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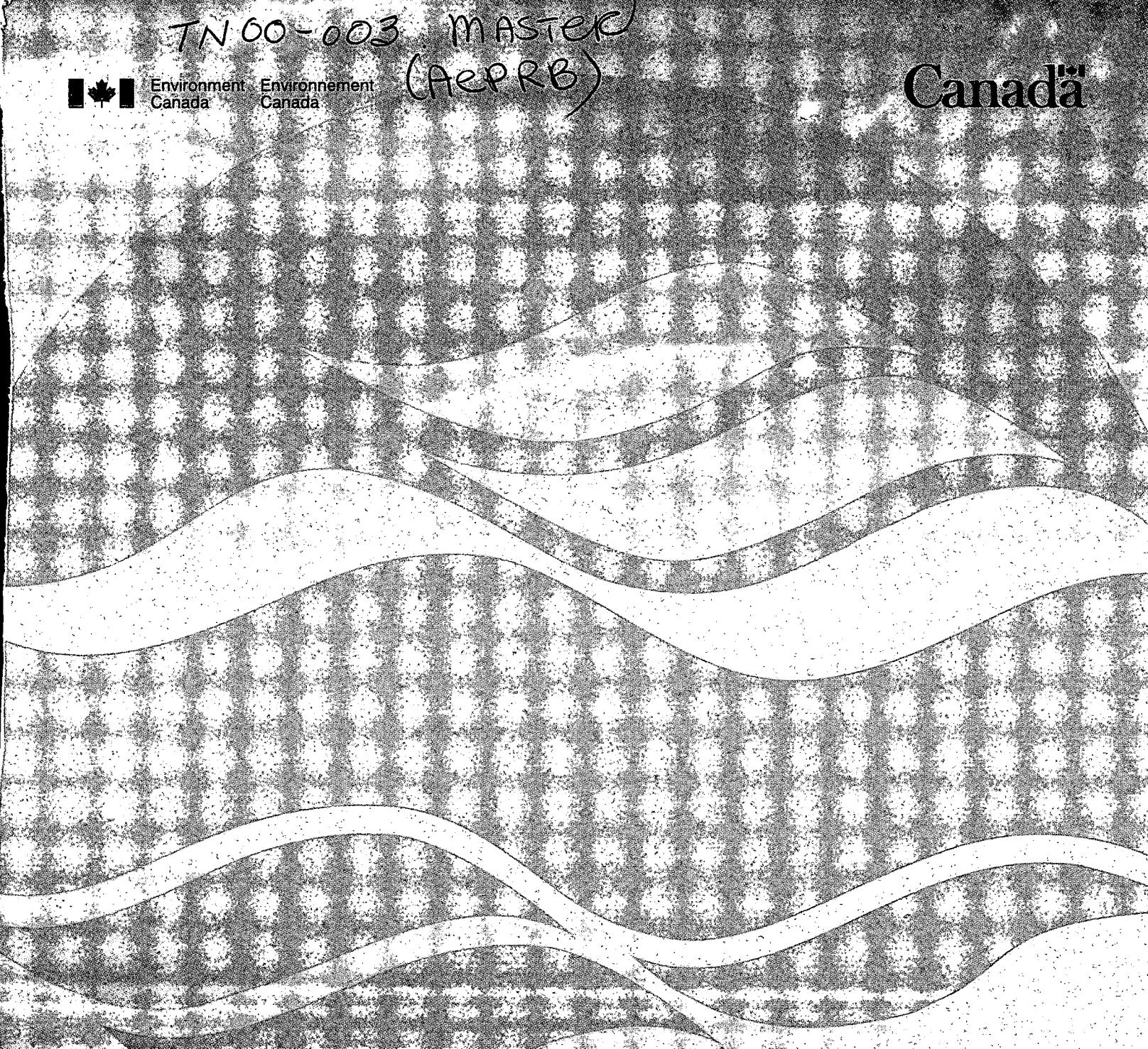

RESULTS OF THE 1998-1999 SURVEY FOR THE OCCURRENCE OF THE NEW ANTIFOULING COMPOUND IRGAROL 1051 IN THE CANADIAN AQUATIC ENVIRONMENT

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by

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MANAGEMENT PERSPECTIVE

Tributyltin (TBT), an antifouling agent, is perhaps the most toxic chemical that has ever been deliberately introduced into the aquatic environment. Irgarol 1051 is a new antifouling biocide intended to replace TBT. A national survey for the presence of Irgarol 1051 in water and sediment took place in 1998 and 1999. It was designed to determine the ambient concentration levels of Irgarol and its stable degradation product M1 in the Canadian freshwater and marine environment. Irgarol was not found in Canada. A review of the literature dealing with the occurrence and toxicity of Irgarol was incorporated into this report to assist those interested in more detail on Irgarol 1051.

