence of stront current/hard bottom species.
Low	Erosional sea floor (silt/clay <33%). Bacterial coverage <25%. Wide diversity of epibenthic macrofauna. Occurrence of strong current/hard bottom species. Conditions under cages similar to control sites.

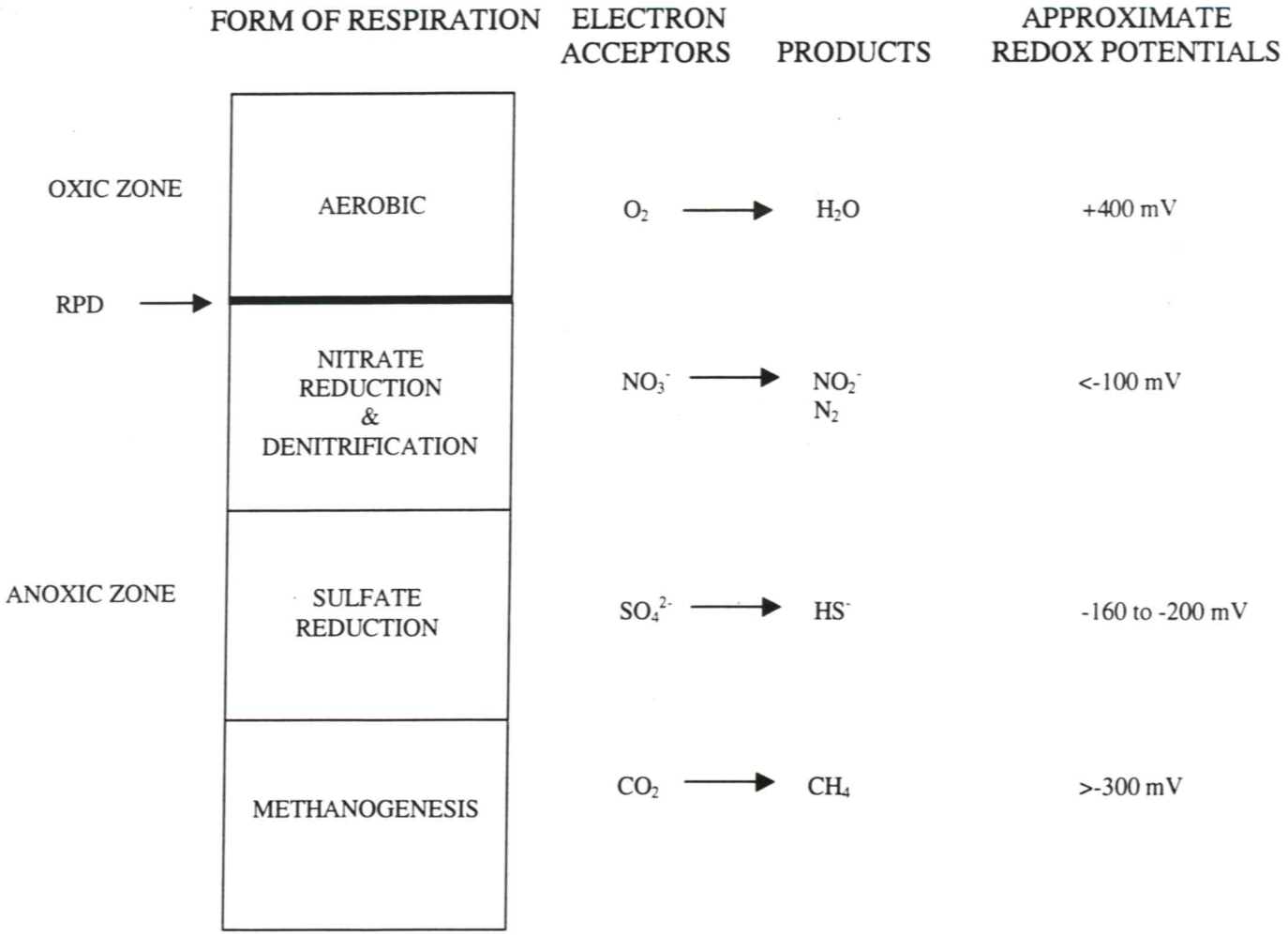
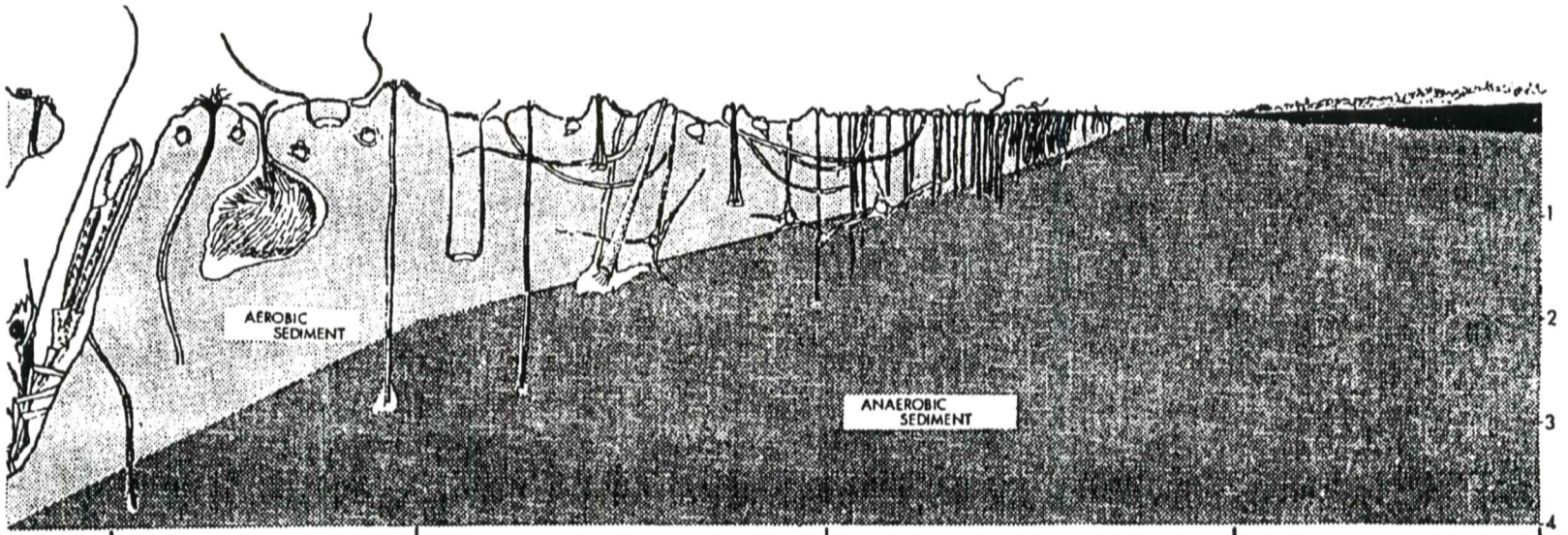


Fig. 1. Relationship between depth and dominant microbial processes occurring in marine/estuarine sediments (from Poole and Wildish 1979).



ZONE	NORMAL	TRANSITORY		POLLUTED	GROSSLY POLLUTED
TYPICAL MACRO-FAUNA DOMI-NANTS	Nucula Amphiura Terebellides Rhodine Echinocardium Nephrops	Labidoplax Corbula Goniada Thyasira Pholoe	Chaetozone Anaitides Pectinaria Myriochele Ophiodromus	Capitella Scolelepis	No MACROFAUNA Surface covered by Fibre 'blanket'

Fig. 2. Diagrammatic representation of changes in macrofauna and sediment structure along an organic enrichment gradient in marine/estuarine conditions (Pearson and Rosenberg 1978).

