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Light Hydrocarbons and the Deepwater Ocean Outfalls Offshore Sydney: Rig Seismic Survey 112

by

D. T. Heggie, D. J. Fredericks, G. P. Bickford and J. H. Bishop

AGSO Record 1997/58

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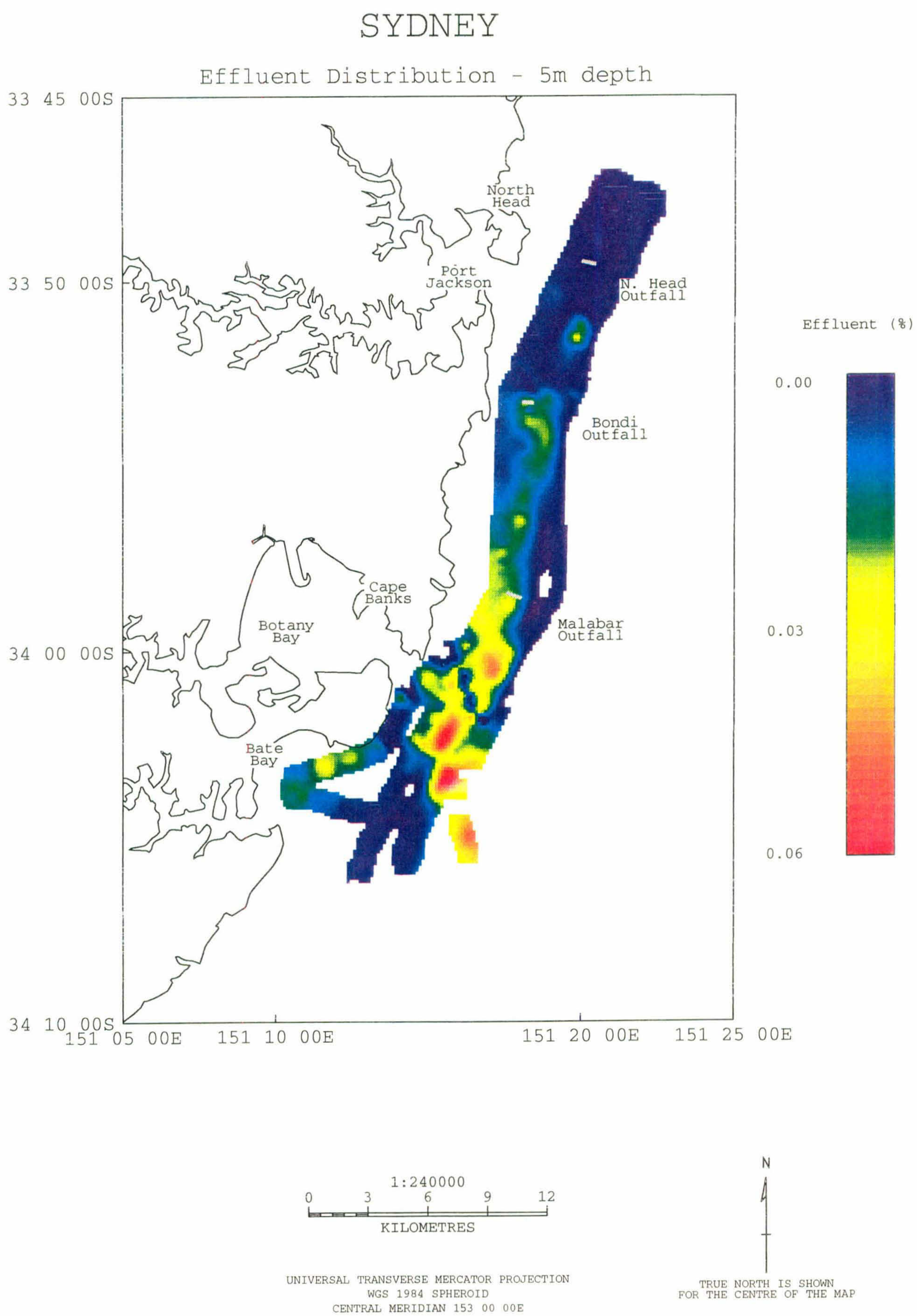

Frontispiece - map of effluent discharged from Sydney's deepwater outfalls

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Projects 121.37 and 243.02

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Australian Geological Survey Organisation

Petroleum and Marine Division

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Executive Summary

AGSO conducted a geochemical survey (Survey 112) aboard *Rig Seismic*, jointly with the Water Board (Sydney), in the coastal zone offshore Sydney during September-October 1992. An overview of the sedimentology, benthic geochemistry and light hydrocarbon geochemistry and the deepwater ocean outfalls are summarised in Heggie *et. al.* (1993). This Record documents the hydrocarbon-related results from the survey and includes contours of hydrocarbon concentrations at three depths (5 m, 25 m and 45 m) offshore Sydney and an analysis of the source of hydrocarbons found in seawater based on their geochemical and isotopic signatures.