SOMMAIRE À L'INTENTION DE LA DIRECTION

L'agent antisalissure tributylétain (TBT) est peut-être l'agent chimique le plus toxique délibérément introduit dans l'environnement aquatique. L'Irgarol 1051 est un nouveau biocide antisalissure destiné à remplacer le TBT. En 1998 et en 1999, on a effectué un relevé national pour déceler la présence de l'Irgarol 1051 dans l'eau et les sédiments, de façon à déterminer les teneurs ambiantes d'Irgarol et de son produit de dégradation stable, le M1, dans les milieux dulcicoles et marins du Canada; les résultats étaient négatifs. On n'a pas décelé la présence d'Irgarol au Canada. Pour plus de précisions sur l'Irgarol 1051, on peut consulter une étude de la documentation incorporée au rapport, qui porte sur l'occurrence et la toxicité de ce produit.

ABSTRACT

A survey for the occurrence of the new antifouling compound Irgarol 1051 and its stable degradation product M1 in Canadian freshwater and marine environments in 1998 and 1999 was conducted. It is possible that Irgarol 1051 may be used as an antifoulant as TBT is phased out. This report, based on research and monitoring data from the National Water Research Institute, Okayama University, Japan, and summarized literature data, was prepared to provide regulatory agencies with background information and references. In this survey, four large ports (Vancouver, Toronto, Montreal, Halifax) and many small ports and marinas were sampled in an attempt to obtain background information which could assist federal and provincial agencies in the management of new antifouling chemicals. The main conclusion of this survey is that as of 1999 the Canadian aquatic ecosystem has not been contaminated by Irgarol 1051.

RÉSUMÉ

En 1998 et 1999, on a effectué un relevé afin de rechercher la présence du nouveau composé antisalissure Irgarol 1051 et de son produit de dégradation stable, le M1, dans les milieux dulçaquicoles et marins. Il est possible qu'on utilise l'Irgarol 1051 comme agent antisalissure pour remplacer le TBT, en voie d'élimination graduelle. On a rédigé ce rapport, basé sur des données de recherche et de surveillance de l'Institut national de recherche sur les eaux et de l'Université Okayama (Japon), ainsi que sur des sommaires de données de la documentation, afin de fournir aux organismes réglementaires des informations sur le milieu et des références. Dans ce relevé, on présente les résultats de l'échantillonnage de quatre grands ports (Vancouver, Toronto, Montréal, Halifax) et d'un grand nombre de petits ports et de marinas, afin d'obtenir des informations sur les conditions du milieu, qui devraient être utiles pour les organismes fédéraux et provinciaux responsables de la gestion des nouveaux agents chimiques antisalissures. La principale conclusion de ce relevé est qu'en 1999, l'écosystème aquatique canadien n'était pas contaminé par l'Irgarol 1051.

INTRODUCTION

Antifouling paints are specifically designed to keep watercraft and aquatic structures free of attached aquatic organisms by continuously releasing a small and constant amount of biocide(s) to discourage the development of biofouling organisms on the surface of hulls and structures (French and Evans, 1986). Therefore, from the perspective of aquatic toxicology, antifouling biocides are toxic chemicals that are deliberately introduced into the aquatic environment in order to prevent or alleviate the problems caused by fouling organisms. For the shipping industry, effective fouling control means lower fuel costs and reduced docking time, crucial factors for a shipping company to survive in the very competitive market place (Voulvoulis *et. al.*, 1999). For example, it has been estimated that for a 250,000-ton tanker, five per cent fouling which is barely visible, could increase the fuel costs by 17 per cent (Lewis, 1997).

Prior to the recognition of the broad spectrum antifouling properties of organotin compounds and the subsequent development of the organotin self-polishing (self-controlled dissolving) copolymer in the 1970s, the effective service life for most antifouling paints rarely exceeded 12 to 18

months. With antifouling paints containing tributyltin self-polishing copolymer formulations, it is not uncommon to achieve a macrofouling-free hull for a ship for 60 or more months (Lewis, 1997). However, the outstanding antifouling performance of triorganotins had also slowed down the research for other antifouling chemicals, until in the early 1980s it was found that ultratrace concentrations of tributyltin were capable of exerting a significant impact on the aquatic ecosystem health (Bryan and Gibbs, 1991; Dahl and Blanck, 1996). This observation resulted in a renewed interest in the search for alternative biocides with more environmentally acceptable properties for use in the antifouling formulations (Voulvoulis *et. al.*, 1999). In general, there has been a trend returning to the use of copper-based antifouling formulations, but these formulations need to incorporate additional booster biocide(s) to improve their efficacy by inhibiting the primary growth of copper resistant fouling organisms such as the green alga *Enteromorpha* spp. and the brown alga *Ectocarpus* spp. (Scarlet *et al.*, 1997; Thomas, 1998).

Many antifouling booster biocides have been developed. Currently there are over 12 organic booster biocides including Irgarol that are approved for use in antifouling products marketed in the UK (Voulvoulis *et al.*, 1999). Since

these new booster biocides were introduced into antifouling paints only after restrictions were imposed on the use of organotins in the late 1980's, there has been very little and/or no monitoring of these biocides in the aquatic environment. Irgarol 1051 is probably one of the very few booster biocides that has received some monitoring attention. Irgarol is highly effective against both freshwater and marine algae, making it an ideal booster biocide to broaden the effective range of the copper-based antifouling paints. Irgarol belongs to the s-triazine group of compounds which act as photosystem-II (PSII) inhibitors, with the inhibition of photosynthetic electron capture transport in chloroplasts as their biochemical mode of action (Dahl and Blanck, 1996).