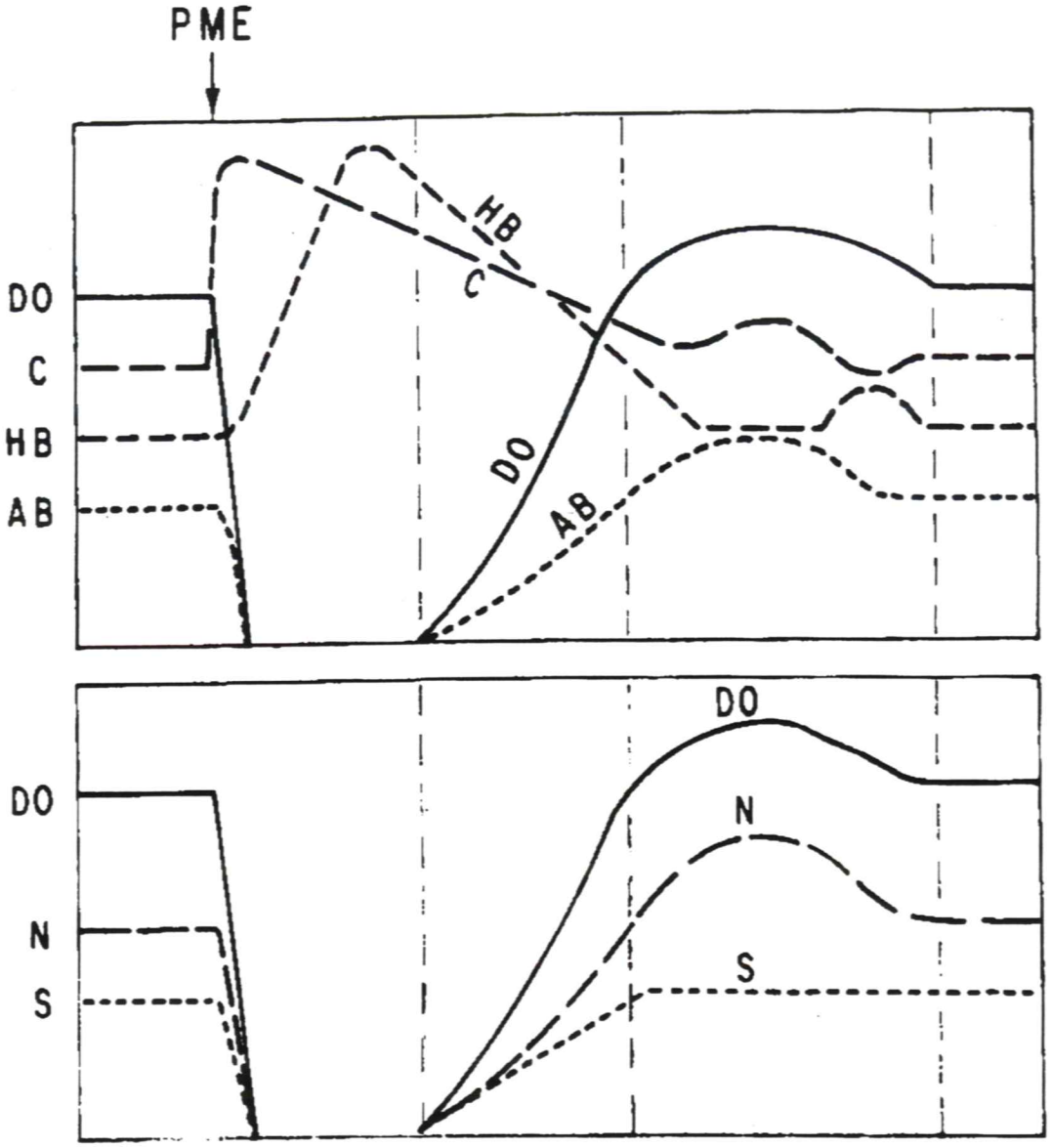


Fig. 3. Concept of stabilization of organic matter along an enrichment gradient from a point source of PME. The x axis may be space (=distance) or time. The y axis indicates relative amounts of materials indicated by letters in the following key. PME = pulp mill effluent, DO = dissolved oxygen, C = available carbon, HB = heterotrophic biomass, AB = autotrophic biomass, N = density and S = species of macrofauna. From Poole et al. (1978).

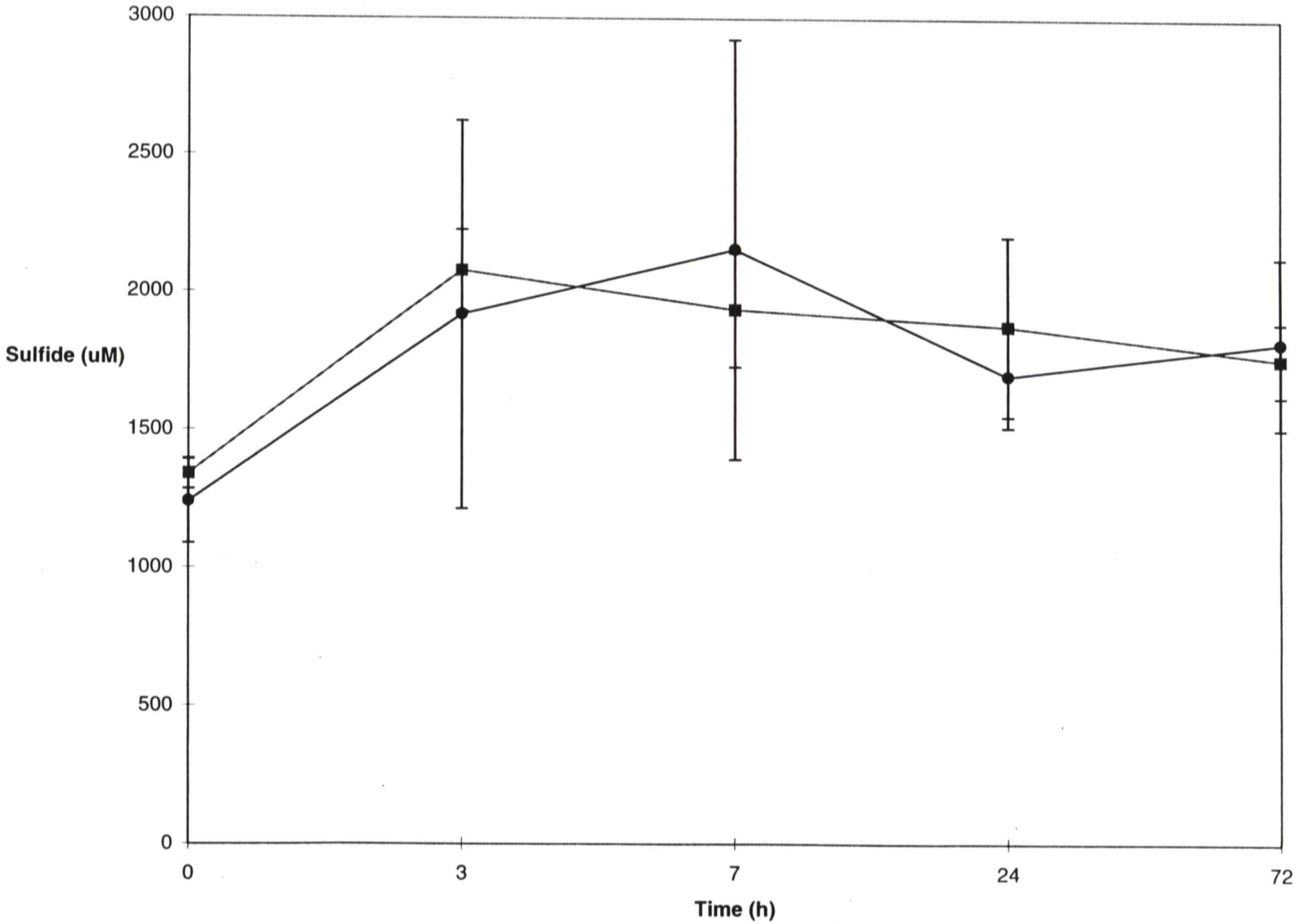


Fig. 4. Time course, in hours, of the sulfide content of sediment subsamples stored in the dark at 5°C.