The primary objective of this work was to evaluate the application of continuous, real-time measurements of light hydrocarbons in seawater as tracers of anthropogenic inputs to the coastal zone, notably the deepwater ocean outfalls. Total Hydrocarbon data (THC) were acquired at 30 second intervals (or at a ship speed of 5 knots every 75 m over the seafloor), and C_1 through C_8 data were acquired at 2 minute intervals (approximately every 250 m over the seafloor). Approximately 500 line-km of direct hydrocarbon detection (DHD) data were obtained during the survey, between Broken Bay and Port Hacking. Eighteen vertical profiles of light hydrocarbon concentrations in seawater were also obtained from near the ocean outfalls and near the entrances to Broken Bay, Port Jackson, Botany Bay and Port Hacking.

Methane was the predominant hydrocarbon measured in the survey area. The highest methane concentrations were found between the Malabar and North Head Ocean Outfalls, and are about fifty-fold background concentrations. Similarly, other light hydrocarbons were elevated above backgrounds indicating anthropogenic inputs to the coastal zone. The vertical distributions of hydrocarbons in the water column indicated plumes of hydrocarbons throughout the water column, with total hydrocarbon concentrations up to about ten-fold background concentrations. The distributions of

the plumes, in the vicinity of the outfalls, varied markedly over the period of a few days, indicating the control the local oceanography plays in plume dispersion.

Cross-plots of light hydrocarbon molecular compositions indicated trends in hydrocarbon composition that distinguish between hydrocarbons emanating from the ocean outfalls from those emanating from Port Jackson and Botany Bay. The ocean outfalls are characterised by high concentrations of methane and low levels of C_{2+} hydrocarbons (low percent hydrocarbon wetness). In contrast, the hydrocarbon mixtures from near the entrances of Botany Bay and Port Jackson are characterised by low methane abundances and increased abundances of C_{2+} hydrocarbons (high percent hydrocarbon wetness) notably ethane, propane and butane.

Light hydrocarbons in seawater have been shown to be sensitive tracers of anthropogenic hydrocarbon inputs to the coastal zone. These types of data, therefore, are useful in testing hydrodynamic models of sewage plume behaviour and the dispersion of the ocean outfall discharges in the coastal zone, and hence, the impact that these discharges may have on the coastal zone. Furthermore, the molecular compositions of light hydrocarbon mixtures in the coastal zone were able to distinguish at least two sources of hydrocarbons to the coastal zone: those from ocean outfall and those from estuaries. Continuous measurement of hydrocarbon concentration in seawater provides a new tool in tracing potential sources of anthropogenic materials added to the coastal zone, and hence will assist in developing monitoring strategies.

1. Introduction

The three deepwater ocean outfalls (Bondi, Malabar and North Head) discharge approximately 1000 ML/d of primary treated effluent to the sea offshore Sydney. A pilot project conducted in October 1991 (Survey 104), aboard the AGSO research vessel *Rig Seismic*, utilising the continuous geochemical tracer [CGT] capability, showed that the analysis of oceanic waters for light hydrocarbon content provides a useful method for characterising pollutants from various sources (BMR Research Newsletter, 16, 1992). These earlier trials were conducted between Botany Bay and North Head; light hydrocarbon anomalies were detected from each of the three deepwater ocean outfalls and near the entrances to estuaries. The results suggested that the molecular compositions of different hydrocarbon mixtures may be useful indicators of hydrocarbon sources mixed together in the coastal zone.

The success of that pilot survey and the implications of the results for the Water Board (Sydney) in developing environmental strategies and managing discharges into the coastal zone, lead to an investigation (Survey 112) during September-October 1992, aboard *Rig Seismic*. A summary of the scientific activities from that survey and the shipboard results, including descriptions of the sedimentology and sediment geochemistry of shelf sediments was presented in Heggie *et al.* (1993a). A preliminary interpretation of the hydrographic (conductivity, temperature, pH and dissolved oxygen content) and Total Hydrocarbon (THC) data collected on the survey were presented in Heggie *et al.* (1993b). This Record describes the distribution and geochemical signatures of light hydrocarbons in the ocean water off Sydney, including contour maps of light hydrocarbon concentrations at three depths (5 m, 25 m and 45 m).

2. Background

Light (C_1-C_4) and intermediate (C_5-C_8) hydrocarbons are present in seawater and sediments principally as a result of the following three processes.

(1) Biological processes.

Hydrocarbons are produced microbially and photochemically in seawater. In addition, during early diagenesis, a variety of hydrocarbons are produced by the activities of microbial organisms during aerobic and anaerobic destruction of organic matter which occurs primarily in the top few tens of metres of sediments. The products of these reactions include methane and minor quantities of both saturated and unsaturated hydrocarbons (Hunt, 1979; Claypool & Kvenvolden, 1983 and references cited therein). The presence of the unsaturated hydrocarbons, which are only produced biochemically (Primrose & Dilworth, 1976; Claypool & Kvenvolden, 1983), provides one criteria to distinguish between biogenic and thermogenic hydrocarbons.

These compounds produced *in-situ* generally occur in low concentrations as background hydrocarbons in seawater (Claypool & Kvenvolden, 1983). However, high concentrations of biogenically-produced hydrocarbons may accumulate in relatively shallow-buried sediments and seep into the overlying water, resulting in biogenic anomalies (Brooks *et al.,* 1974; Bernard *et al.*, 1976).

(2) Thermogenic processes.