With the widespread occurrence of Irgarol in European and Asian aquatic environments, it would seem appropriate to anticipate the inevitable introduction of Irgarol 1051 into the Canadian aquatic environment through foreign ships painted with Irgarol containing antifouling paints and the possible import of some antifouling paints with Irgarol as an ingredient. A joint long-term study between Canada and Japan was initiated on Irgarol in 1996 to determine whether Irgarol 1051 is present in the Canadian or Japanese aquatic environment.. This report summarizes the results of our

second two-year study (1998-1999), focusing on determining the distribution of Irgarol in the dissolved phase in the Canadian aquatic environment. The first two-year Irgarol monitoring study (1996-1997) has been documented by Liu et al (1999b).

MATERIALS AND METHOD

Chemicals

Irgarol 1051 [(2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine), identification no. 84611.0] of high grade (95%) was a gift of the Ciba-Geigy Canada Ltd., Mississauga, Ontario L5M 5N3. Pesticide grade organic solvents were obtained from Caledon Laboratories, Georgetown, Ontario. The sodium sulphate used for drying organic extracts was heated to 500°C for 24 h before use. All glassware were rinsed with pesticide grade solvents before use. All other chemicals used in the experiments were reagent grade or better.

Sampling Sites

In this two-year (1998-1999) Canadian survey, subsurface water samples were collected from four large ports (Vancouver, Toronto, Montreal, Halifax) and numerous small ports and marinas, and were analyzed for Irgarol 1051 and its degradation product M1. All the four large ports have industrial establishments and busy commercial shipping activities, which would presumably contribute to the leaching of Irgarol 1051 in the Canadian aquatic environment. Detailed Irgarol 1051 sampling sites for each of the four large ports are shown in Figures 1-4. In the figures each sampling site is given a numerical number, followed by a slash. The number before the slash indicates the site number and the one after the slash denotes the water depth (in meters) at that particular site. The small ports and marinas surveyed for Irgarol included Windsor (Ontario), Port Stanley (Ontario), Hamilton (Ontario), Kingston (Ontario), Midland (Ontario), Sorel (Quebec), Miramichi (New Brunswick), Bathurst (New Brunswick), Charlottetown (P.E.I.), Pictou (Nova Scotia), Pt. Hawkesbury (Nova Scotia), Sydney (Nova Scotia), Victoria (British Columbia), Nanaimo (British Columbia), Deep Cove (British Columbia), Patricia Bay (British Columbia), Sydney (British Columbia), Esquimalt (British Columbia), and Fraser River (British Columbia).

Sample Collection and Storage

Subsurface (0.5 m depth) freshwater (i.e., river and lake water) and enclosed coastal water (i.e., harbours, bays and coves) samples were collected from a 4-m aluminium boat which had not been painted with any antifouling paint. Samples were taken using precleaned 4-L glass bottles held in a weighted stainless-steel frame fitted with a stopper and a subsurface trigger to avoid surface contamination. At least 4 bottles (4 x 4 L) of water were collected from each sampling site, and the collected samples were extracted on the day of collection.

Sample Preparation

Liquid-liquid extraction (LLE) procedure was used to extract Irgarol 1051 from the collected water samples, because of the anticipated very low ambient concentrations of Irgarol 1051 in the water samples and the resulting necessity to process a large volume of water. In brief, 4 L of the water sample were transferred to a flat-bottom 4.3-L glass bottle containing 200 mL of dichloromethane (DCM) and a 7.5-cm magnetic stirring bar. The contents

were thoroughly mixed for 30 min and then transferred to a 5-L glass separatory funnel. The extraction was repeated three times each with 200 mL of fresh DCM. For each sampling site, 16 L of water sample were processed and the pooled DCM extracts were dried through anhydrous sodium sulphate. A toluene keeper was added to the resulting extracts which were then concentrated to 5 mL on a rotary evaporator. Further concentration and solvent exchange into toluene were performed under a gentle stream of nitrogen. The toluene extract was analyzed for Irgarol 1051 and its degradation product M1 (Liu et al., 1997) by GC-NPD and GC-MS. Under such conditions detection limits for Irgarol 1051 in natural water samples are generally in the order of 1-2 ng/L.

Chemical Analysis

The toluene extracts were analyzed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a nitrogen-phosphorus detector (300°C) and a flame ionization detector (300°C) utilising an oven program with a 2-min hold at 80°C and a temperature ramp of 10°C/min to 150°C followed by a temperature ramp of 4°C/min to 280°C and a final temperature ramp of 8°C/min to 300°C. The columns used were dual DB5 coated capillary

columns (0.25 mm x 27 m) which had been installed into the injector (200°C) in the splitless mode with a constant helium carrier flow of 0.8 mL/min. Mass spectral analysis was performed using the same temperature program and column stationary phase (0.25 mm x 30 m) on a Hewlett Packard 5971A mass selective detector (MSD), and MS Chem Station. The MSD was operated in electron impact (EI) mode with an ionization potential of 70 eV and a source temperature of 190°C. The scan range was 50-500 amu and quantification of Irgarol 1051 was obtained using selective ion monitoring (SIM). Three selective ions, m/z 182, 238 and 253, were used to confirm the presence of Irgarol 1051.