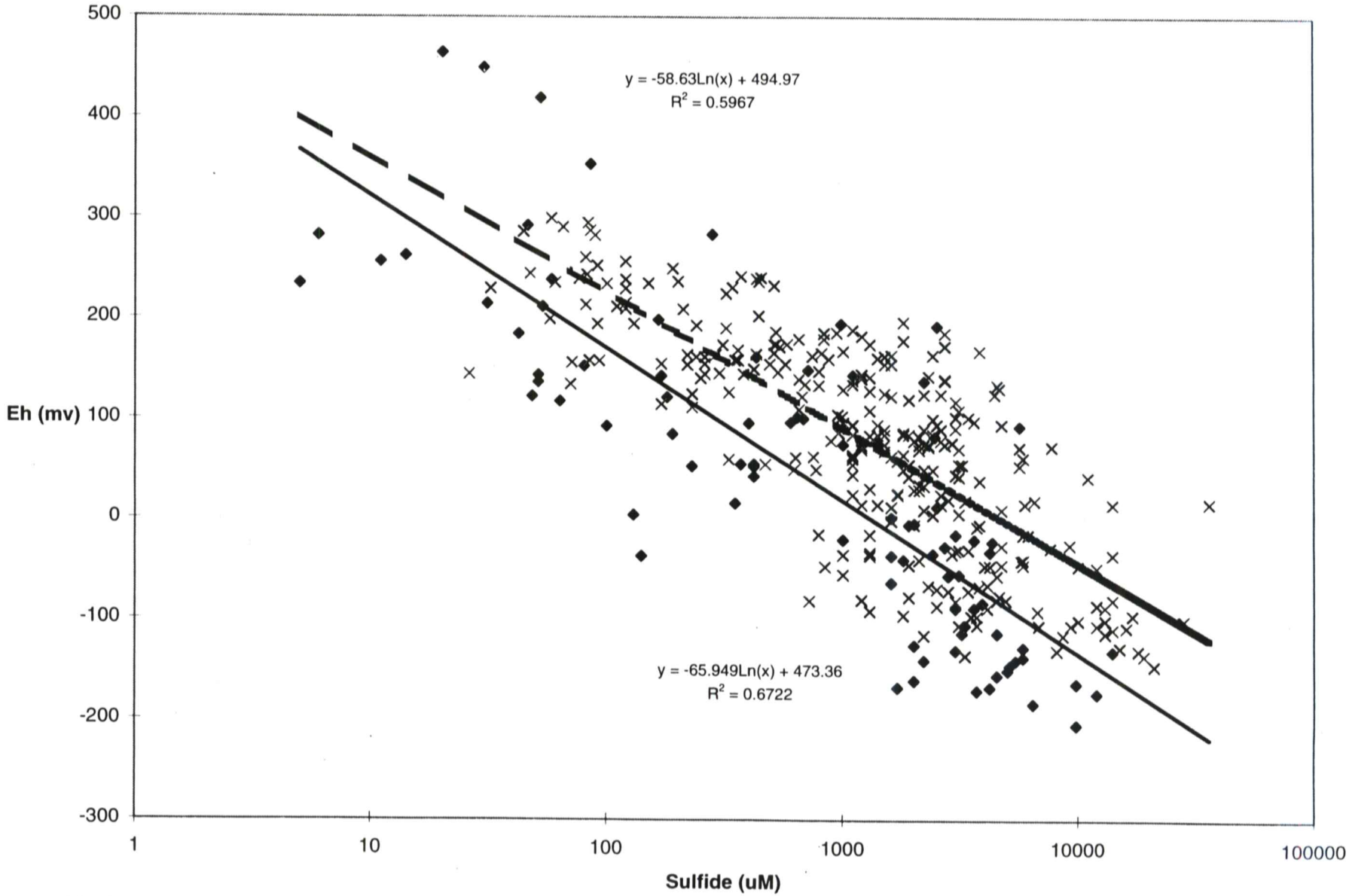


Fig. 5. Eh:sulfide plot of sediment subsamples from the Fundy Isles area in 1994 and 1995 (squares) (Hargrave et al. 1997) and from the environmental monitoring program stations visited in 1998.

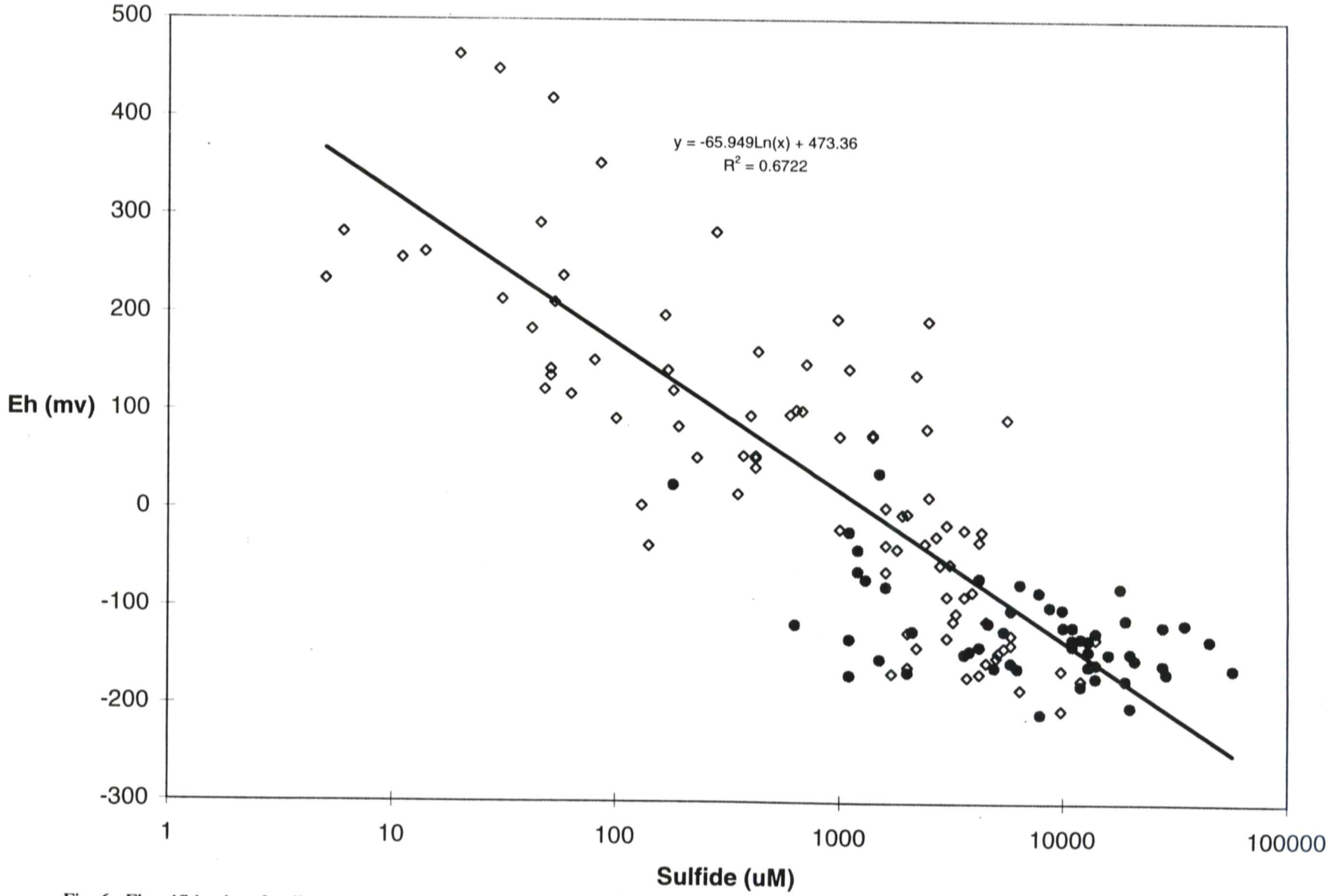


Fig. 6. Eh:sulfide plot of sediment subsamples from Tracadie Bay, PEI in August 1998 (circles) compared to 1994/95 Fundy Isles data from Hargrave et al. (1997).