The effect of heat on organic matter (catagenesis and metagenesis) buried to depths of several kilometres in sedimentary basins produces thermogenic hydrocarbons (Hunt, 1979; Tissot & Welte, 1984). The products of these reactions include methane and the saturated (C_2-C_8) hydrocarbons. Light hydrocarbons may migrate kilometres to permeate the near-surface sediments and seep into the overlying bottom-water resulting in thermogenic anomalies. Naturally occurring thermogenic hydrocarbon seeps are not expected offshore Sydney, but abundant C_{2+} hydrocarbons are indicators of anthropogenic hydrocarbons of a petrogenic (thermogenic) origin.

(3) Anthropogenic processes.

Human activities can introduce anthropogenically-sourced hydrocarbons into the marine environment. Anthropogenic hydrocarbons may be of a petrogenic origin e.g., ship spills, refined petroleum products and other hydrocarbons used in industrial processes and contain low abundances of methane relative to higher hydrocarbons. Anthropogenic biogenic hydrocarbons in contrast, such as those produced from urban sewage degradation are known to be characterised by abundant methane.

3. The mixing model of hydrocarbon sources

We have utilised a modified version of a molecular compositional mixing model (used in the offshore petroleum exploration industry) to investigate hydrocarbon sources offshore Sydney. One approach to defining anomalies and distinguishing between different types of sources requires that a mean background concentration be defined (either statistically or graphically), and this mean concentration is then subtracted from the measured concentrations. Because of variability in the background concentrations, this approach may be problematic, particularly where inputs are highly diluted and the anomalies are subtle.

Our approach was to initially review the data on a line-by-line basis and compare measured concentrations with the regional background. Then, a variety of hydrocarbon cross-plots were constructed, particularly methane versus percent hydrocarbon wetness (wetness % = $\sum(C_2\text{-}C_4)/\sum(C_1\text{-}C_4) \times 100$) to differentiate between biogenic and anthropogenic petrogenic sources. The rationale behind this approach (Figure 1) is that different hydrocarbon sources e.g., biogenic versus petrogenic-sourced hydrocarbons can be distinguished on the basis of their light hydrocarbon molecular compositions (Hunt, 1979; Tissot & Welte, 1984; Claypool & Kvenvolden, 1983). The background hydrocarbons in this model plot in a narrow range towards the left origin (low concentrations), while end-member source hydrocarbons plot to the right (high concentrations).

As the hydrocarbons in bottom-waters represent mixtures of the two end-members, the trends between them are indicative of the source of the hydrocarbons comprising the anomalies (Fig.1). For example, when the hydrocarbon wetness increases with increasing methane concentration, the trend indicates that the anomaly was probably derived from a petrogenic (either naturally occurring or anthropogenic) source. In contrast, increasing methane concentrations, coupled with decreasing hydrocarbon wetness, suggests that the anomaly was derived from either a 'dry' gas petrogenic source or is of a biogenic origin. This model has been utilised here to investigate the potential hydrocarbon sources offshore Sydney *ie* naturally occurring and anthropogenic biogenic sources and anthropogenic petrogenic sources. Carbon isotopic data of methane (Fuex, 1977; Bernard *et al.*, 1977), have been utilised to further investigate hydrocarbon source.

4. Objectives

The direct hydrocarbon detection (DHD) component of the survey aimed to identify and characterise the hydrocarbon signals from a number of possible sources along the Sydney coastline and to determine the origin of anthropogenic light hydrocarbon gases (whether biogenic or petrogenic). In addition, the distributions of light hydrocarbons in seawater, together with the hydrographic and oxygen data, provide a 'baseline' reference and enable the assessment of geochemical and oceanographic processes in the vicinities of ocean outfalls and where estuaries exchange with the coastal waters.