Confirmation of Irgarol 1051 in the toluene extracts was based on comparing the three major ions (m/z 253, 238, and 182) with those obtained from the Irgarol 1051 standards. Quantification of Irgarol 1051 in the toluene extracts was based on the peak area of the molecular ion m/z 253.

RESULTS AND DISCUSSION

Since Irgarol 1051 has never been used in Canada before, the 1993-1994 Canadian survey for tributyltin (Chau et al., 1996; 1997) was used as a guide for the selection of sampling sites for both of our 1996-1997 and 1998-1999 Canadian survey for Irgarol 1051. Tributyltin was the most widely used antifouling agent in Canada until its use was regulated in 1989 (Chau et al., 1997). It was thought that the new antifouling biocide Irgarol 1051 could be found at sites where high concentrations of tributyltin had occurred. For example, the Irgarol sampling site of 11/5m in Figure 1 is the Vancouver Shipyards, which had a high concentration level of TBT during the 1993-1994 national survey for tributyltin.

Irgarol 1051 was not detected at any of the Canadian sampling sites during this second two-year (1998-1999) national survey for Irgarol (data not shown). A similar observation was also noted in the first two-year (1996-1997) Canadian survey for Irgarol 1051 (Liu *et al.*, 1999b). Therefore, it appears that the Canadian aquatic ecosystem is currently free from Irgarol contamination. Several reasons may explain why Irgarol was not found in the above two surveys. First, Irgarol at this time has not been registered in Canada and as a result it is unlikely that this chemical has been utilized in the

antifouling paint formulations in Canada. Second, Irgarol is a new chemical and it takes time for Irgarol to build up a detectable level in the Canadian aquatic environment. For example, Irgarol 1051 and copper based products replaced the organotins containing antifouling paints in Switzerland in 1990, but the detection of Irgarol 1051 in the Swiss aquatic environment was only accomplished in 1996 (Toth et al., 1996).

Although Irgarol has not yet been found in the Canadian aquatic environment, this does not mean that Canada will be immune from the contaminantion of Irgarol in the near future. Irgarol has aleady become widespread in the European aquatic environment (Table 1) since its introduction into Europe in the mid-1980s, a span of merely a decade between the application and its environmental detection. With its recent detection in Australian coastal waters and the Seto Inland Sea in Japan (Liu *et al.*, 1999b; Scarlet *et al.*, 1997; 1999; Voulvoulis *et al.*, 1999; Okamura *et al.*, 2000a), Irgarol could rapidly become a real global aquatic contaminant just like the organotins. Organotins were first formulated into antifouling paints in the mid-1960s (Voulvoulis *et al.*, 1999) and by late 1970s and early 1980s, in approximately a decade, their environmental occurrence and impacts on the aquatic ecosystem had become evident

(Beaumont and Newman, 1986). Therefore, it would appear that Irgarol may have a potential almost as strong as the organotins to become a true global aquatic contaminant.

Fate and transformation pathway of Irgarol 1051 in the ambient aquatic environment are not yet fully understood. A laboratory study (Liu *et al.*, 1997) showed that Irgarol resisted bacterial degradation, but the white rot fungus *Phanerochaete chrysosporium* could biotransform Irgarol via N-dealkylation at the cyclopropylamino group. This would result in the formation of the metabolite M1 (2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine). Chemical degradation of Irgarol by mercuric chloride appeared to follow the reaction of a catalyzed hydrolysis (Liu *et al.*, 1999a), and the mechanism apparently involved the formation of bidentate chelation, which weakened the cyclopropylamino bond and resulted in the formation of a hydrolysis product M1. Since photodegradation of Irgarol by natural sunlight in sea water also led to the formation M1 (Okamura *et al.*, 1999), it can be reasonably concluded that M1 could be a major and perhaps ultimate degradation product during the biological, chemical and photo degradations of Irgarol. This deduction was supported by the very recent finding that both M1 and Irgarol have been positively identified in environmental samples

taken from the Seto Inland Sea in Japan (Okamura *et al.*, 2000a). Since the concentration levels of M1 in these samples were generally higher than those of Irgarol, it would further suggest that M1 may have an environmental persistence much greater than its parent compound Irgarol 1051.

Tables 2 and 3, as well as the study of Okamura *et al* (2000b) have amply demonstrated that both Irgarol and its degradation product M1 have a high biocidal activity againt many aquatic plants and algae. Therefore, it can be assumed that the rapid accumulation of Irgarol and M1 in the environment could have far reaching long term impacts on function of the aquatic ecosystem. When the literature data in Table 1 are compared with those in Table 4, it is evident that the ambient concentration levels of Irgarol 1051 in some localities are already high enough to negatively impact the periphyton community in the marine environment. Since the use of Irgarol in antifouling paints is inevitable and for the sake of protecting the Canadian aquatic ecosystem from Irgarol and related compounds, it would be advisable that Environment Canada have some in-house expertise on new antifouling chemicals.