Appendix 1. Sediment geochemical data from the 1998 environmental monitoring conducted by Dominator Environmental Diving Services. Station numbers refer only to the temporal order in which the sites were visited to protect site identity.

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV $_{NHE}$	Time DST/AST
1998							
16-Aug	1	1	A	620			13:00
		1	B	570			
		1	C	1100			
26-Aug	2	1	A	14000	-199.6	14.4	
		1	B	11000	-172.7	41.3	
		1	C	36000	-198.2	15.8	
		2	A	5600	-161.3	52.7	
		2	B	5600	-142.8	71.2	
		2	C	5800	-153.3	60.7	
	3	1	A	1100	-76	138	
		1	B	2700	-42	172	
		1	C	1600	-51	163	
		2	A	5900	-199.4	14.6	
		2	B	6500	-196	18	
		2	C	7700	-141.9	72.1	
		3	A	3700	-319.6	-105.6	
		3	B	13000	-315	-101	
		3	C	6700	-306	-92	
	4	1	A	2700	-75	139	
		1	B	3100	-144	70	
		1	C	3100	-106	108	
		2	A	4600	-291	-77	
		2	B	3800	-282	-68	
		2	C	4000	-261	-47	
27-Aug	5	1	A	1800	-150	64	
		1	B	2600	-136	78	
		1	C	2300	-140	74	
		2	A	3400	-245	-31	
		2	B	4700	-260	-46	
		2	C	2900	-249	-35	
	6	1	A	3300	-196	18	
		1	B	3100	-209	5	
		1	C	2600	-190	24	
	7	1	A		-185	29	
		1	B		-178	36	
		1	C		-130	84	
31-Aug	8	1	A	4700	-241	-27	
		1	B	6100	-230	-16	
		1	C	5700	-256	-42	
		2	A	2100	-180	34	
		2	B	1900	-172	42	
		2	C	3000	-124	90	
	9	1	A	1100	-26	188	

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		1	B	2300	-72	142	
		1	C	1100	-80	134	
		2	A	3400	-113	101	
		2	B	2200	-125	89	
		2	C	2900	-138	76	
1-Sep	10	1	A	1800	-130	84	
		1	B	2000	-136	78	
		1	C	1600	-152	62	
		2	A	1500	-60	154	
		2	B	1300	-73	141	
		2	C	1200	-70	144	
3-Sep	11	1	A	1300	-131	83	
		1	B	1200	-142	72	
		1	C	1400	-120	94	
		2	A	950	-110	104	
		2	B	890	-136	78	
		2	C	960	-128	86	
9-Sep	12	1	A	1200	-140	74	10:10
		1	B	2100	-132	82	
		1	C	2200	-165	49	
	13	1	A	12000	-300	-86	11:10
		1	B	14000	-295	-81	
		1	C	2700	-140	74	
	14	1	A	1200	-74.1	139.9	11:50
		1	B	1300	-86.2	127.8	
		1	C	690	-80.1	133.9	
	15	1	A	3700	-311	-97	12:45
		1	B	3000	-296	-82	
		1	C	6800	-320	-106	
		2	A	17000	-310	-96	13:15
		2	B	16000	-322	-108	
		2	C	13000	-302	-88	
	16	1	A	740	-52	162	14:15
		1	B	1000	-47	167	
		1	C	1300	-40	174	
		2	A	2100	-145	69	14:35
		2	B	1100	-150.1	63.9	
		2	C	1100	-130	84	
10-Sep	17	1	A	1100	-154	60	9:15
		1	B	1100	-160	54	
		1	C	1200	-145	69	
		2	A	5800	-260	-46	9:45
		2	B	4500	-271	-57	
		2	C	3100	-245	-31	
	18	1	A	1300	-184	30	
		1	B	1100	-170	44	
		1	C	1100	-152	62	

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		2	A	4500	-295	-81	
		2	B	3500	-311	-97	
		2	C	2800	-286	-72	
		3	A	2500	-301	-87	
		3	B	1300	-306	-92	
		3	C	3400	-286	-72	
14-Sep	19	1	A	1500	-146.3	67.7	10:00
		1	B	2100	-140	74	
		1	C	1800	-17.9	196.1	
		2	A	4600	-84	130	10:30
		2	B	4400	-90	124	
		2	C	3000	-97	117	
	20	1	A	13000	-328	-114	11:45
		1	B	28000	-315	-101	
		1	C	9300	-320	-106	
		2	A	3200	-160	54	12:15
		2	B	3100	-172	42	
		2	C	1700	-189	25	
	21	1	A	3000	-112.8	101.2	13:45
		1	B	2400	-114.6	99.4	
		1	C	1800	-36.5	177.5	
		2	A	3800	-47	167	14:15
		2	B	2400	-51	163	
		2	C	2700	-29	185	
15-Sep	22	1	A	14000	-324	-110	9:45
		1	B	8600	-330	-116	
		1	C	3100	-320	-106	
		2	A	21000	-360	-146	10:15
		2	B	19000	-350	-136	
		2	C	18000	-345	-131	
	23	1	A	2300	-142	72	11:00
		1	B	2200	-140	74	
		1	C	1800	-165	49	
		2	A	1100	-120	94	11:25
		2	B	990	-112	102	
		2	C	1900	-95	119	
		3	A	3000	-170	44	12:00
		3	B	2000	-185	29	
		3	C	2600	-90	124	
		4	A	3100	-160	54	12:15
		4	B	2800	-195	19	
		4	C	2400	-165.1	48.9	
		5	A	1400	-200	14	12:50
		5	B	2000	-220	-6	
		5	C	1700	-190	24	
	24	1	A				
		1	B				

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		1	C				
16-Sep	25	1	A	830	-35.1	178.9	10:20
		1	B	510	-40.6	173.4	
		1	C	540	-42.8	171.2	
	26	1	A	830	-28.9	185.1	11:10
		1	B	940	-28.6	185.4	
		1	C	440	-11.9	202.1	
	27	1	A	1100	-121	93	11:40
		1	B	1200	-32	182	
		1	C	520	-40	174	
		2	A	240	-21.6	192.4	12:05
		2	B	320	-24.1	189.9	
		2	C	580	-40.2	173.8	
17-Sep	28	1	A	4900	-295	-81	10:05
		1	B	4100	-303	-89	
		1	C	2200	-330	-116	
		2	A	1700	-156	58	10:30
		2	B	1900	-160	54	
		2	C	1600	-202	12	
		3	A	4100	-280	-66	11:00
		3	B	1800	-310	-96	
		3	C	1200	-295	-81	
	29	1	A	1500	-52	162	12:00
		1	B	870	-55	159	
		1	C	810	-49	165	
		2	A	1600	-60	154	12:30
		2	B	1400	-54	160	
		2	C	430	-50	164	
	30	1	A	1500	-125	89	9:20
		1	B	1500	-130	84	
		1	C	1400	-130	84	
21-Sep	31	1	A	70	-80	134	13:45
		1	B	57	-15	199	
		1	C	91	-20	194	
		2	A	120	-5	209	14:10
		2	B	110	-3	211	
		2	C	130	-20	194	
	32	1	A	10000	-315	-101	17:15
		1	B	12000	-320	-106	
		1	C	1900	-292	-78	
		2	A	3300	-350	-136	17:45
		2	B	8100	-345	-131	
		2	C	15000	-342	-128	
	33	1	A	71	-58.6	155.4	14:45
		1	B	93	-57	157	
		1	C	790	-67	147	