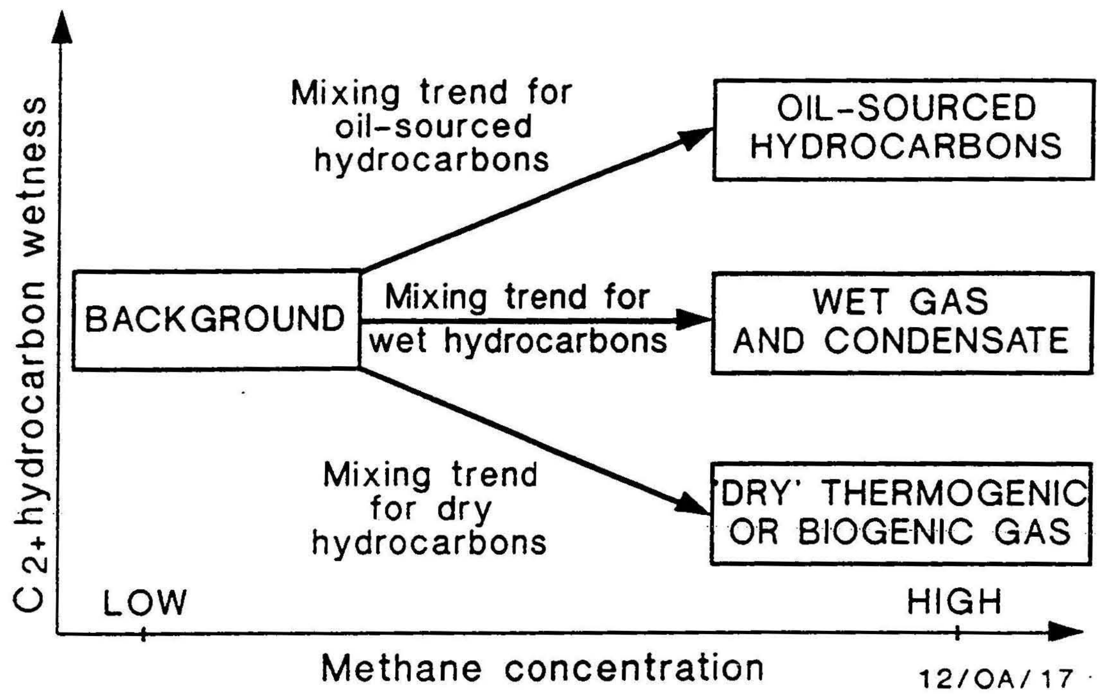


Figure 1 Cross-plot of methane versus percent hydrocarbon wetness, showing the general decrease in wetness with increasing methane for gas-prone or biogenic sources. Conversely, oil-prone sources are indicated by increasing wetness with increasing methane. Gas-condensate sources fall between the dry gas and oil-prone trends.

The objectives of the program were:

1. To determine the concentrations and distributions of light hydrocarbons entering the coastal zone from the deepwater ocean outfall sites located at North Head, Bondi and Malabar.
2. To determine the concentrations and distributions of light hydrocarbons entering the coastal zone from major estuaries including Broken Bay, Port Jackson, Botany Bay and Port Hacking.
3. To characterise the molecular and isotopic compositions of light hydrocarbons entering the coastal zone and determine whether these data can be used as tracers of hydrocarbon source.

5. Methods

A schematic of the CGT system installed on *Rig Seismic* is shown in Figure 2. The CGT system includes two different modes of data collection: Direct Hydrocarbon Detection (DHD) refers to analyses of light and intermediated hydrocarbons (C_1 through C_8) in seawater by automated gas-chromatography. SDL (Submersible Data Logger) data refers to measurement of seawater temperature, conductivity (and calculated salinity), pH, depth and dissolved oxygen with a Yeo-Kal submersible probe system.

The equipment comprises four major components (Figure 3):

1. **SDL** - Submersible Data Logger consisting of a towed fish (tow-fish) fitted with a submersible pump which delivers seawater to the geochemical laboratory on the ship via a hollow cable. A conductivity/temperature/depth sensor (CTD) in the tow-fish, measures the depth of the tow-fish as well as the temperature and salinity of the seawater. This enables the depth of sampling to be related to the depth of the thermocline, and detection of the hydrographic 'fronts' and freshwater inputs from estuaries and discharged wastewater.

2. **Cable** - A hollow cable (consisting of medical grade nylon) delivers bottom-water to the geochemical laboratory. The nylon tubing is wrapped with insulated conductors which both transmit power to the tow-fish and relay SDL and sonar data from the tow-fish and conductors. The tubing and conductors are further wrapped in a stainless steel braid with plastic fairings which are attached to the cable to reduce frictional drag, and allow the tow-fish to be towed almost directly beneath the ship.
3. **Direct Hydrocarbon Detection** The analytical equipment consists of a gas extraction unit followed by a series of gas chromatographs connected in parallel to measure the concentration of a variety of (C_1-C_8) hydrocarbons extracted from seawater (Table 1). The total hydrocarbon concentrations are measured every 30 seconds or at a ship speed of 5 knots, a distance of about 75 m on the seafloor. The light hydrocarbons (C_1-C_4) are measured at 2 minute intervals (approximately 300 m on the seafloor), whereas the C_5-C_8 hydrocarbons are measured every 8 minutes (approximately 1200 m). Sub-samples of extracted gas were taken and stored for subsequent shore-based isotopic analyses. The reported hydrocarbon concentrations are in parts per million (ppm) in the headspace (*ie* concentration of hydrocarbons in the gas removed from seawater under vacuum) and they have not been converted to seawater concentrations.
4. **Data Acquisition System.** A PC-based data processing system on which all data are displayed, edited and stored in a database for plotting at sea.

The tow-fish is deployed amidships from *Rig Seismic* so that geochemical data can be acquired concurrently with other data, such as high-resolution seismic, side-scan sonar, magnetic and gravity data. All data are recorded continuously so that any hydrocarbon anomalies in the water column can be quickly recognised and additional measurements (or samples can be collected) when appropriate.

Detector sensitivity for the GC is < 10 parts per billion in the stripped headspace sample. Calibrations were conducted on a daily basis and were within 10 % for the entire program and system blanks were less than 2 ppm for methane and 5 ppb for C_{2+} compounds.