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Table 1. Concentrations of Irgarol 1051 in aquatic environments (ng/L)

Locations	Regime	Ports	Marinas	Fishery habours, river, lake, sea	References
Vancouver B.C.	coastal	n.d.	n.d.		this study
Toronto, Ontario	riverine	n.d.	n.d.		this study
Montreal, Quebec	riverine	n.d.	n.d.		this study
Halifax, N.S.	coastal	n.d.	n.d.		this study
Other locations in Canada	coastal, riverine lake	n.d.	n.d.		this study
Cote d'Azur, France	coastal	5-280	110-1700		Readman *et al.*, 1993
Kent, Sussex, Hampshire UK	coastal estuarine	9-14	52-500		Gough *et al.*, 1994
Riviera, France, Monaco	coastal	13.8-264	22-640		Tolosa *et al.*, 1996b
Humber, UK	estuarine		169-682		Zhou *et al.*, 1996

Fiskeback-ski, Sweden	estuarine		30-400		Tolosa *et al.*, 1996a
Port d'Ouchy, Switzerla-nd	lake		2.5-145		Toth *et al.*, 1996
Plymouth, UK	estuarine		28-127		Scarlet *et al.*, 1997
Scheldt, Netherland	riverine, estuary			1-10	Steen *et al.*, 1997
Masnou, Ebre Delta Spain	coastal	10-325	7-325		Ferrer *et al.*, 1997a 1997b
Mizushim a Japan	coastal	n.d.-19.5			Liu *et al.*, 1999b
Seto Inland Sea Japan	coastal		n.d-264	n.d-142	Liu *et al.*, 1999b
Valencia, Spain	riverine, lake, coastal			<100	Penalva *et al.*, 1999
Queensla-nd Australia	coastal	n.d.-100 (estimated)			Scarlett *et al.*, 1999
North and Baltic Sea, Germany	coastal			11-440	Biselli *et al.*, 2000

Table 2. Irgarol 1051 toxicity to aquatic plants*

Species (ng/L)	NOEC(ng/L)	IC50 3d	IC50 5d
Anabaena flos-aquae	542	>2870	2070
Selenastrum capricornutum	652	1580	1460
Dunaliella tertiolecta	130		560
Isochrysis galbana	110		440
Skeletonema costatum	146	357	430
Chlorococcum sp.	110		420
Navicula pelliculosa	<75.6	59	136
Selenastrum capricornutum		7430	

* From literature data modified by Lenwood *et al.*, 1999.

Table 3. Effects of Irgarol 1051 on *Fucus vesiculosus**

Toxicity endpoints (ng/L)	Toxicity		
	NOEC[a]	LOEC[b]	IC50
Fertilization	800	4,000	>100,000
Germination (exposed during fertilization)	<160	160	325
Germination (exposed after fertilization)	4,000	20,000	11,400
Growth (apical hair formation)	<160	160	1,690

*Literature data modified by Lenwood *et al.*, 1999

[a]No Observed Effect Concentration, the highest concentration tested that caused no significant effect on the measured endpoint.

[b]Lowest Observed Effect Concentration, the lowest concentration tested that caused a signficant effect on the measured endpoint.

[c]Estimated by graphical interpolation.

Table 4. Effect of Irgarol 1051 on periphyton in microcosms*

Endpoint (ng/L)	Toxicity			
	NOEC	LOEC	MATC	IC50
Photosynthesis/ chlorophyll-a	16	64	32	185
Photosynthesis/ long-term	64	257	128	211
Photosynthesis/ short-term	257	824	480	1,210
Chlorophyll-a	257	1,030	514	695
Community Structure	64	257	128	1,390
Number of algal taxa	257	1,030	514	3,860

*Literature data modified by Lenwood *et al.*, 1999.