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		2	A	290	-51	163	15:10
		2	B	260	-53	161	
		2	C	360	-56	158	
		3	A	300	-69	145	15:40
		3	B	260	-70	144	
		3	C	380	-70	144	
22-Sep	34	1	A	3800	-220	-6	16:25
		1	B	5800	-230	-16	
		1	C	4700	-205	9	
		2	A	2500	-120	94	16:45
		2	B	1500	-140	74	
		2	C	1300	-106	108	
		3	A		-300	-86	
		3	B		-310	-96	
		3	C		-340	-126	
	35	1	A	26	-70	144	17:15
		1	B	230	-90	124	
		1	C	170	-60	154	
		2	A	530	-68	146	17:40
		2	B	670	-92	122	
		2	C	650	-105	109	
23-Sep	36	1	A	120	0.8	214.8	14:45
		1	B	81	-1	213	
		1	C	210	-5.6	208.4	
		2	A	260	-60	154	15:15
		2	B	220	-51	163	
		2	C	220	-61	153	
22-Sep	37	1	A	650	-35	179	18:30
		1	B	520	-28	186	
		1	C	250	-74	140	
		2	A	310	-41	173	18:50
		2	B	360	-46	168	
		2	C	350	-56	158	
23-Sep	38	1	A	76	25	239	16:15
		1	B	47	30	244	
		1	C	32	15	229	
		2	A	370	27	241	16:40
		2	B	450	26	240	
		2	C	100	20	234	
	39	1	A	190	35	249	19:00
		1	B	120	15	229	
		1	C	200	22	236	
		2	A	60	21	235	19:25
		2	B	120	24	238	
		2	C	81	46	260	
	40	1	A	1100	-190	24	13:00

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		1	B	2100	-185	29	
		1	C	1200	-200	14	
		2	A	330	-155	59	13:25
		2	B	470	-160	54	
		2	C	770	-165	49	
		3	A	420	-65	149	13:50
		3	B	570	-60	154	
		3	C	490	-60	154	
		4	A		-120	94	
		4	B		-122	92	
		4	C		-140	74	
24-Sep	41	1	A	44	72	286	9:45
		1	B	89	68	282	
		1	C	58	85.2	299.2	
		2	A	65	76.3	290.3	10:15
		2	B	83	80.6	294.6	
		2	C	85	72.8	286.8	
	42	1	A	440	22	236	11:45
		1	B	340	16	230	
		1	C	150	20.1	234.1	
24-Sep	43	1	A	170	-100	114	17:50
		1	B	330	-88	126	
		1	C	230	-103	111	
		2	A	84	-56.7	157.3	18:20
		2	B	240	-53	161	
		2	C	510	-49	165	
	44	1	A	1800	-128	86	14:50
		1	B	1100	-130	84	
		1	C	1000	-118	96	
		2	A	91	37.9	251.9	15:15
		2	B	82	29.1	243.1	
		2	C	120	42	256	
	45	1	A	2400	-130	84	15:30
		1	B	1900	-130	84	
		1	C	2600	-125	89	
		2	A	320	10	224	16:00
		2	B	510	18	232	
		2	C	430	25	239	
29-Sep	46	1	A	2200	-205	9	10:30
		1	B	2400	-210	4	
		1	C	2600	-199.7	14.3	
		2	A	840	-262	-48	11:00
		2	B	1000	-270	-56	
		2	C	1300	-230	-16	
		3	A	1300	-251	-37	11:30
		3	B	1300	-250	-36	

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		3	C	790	-230	-16	
	47	1	A	630	-153	61	12:10
		1	B	750	-152	62	
		1	C	620	-165	49	
		2	A	1000	-250	-36	12:40
		2	B	1300	-248	-34	
		2	C	650	-75	139	
	48	1	A	1900	-260	-46	14:50
		1	B	2100	-255	-41	
		1	C	4200	-261	-47	
		2	A	3700	-222	-8	15:20
		2	B	1600	-216	-2	
		2	C	3000	-246	-32	
	49	1	A	2500	-284	-70	16:30
		1	B	2300	-281	-67	
		1	C	720	-296	-82	
30-Sep	50	1	A	1600	-92	122	11:00
		1	B	2200	-90	124	
		1	C	2700	-76	138	
		2	A	1000	-85	129	11:30
		2	B	790	-81	133	
		2	C	1500	-89	125	
	51	1	A	10000	-261	-47	12:10
		1	B	12000	-263	-49	
		1	C	5800	-255	-41	
		2	A	3600	-117	97	12:40
		2	B	4700	-120	94	
		2	C	4500	-81	133	
	52	1	A	9200	-240	-26	13:10
		1	B	14000	-250	-36	
		1	C	7600	-243	-29	
		2	A	2200	-181	33	13:15
		2	B	2200	-172	42	
		2	C	3800	-176	38	
4-Nov	53	1	A	6300	-126	88	10:00
		1	B	8200	-150	64	
		1	C	5800	-161	53	
		2	A	11000	-182	32	10:30
		2	B	8400	-180	34	
		2	C	7700	-184	30	
	54	1	A	6900	-332	-118	11:30
		1	B	13000	-340	-126	
		1	C	12000	-336	-122	
		2	A	10000	-305	-91	12:00
		2	B	23000	-345	-131	
		2	C	29000	-350	-136	

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
5-Nov	55	1	A	6100	-134	80	7:00
		1	B	6200	-126	88	
		1	C	4100	-128	86	
		2	A	3100	-16.8	197.2	7:35
		2	B	7300	-111	103	
		2	C	6700	-121	93	
	56	1	A	19000	-288	-74	8:45
		1	B	16000	-334	-120	
		1	C	20000	-327	-113	
		2	A	18000	-331	-117	9:20
		2	B	8800	-336	-122	
		2	C	17000	-335	-121	
	57	1	A	3800	-67	147	10:15
		1	B	4300	-106	108	
		1	C	5600	-91	123	
6-Nov	58	1	A	1100	-175	39	7:10
		1	B	1300	-227	-13	
		1	C	2100	-218	-4	
		2	A	750	-71	143	7:35
		2	B	2200	-304	-90	
		2	C	2100	-291	-77	
	59	1	A	1100	-116	98	8:00
		1	B	3200	-240	-26	
		1	C	2100	-211	3	
		2	A	1700	-250	-36	8:35
		2	B	1600	-270	-56	
		2	C	1500	-262	-48	
	60	1	A	1600	-237	-23	10:00
		1	B	2500	-235	-21	
		1	C	1800	-230	-16	
		2	A	1500	-286	-72	10:30
		2	B	1800	-260	-46	
		2	C	1400	-263	-49	
		3	A	2500	-313	-99	11:05
		3	B	1000	-290	-76	
		3	C	2400	-289	-75	
30-Nov	61	1	A	3600	-230	-16	11:45
		1	B	1200	-196	18	
		1	C	1100	-218	-4	
		2	A	3500	-270	-56	12:00
		2	B	4900	-240	-26	
		2	C	3900	-261	-47	
		3	A	3200	-220	-6	12:15
		3	B	3300	-200	14	
		3	C	3200	-226	-12	
2-Dec	62	1	A	3300	-225	-11	11:00

Date	Station #	Transect #	Sub-sample #	Sulfide µM	Eh mV	Eh mV_{NHE}	Time DST/AST
		1	B	2900	-221	-7	
		1	C	2000	-196	18	
		2	A	1900	-216	-2	11:15
		2	B	1500	-205	9	
		2	C	1000	-210	4	
30-Nov	63	1	A	120	45	259	11:00
		1	B	130	15	229	
		1	C	20	30	244	
2-Dec	64	1	A	2500			13:00
		1	B	2300			
		1	C	1700			
3-Dec	64	1	A	1300	-192	22	9:30
		1	B	1400	-186	28	
		1	C	1400	-198	16	
		2	A	990	-210	4	10:00
		2	B	830	-200	14	
		2	C	1100	-176	38	
8-Dec	65	1	A	1100	-272	-58	9:30
		1	B	1000	-268	-54	
		1	C	1300	-241	-27	
		2	A	740	-229	-15	10:15
		2	B	780	-236	-22	
		2	C	680	-216	-2	

Appendix 2. Sediment geochemical data from SCUBA-diver collected cores in Tracadie Bay in August 1998, under and near blue mussel culture lines. Asterisks indicate reference locations away from the mussel lines.