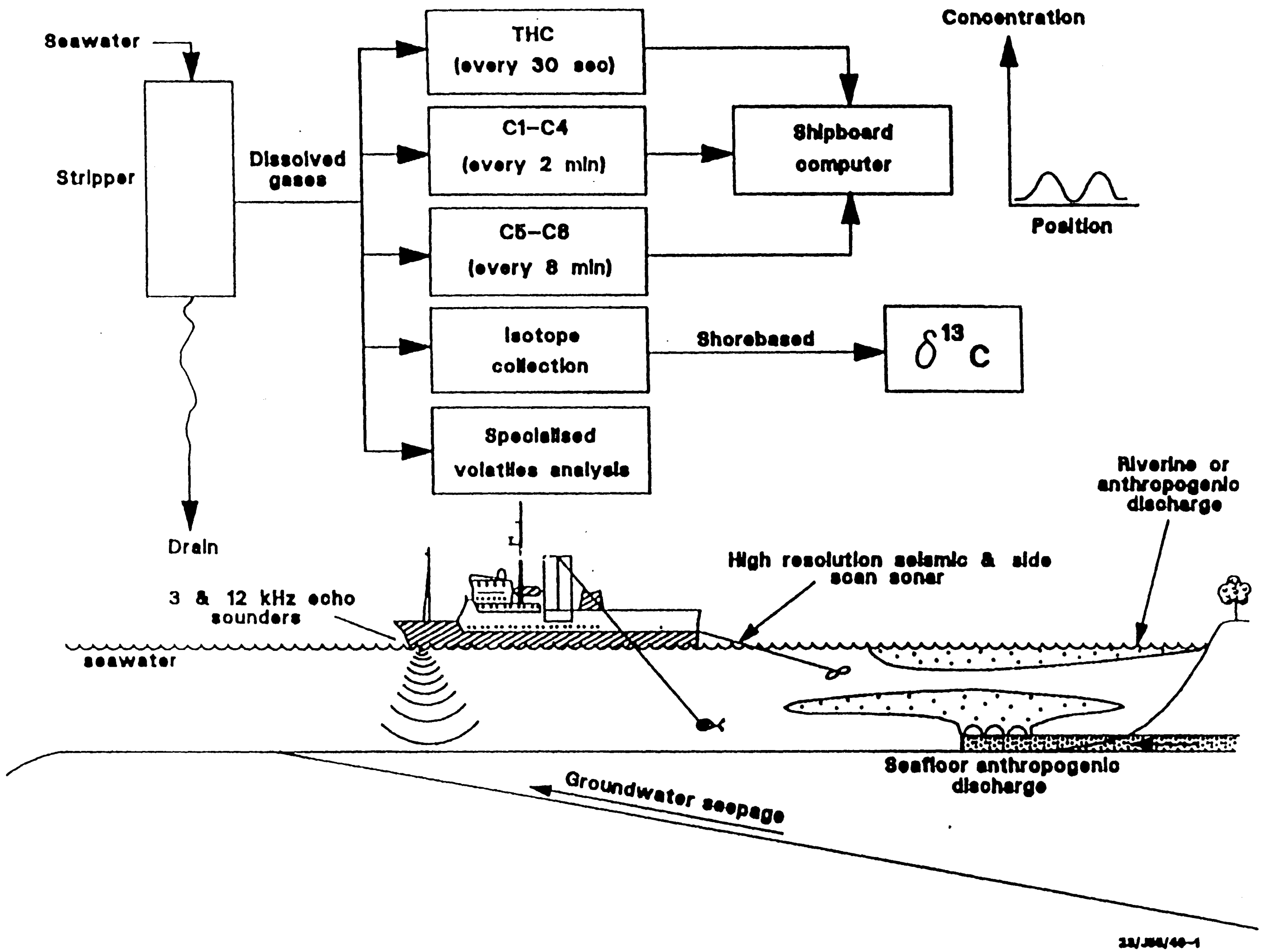


Figure 2. Schematic of the Continuous Geochemical Tracer (CGT) system.