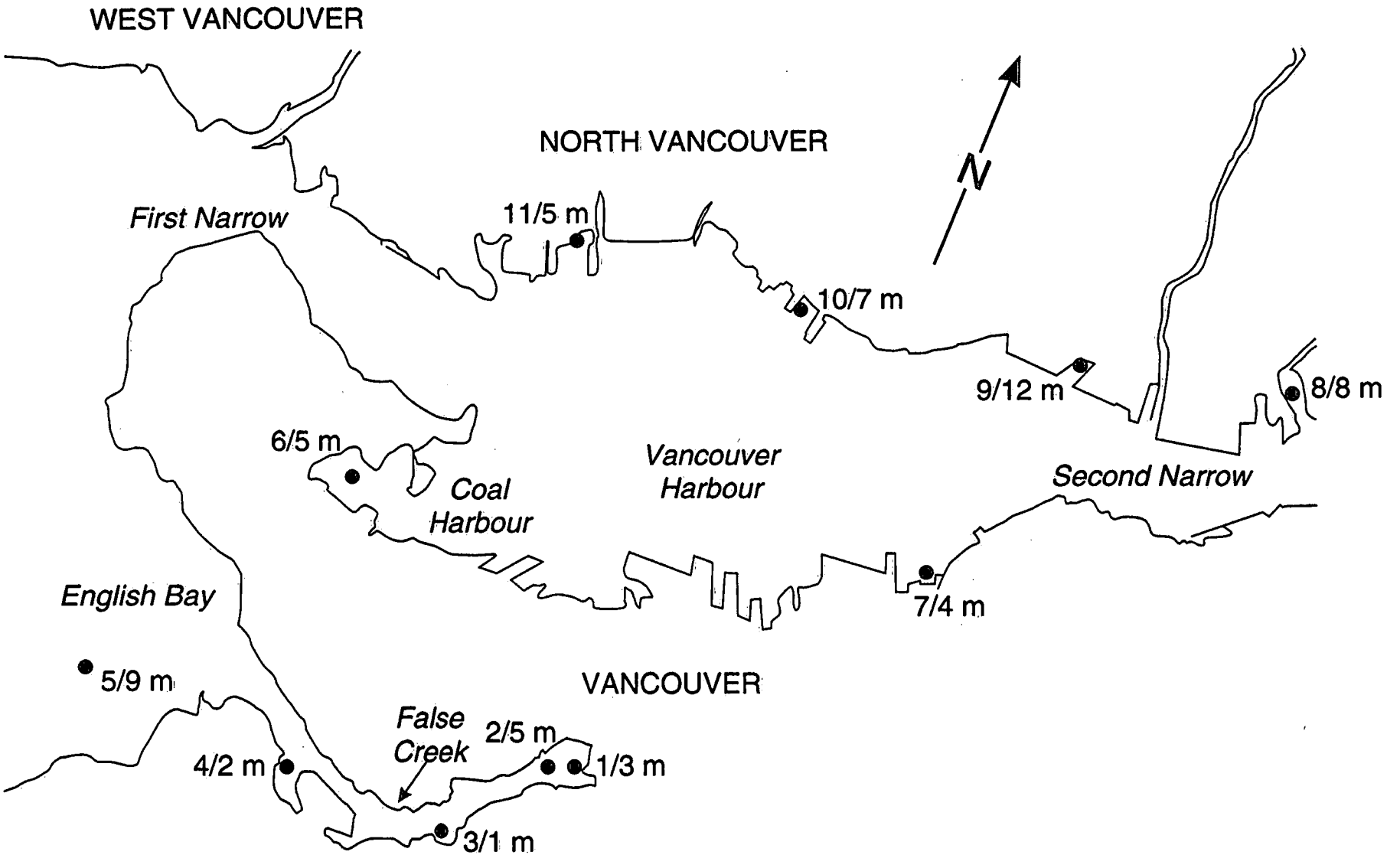
Legends

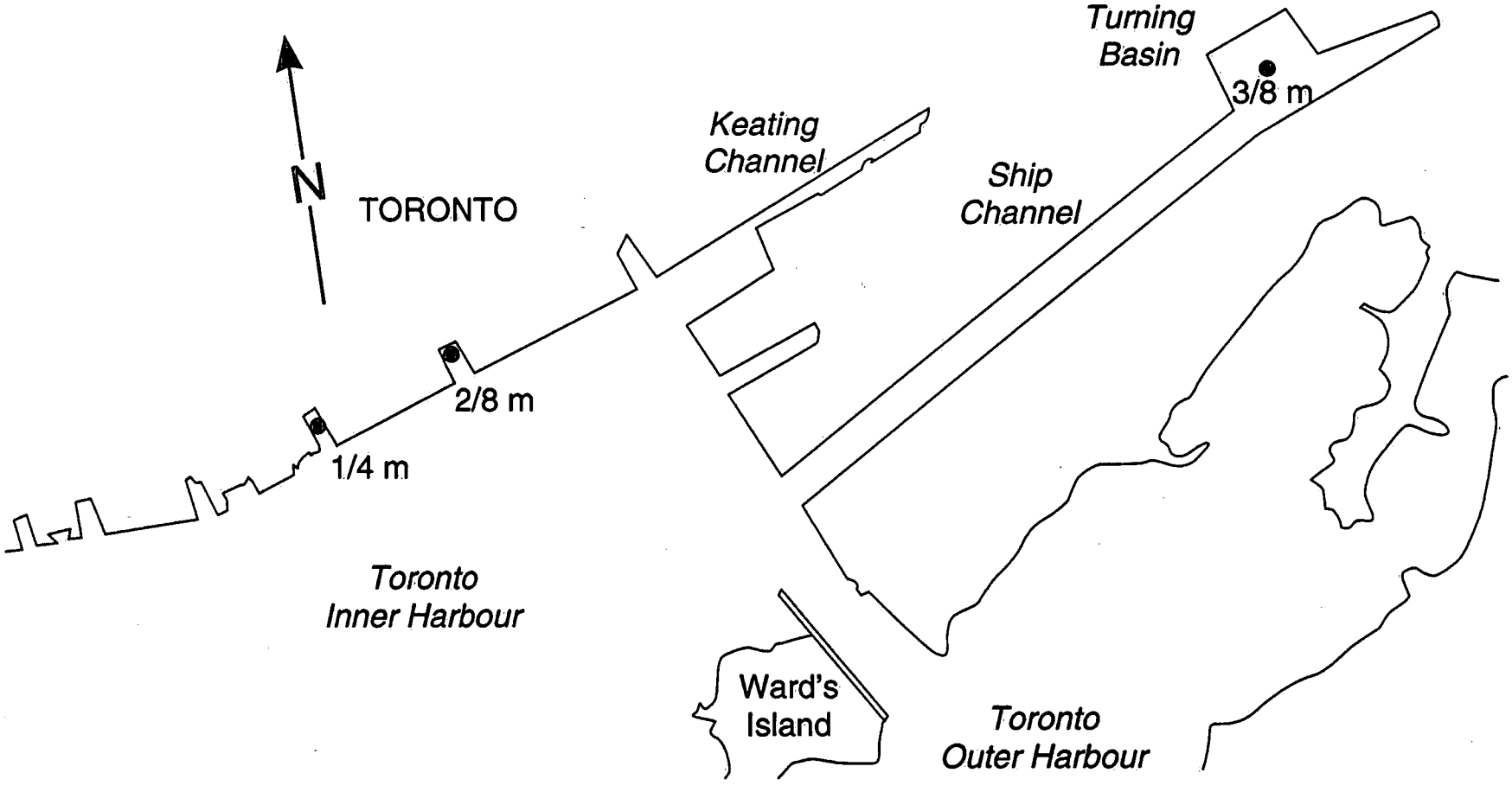
Figure 1. Location of sampling stations in Vancouver Harbour.