Date	Sample #	Latitude	Longitude	Eh, mV	Eh_{NHE}	Sulfide µM
18-08-98	1A	46 24 30	62 59 26	-323.3	-119.3	28000
	1B			-378.3	-174.3	19000
	1C			-361.8	-157.8	14000
	2A	46 24 30	62 59 26	-284.3	-80.3	18000
	2B			-335.4	-131.4	12000
	2C			-365.9	-161.9	6200
	3A *	46 24 23	62 58 36	-283.6	-79.6	1600
	3B *			-246.2	-42.2	1200
	3C *			-168.2	35.8	1500
	4A	46 24 16	62 58 39	-374.4	-170.4	1100
	4B			-337.4	-133.4	1100
	4C			-322.6	-118.6	630
	5A *	46 24 30	62 59 33	-360.5	-156.5	5800
	5B *			-357.8	-153.8	1500
	5C *			-344.7	-140.7	4200
19-08-98	6A *	46 22 55	63 02 01	-320.9	-116.9	35000
	6B *			-303.6	-99.6	8700
	6C *			-280.5	-76.5	6400
	7A	46 22 54	63 01 52	-288.6	-84.6	7800
	7B			-306	-102	9900
	7C			-276.4	-72.4	1300
	8A *	46 21 54	62 59 17	-274.4	-70.4	4200
	8B *			-320	-116	4600
	8C *			-180	24	180
	9A	46 21 55	62 59 16	-328.8	-124.8	2100
	9B			-228	-24	1100
	9C			-268	-64	1200
	10A	46 22 44	62 59 36	-351.9	-147.9	3600
	10B			-371	-167	2000
	10C			-384	-180	12000
20-08-98	11A	46 23 51	63 00 00	-365.5	-161.5	4900
	11B			-350.8	-146.8	20000
	11C			-370.9	-166.9	29000
	12A *	46 23 53	63 00 06	-307.2	-103.2	5800
	12B *			-328.4	-124.4	5400
	12C *			-413	-209	7900
	13A	46 23 55	63 00 15	-348.7	-144.7	3800
	13B			-323.6	-119.6	10000
	13C			-343	-139	11000
	14A *	46 22 29	62 59 40	-351.4	-147.4	16000
	14B *			-323.6	-119.6	11000
	14C *			-336.8	-132.8	11000
	15A	46 22 53	62 59 58	-363.8	-159.8	13000

Date	Sample #	Latitude	Longitude	Eh, mV	Eh_{NHE}	Sulfide µM
	15B			-375.9	-171.9	14000
	15C			-357.2	-153.2	21000
	16A	46 21 52	63 01 34	-337.3	-133.3	11000
	16B			-337.2	-133.2	13000
	16C			-329.6	-125.6	14000
	17A *	46 22 57	63 00 34	-337.3	-133.3	45000
	17B *			-316.4	-112.4	19000
	17C *			-348.5	-144.5	13000
	18A	46 23 51	62 59 03	-405.8	-201.8	20000
	18B			-362.5	-158.5	28000
	18C			-366.6	-162.6	57000

Attached is an insert for the following report. Please attached to this report:

Martin, J.L., K. Haya (editors). 1999. Proceedings of the Sixth Canadian Workshop on Harmful Marine Algae
Canadian technical report of fisheries and aquatic sciences 2261