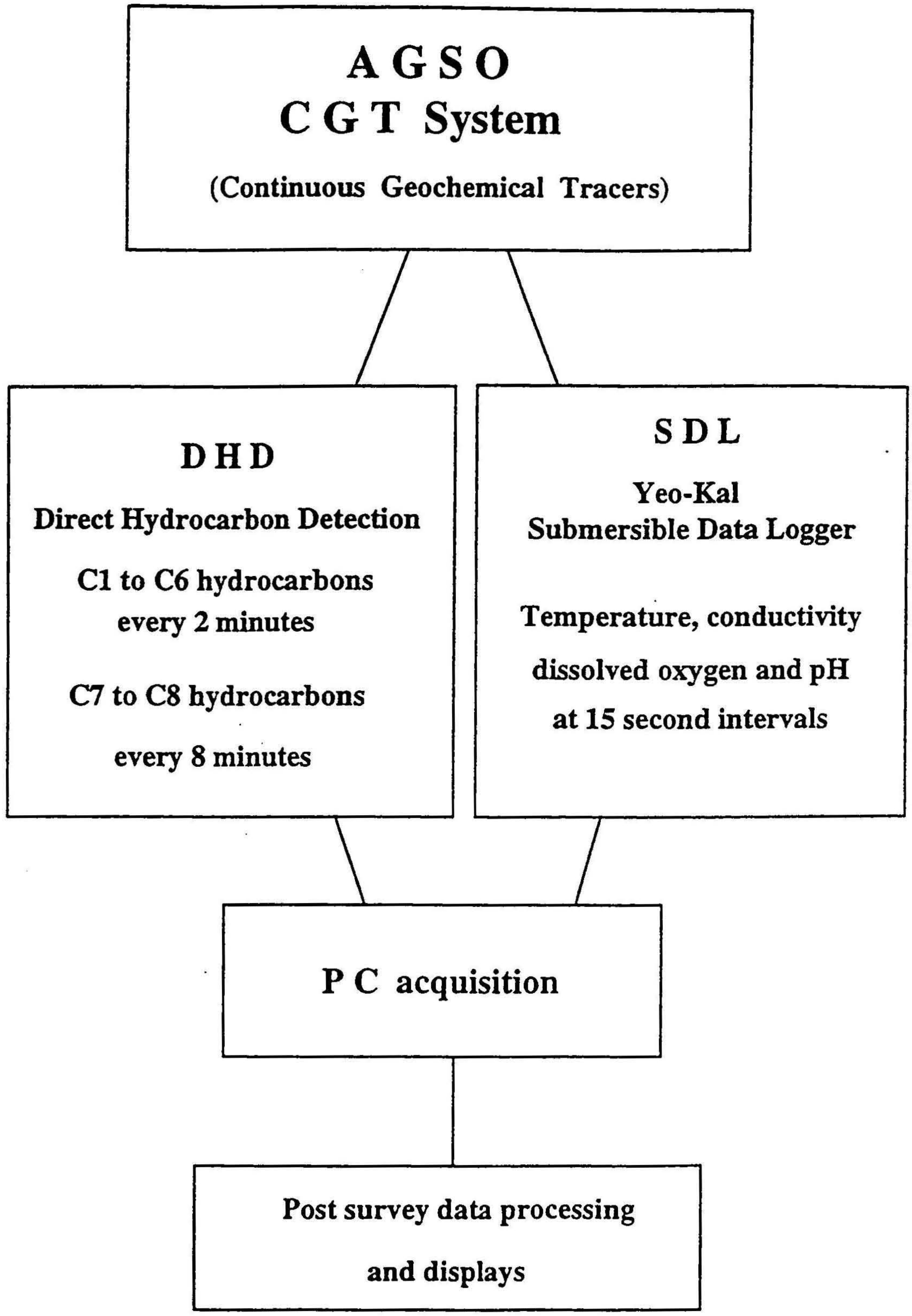


Figure 3. Schematic of the CGT system, installed and operated aboard the "Rig Seismic"

Table 1 Parameters measured using Continuous Geochemical Tracer System:

Parameter	Units	Equipment Used
Total Hydrocarbon (THC)	ppm	Shimadzu GC with FID Detector using 6" Glass bead column
Methane	ppm	Shimadzu GC with FID Detector using 42" activated alumina column
Ethane	ppm	"
Ethylene	ppm	"
Propane	ppm	"
Propylene	ppm	"
i-Butane	ppm	"
n-Butane	ppm	"
		"
i-Pentane	ppm	Shimadzu GC with FID Detector using 30 Megabore DB1 column
n-Pentane	ppm	"
i-Hexane	ppm	"
n-Hexane	ppm	"
Water depth	metres	On-board echo sounders
Tow-fish altitude	metres	Tow-fish echo sounder
Conductivity	mmhos/cm	Conductivity prober
Water temperature	°Celsius	Temperature thermistor
Tow-fish depth	d-bar	Pressure transducer

6. Experimental Design

In order to characterise the signature of potential hydrocarbon sources, concentrations of C_1 through C_8 hydrocarbons were measured with supporting hydrographic data (temperature, salinity, dissolved oxygen, pH, turbidity and percentage light transmission) from eighteen vertical profiles located in the vicinities of the Ocean Outfalls (North Head, Bondi and Malabar) and near the entrances to estuaries (Broken Bay, Botany Bay, Port Hacking/Bate Bay and Port Jackson). The locations of the vertical profiles are listed in Table 2 and shown in Figure 4. Table 3 provides a summary of the data collected at each station.

To determine the spatial distribution of hydrocarbons offshore Sydney and specifically in the vicinity of the deep ocean outfalls, a series of longitudinal transects were conducted between the North Head Ocean Outfall and Port Hacking. The CGT tow-fish was set at three different water-depths: 5 m, 25 m, 45 m and additionally in one survey the tow-fish was deployed 15 m above the sea-floor. Survey tracks for each depth of the CGT tow-fish are shown in Figure 5 to 9 and the data collected on each leg of the survey are listed in Table 4.