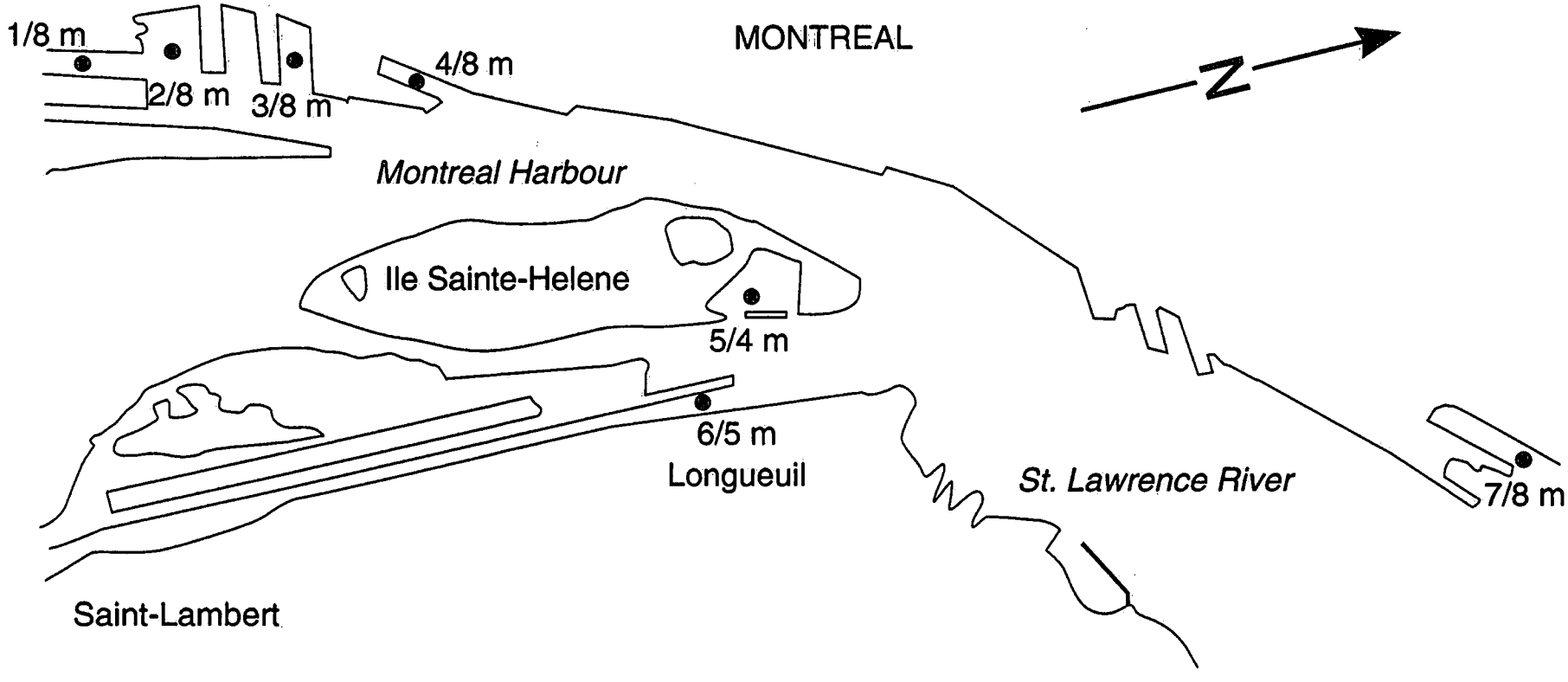
Figure 2. Location of sampling stations in Toronto Harbours.