Figure 1. Eastern New Brunswick

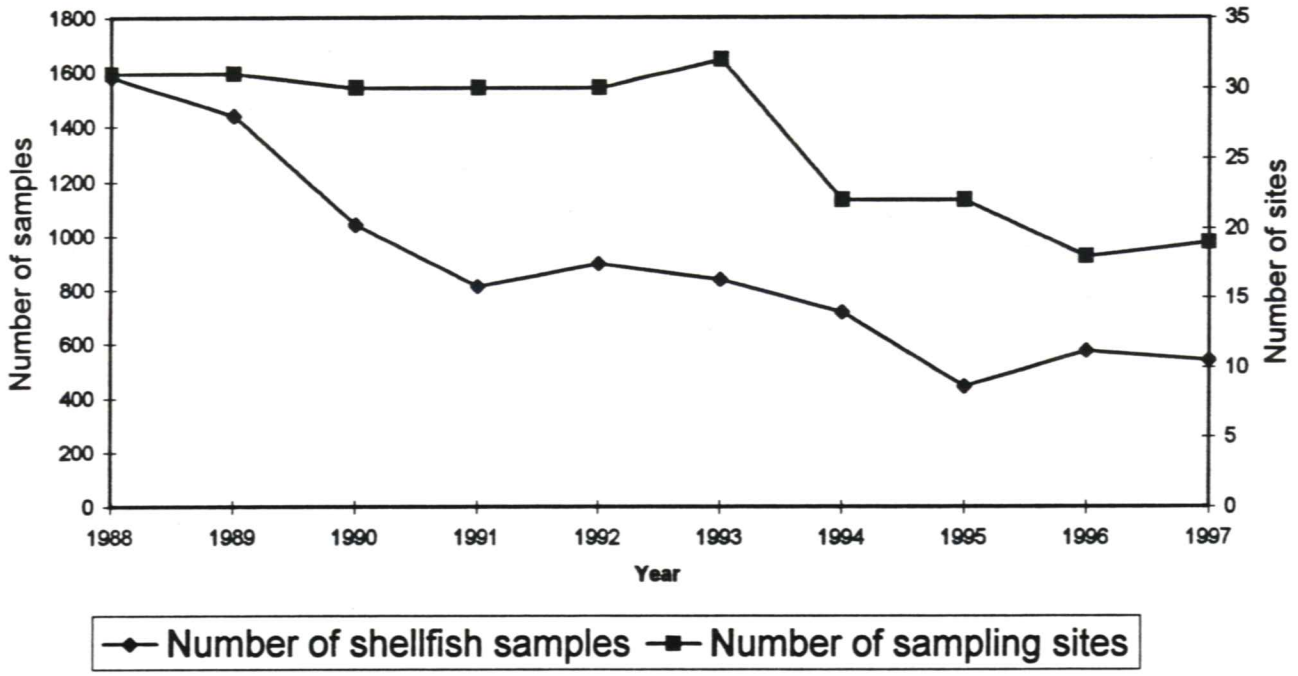


Figure 2. Prince Edward Island

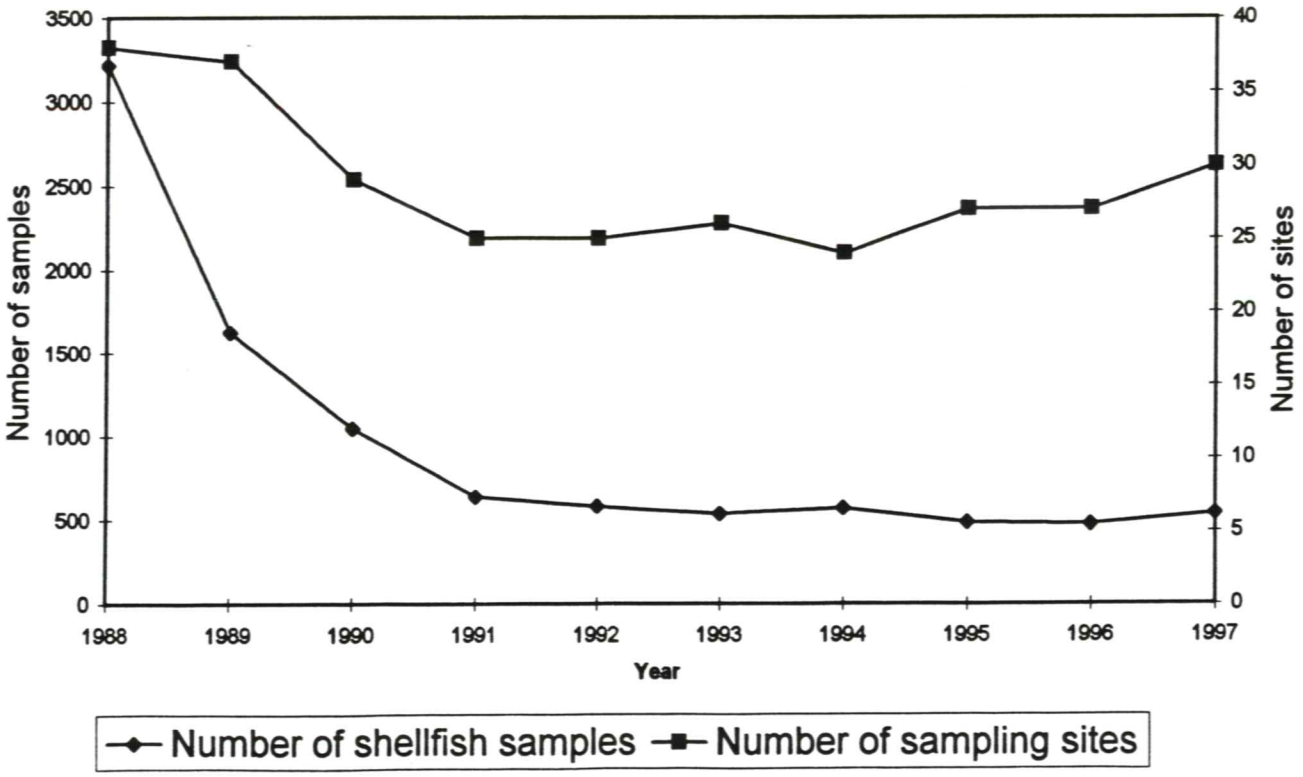


Figure 3. Gulf side of Nova Scotia

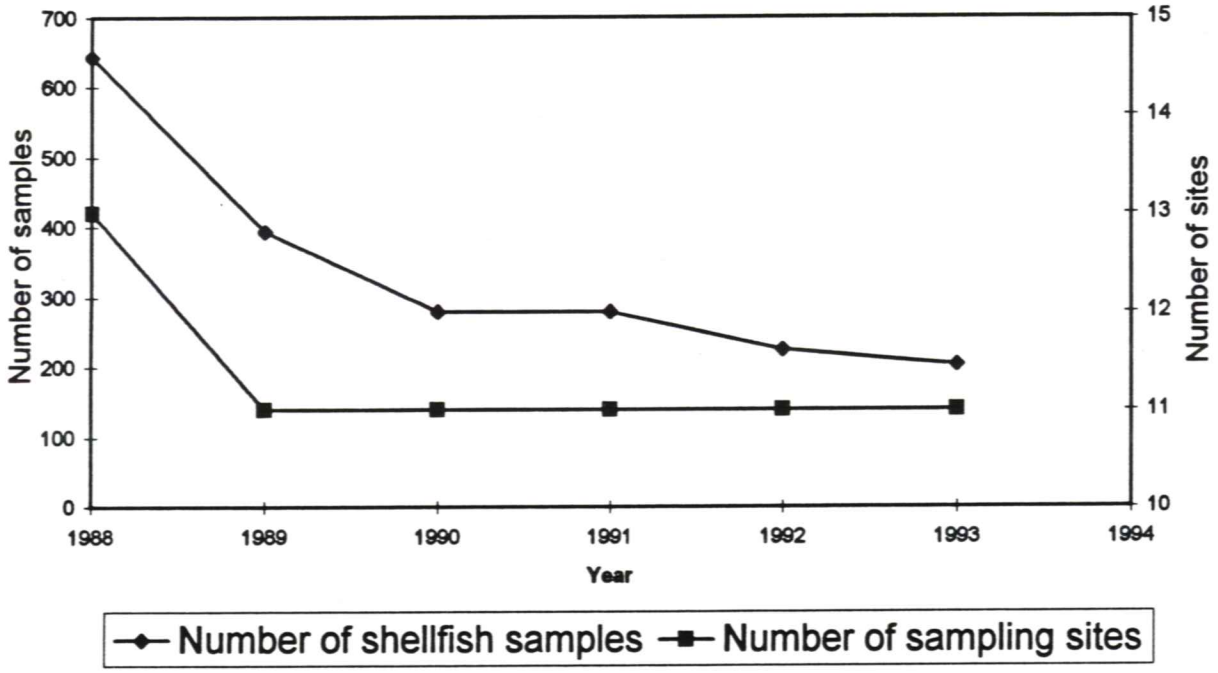


Figure 4. Southwest New Brunswick

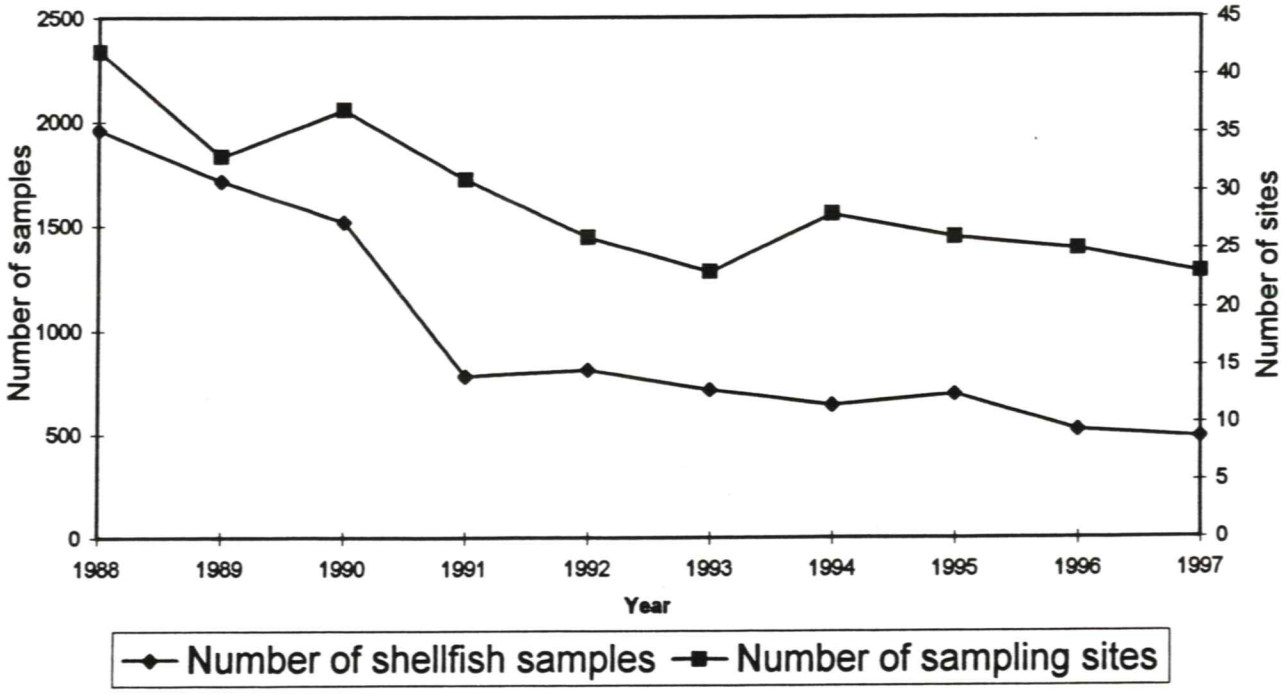