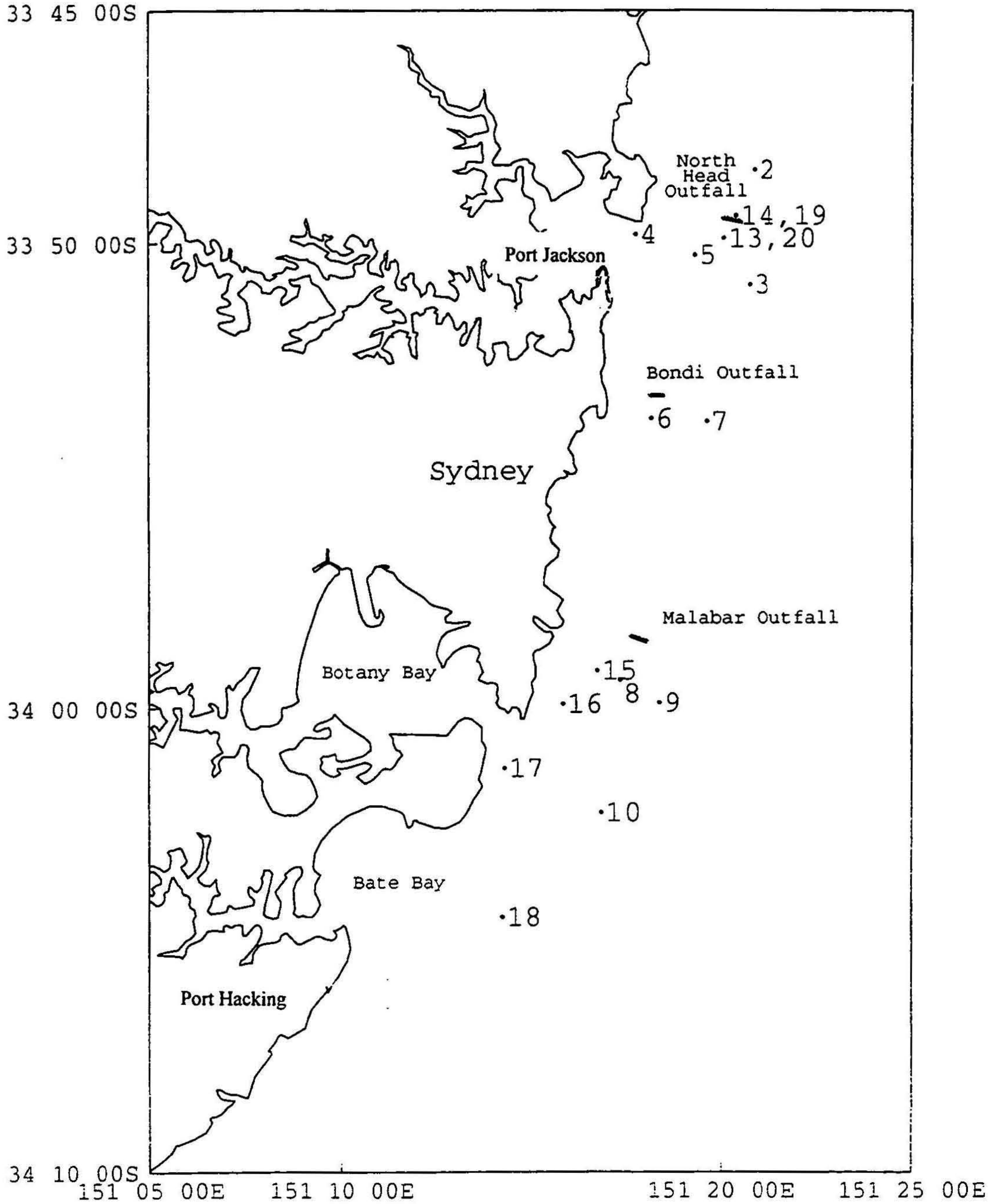
During sea trials conducted aboard *Rig Seismic* (Survey 113), immediately after the termination of Survey 112, the opportunity was taken to analyse light hydrocarbons in seawater during the transit of *Rig Seismic* from offshore North Head to Pyrmont Wharf No. 8. During this transit, the DHD tow-fish was not deployed, and seawater was pumped into the gas extractor using the ship's pump. The intake for this pump is approximately 4 metres below the water line, and located on the forward-port side of the ship.

Table 2 Locations of vertical profiles

VP	WP	Lat. (deg S)	Long. (deg E)	WD (m)	Location
VP112001	WP 2	33.569	151.323	49	Entrance to Broken Bay
VP112002	WP 5	33.808	151.348	65	1 nm north of North Head Outfall
VP112003	WP 6	33.848	151.345	72	1.5 nm south of North Head Outfall
VP112004	WP 8	33.831	151.296	30	Entrance to Port Jackson
VP112005	WP 7	33.838	151.321	50	2 nm east of South Head
VP112006	WP 9	33.897	151.303	67	0.5 nm south of Bondi Outfall
VP112007	WP 10	33.898	151.327	71	1.5 nm east of Bondi Outfall
VP112008	WP 11	33.990	151.289	85	1 nm south of Malabar Outfall
VP112009	WP 12	33.998	151.307	93	1.5 nm south of Malabar Outfall
VP112010	WP 13	34.038	151.281	103	3 nm southeast of Botany Bay entrance
VP112013	WP 35	33.832	151.334	62	0.5 nm southwest of North Head Outfall
VP112014	WP 36	33.824	151.340	60	Middle of North Head diffuser pipe
VP112015	WP 37	33.987	151.279	56	1 nm southwest of Malabar Outfall
VP112016	WP 38	33.999	151.265	54	1.5 nm southwest of Malabar Outfall
VP112017	WP 39	34.022	151.239	49	0.5 nm east of Botany Bay entrance
VP112018	WP 26	34.075	151.238	100	3 nm southeast of Bate Bay
VP112019	WP 34	33.827	151.338	60	Middle of North Head diffuser pipe
VP112020	WP 35	33.832	151.335	63	0.5 nm southeast of North Head Outfall