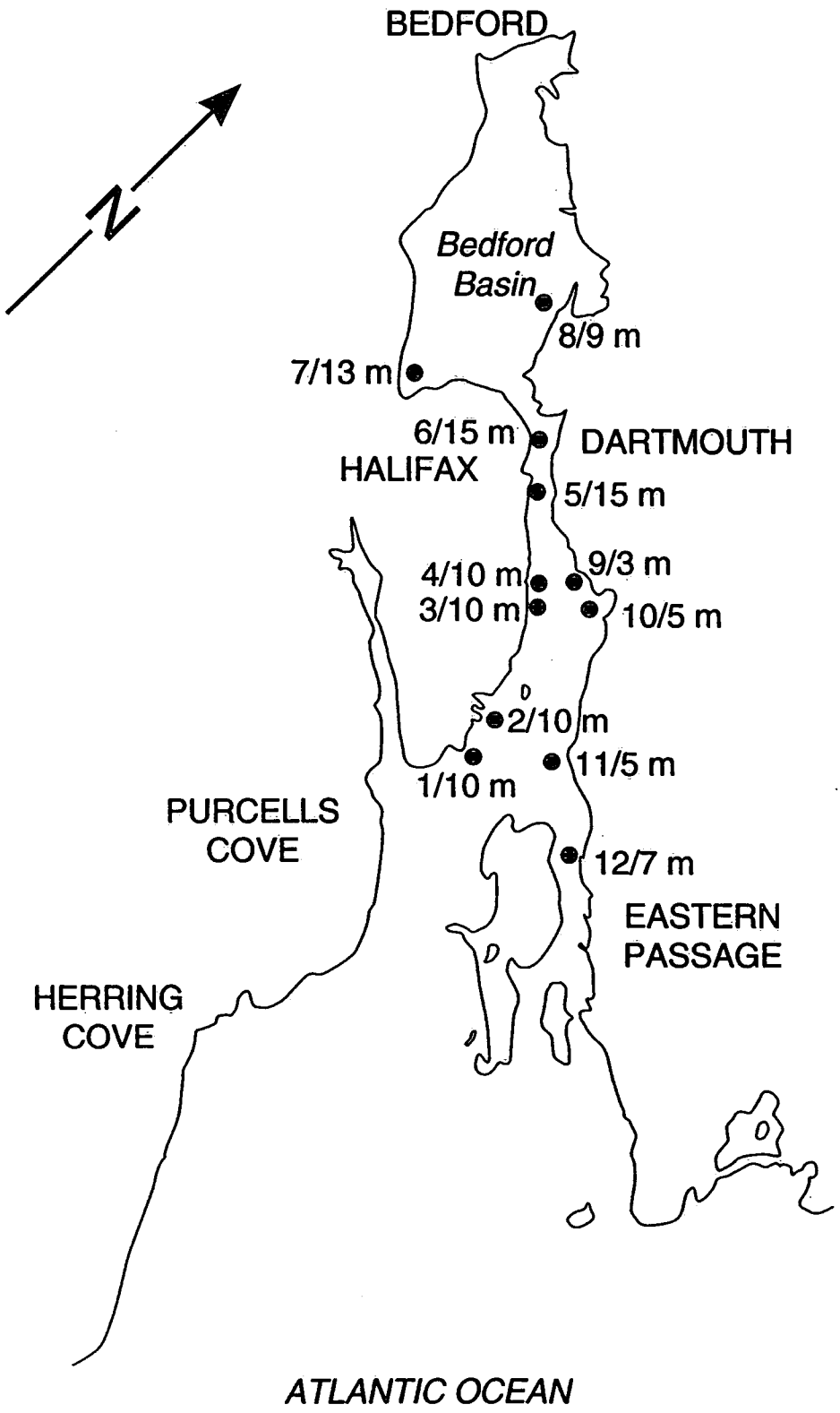
Figure 3. Location of sampling stations in Montreal Harbours.

Figure 4. Location of sampling stations in Halifax Harbours.


WEST VANCOUVER
NORTH VANCOUVER
N
First Narrow
11/5 m
10/7 m
9/12 m
8/8 m
6/5 m
Coal
Harbour
Vancouver
Harbour
Second Narrow
English Bay
7/4 m
5/9 m
VANCOUVER
False
Creek
2/5 m
4/2 m
1/3 m
3/1 m


N
TORONTO
Keating
Channel
Turning
Basin
3/8 m
Ship
Channel
2/8 m
1/4 m
Toronto
Inner Harbour
Ward's
Island
Toronto
Outer Harbour


1/8 m
2/8 m
3/8 m
4/8 m
MONTREAL
N
Montreal Harbour
Ile Sainte-Helene
5/4 m
6/5 m
Longueuil
St. Lawrence River
7/8 m
Saint-Lambert


BEDFORD
N
Bedford
Basin
8/9 m
7/13 m
6/15 m
DARTMOUTH
HALIFAX
5/15 m
9/3 m
4/10 m
3/10 m
10/5 m
2/10 m
11/5 m
1/10 m
PURCELLS
COVE
12/7 m
EASTERN
PASSAGE
HERRING
COVE
ATLANTIC OCEAN

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