Figure 5. Total number of shellfish samples from New Brunswick and PEI

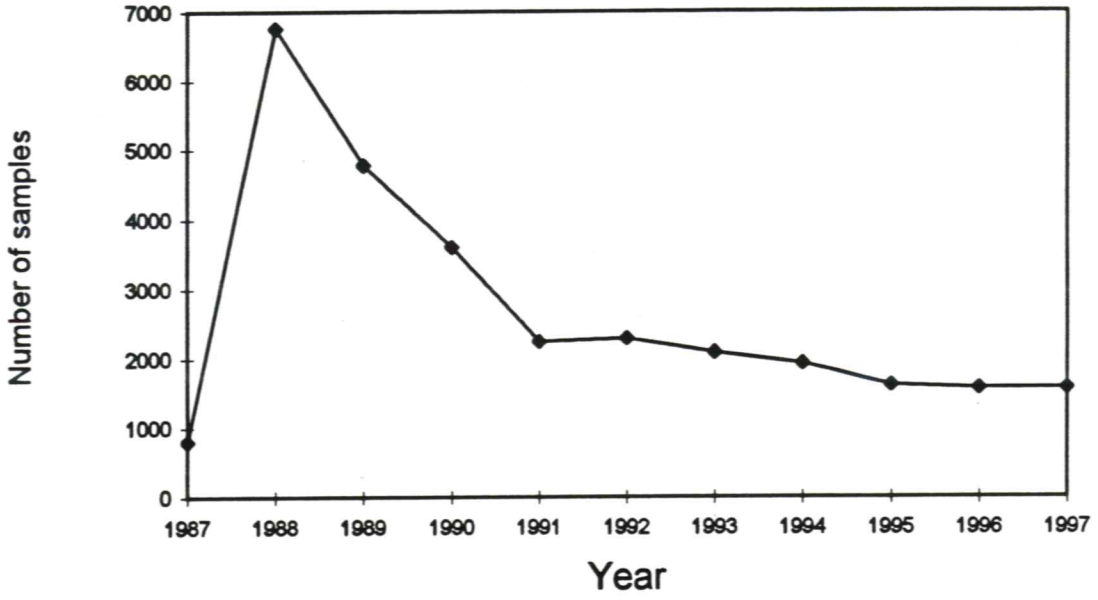


Figure 6. Phytoplankton Monitoring

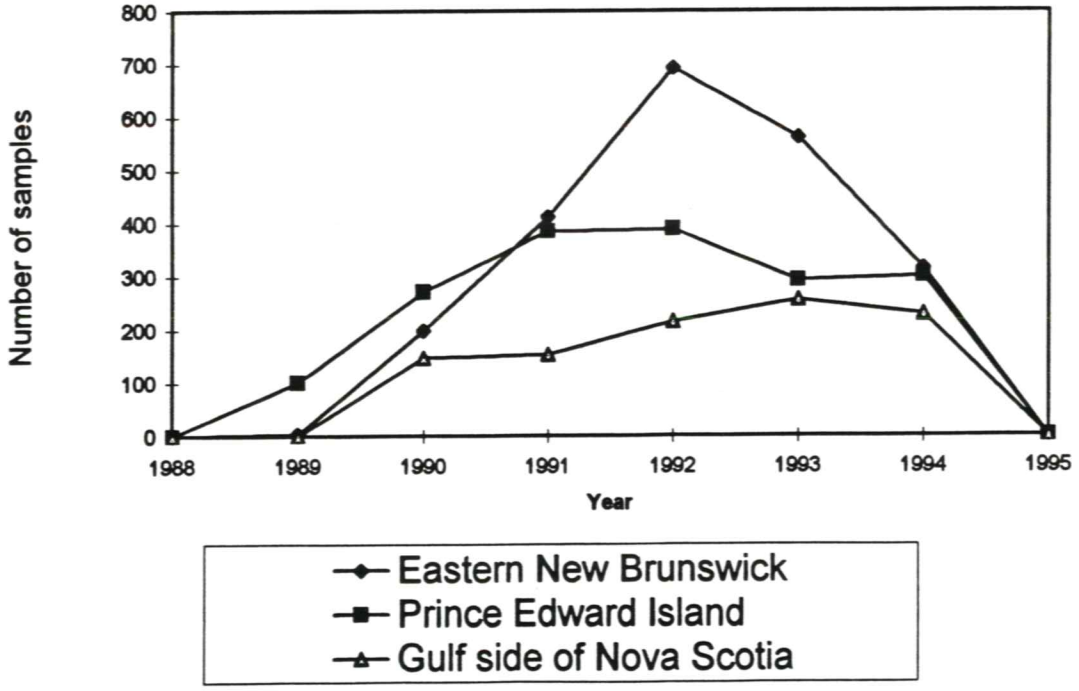
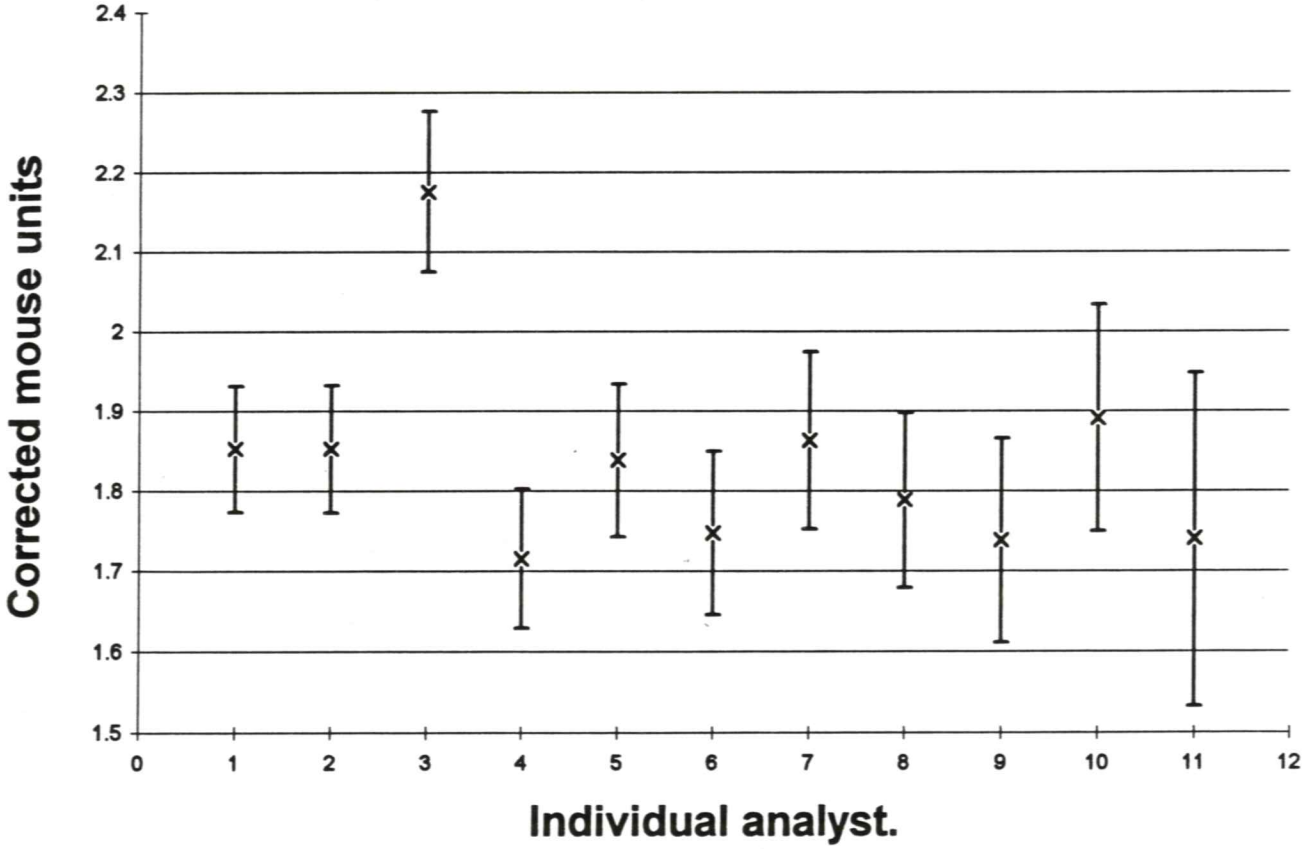


Figure 1. Mean and confidence interval (95%) for all analysts. Ranked by precision.



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