SYDNEY

Location of Vertical Profiles



VP 1 is located in Broken Bay near the entrance to Pittwater

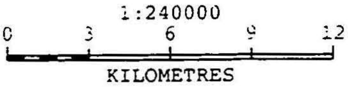


Figure 4

UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E

Table 3 Summary of data for vertical profiles

Vertical Profile	Comments	Approximate Location
VP112001	DHD but no hydrography	Broken Bay
VP112002	DHD and hydrography	North Head Outfall
VP112003	DHD and hydrography	North Head Outfall
VP112004	DHD and hydrography	Entrance to Port Jackson
VP112005	DHD and hydrography	East of South Head
VP112006	DHD and hydrography	Bondi Outfall
VP112007	DHD and hydrography	Bondi Outfall
VP112008	DHD and hydrography	Malabar Outfall
VP112009	DHD and hydrography	Malabar Outfall
VP112010	DHD and hydrography	Southeast of Botany Bay
VP112013	DHD and hydrography	Southwest of North Head Outfall
VP112014	DHD but no hydrography	North Head Outfall
VP112015	DHD and hydrography	Southwest of Malabar Outfall
VP112016	DHD and hydrography	Southwest of Malabar Outfall
VP112017	DHD and hydrography	Entrance to Botany Bay
VP112018	DHD and hydrography	Southeast of Bate Bay
VP112019	DHD but no hydrography	North Head Outfall
VP112020	DHD and hydrography	North Head Outfall

C. G. T. at 5 m WATER DEPTH.
Lines 112004 - 112007 and Bate Bay

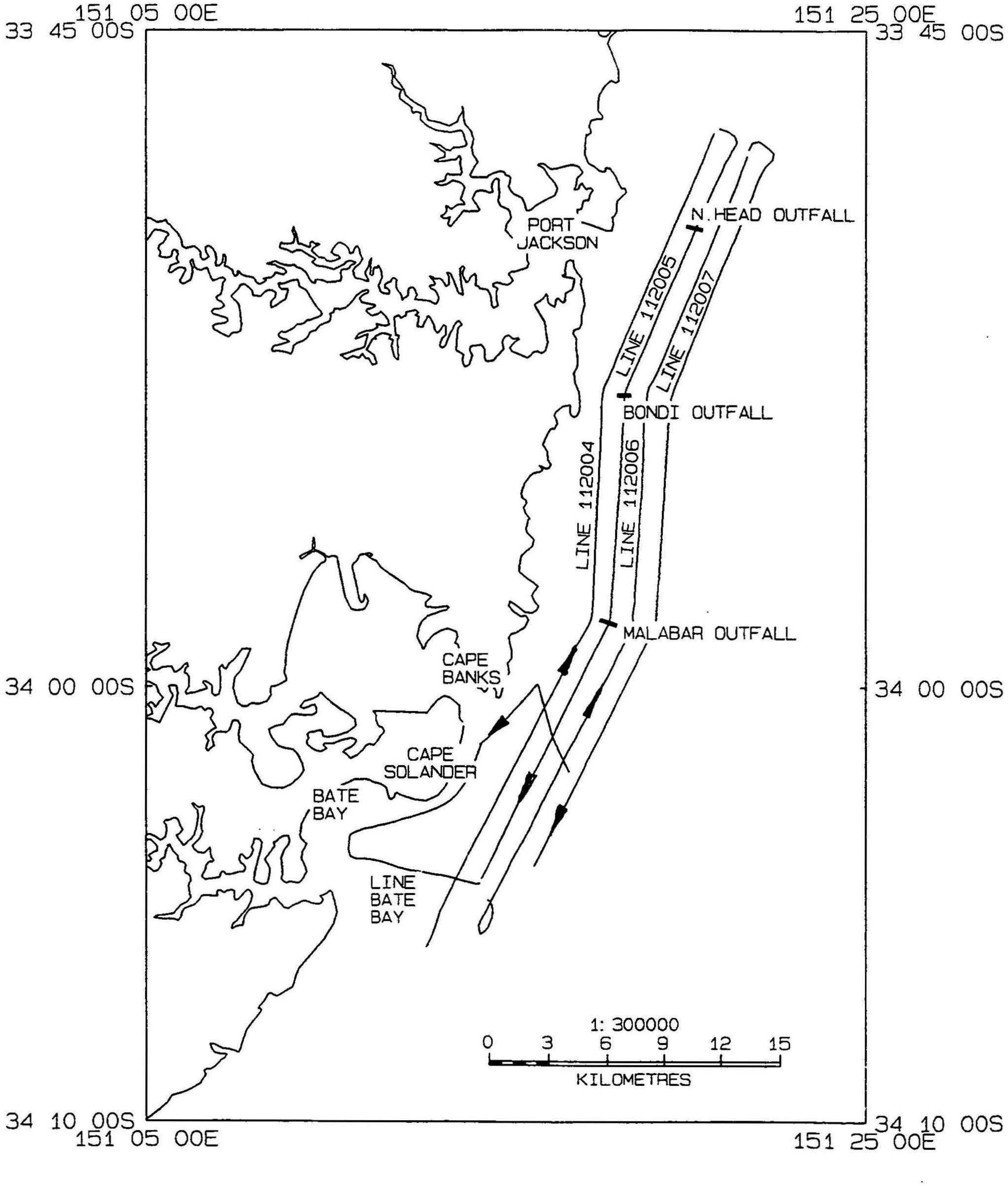


Figure .5. Survey track of the CGT the tow-fish at 5 metres water depth.

C. G. T. at 25 m WATER DEPTH.
Lines 112008 - 112011

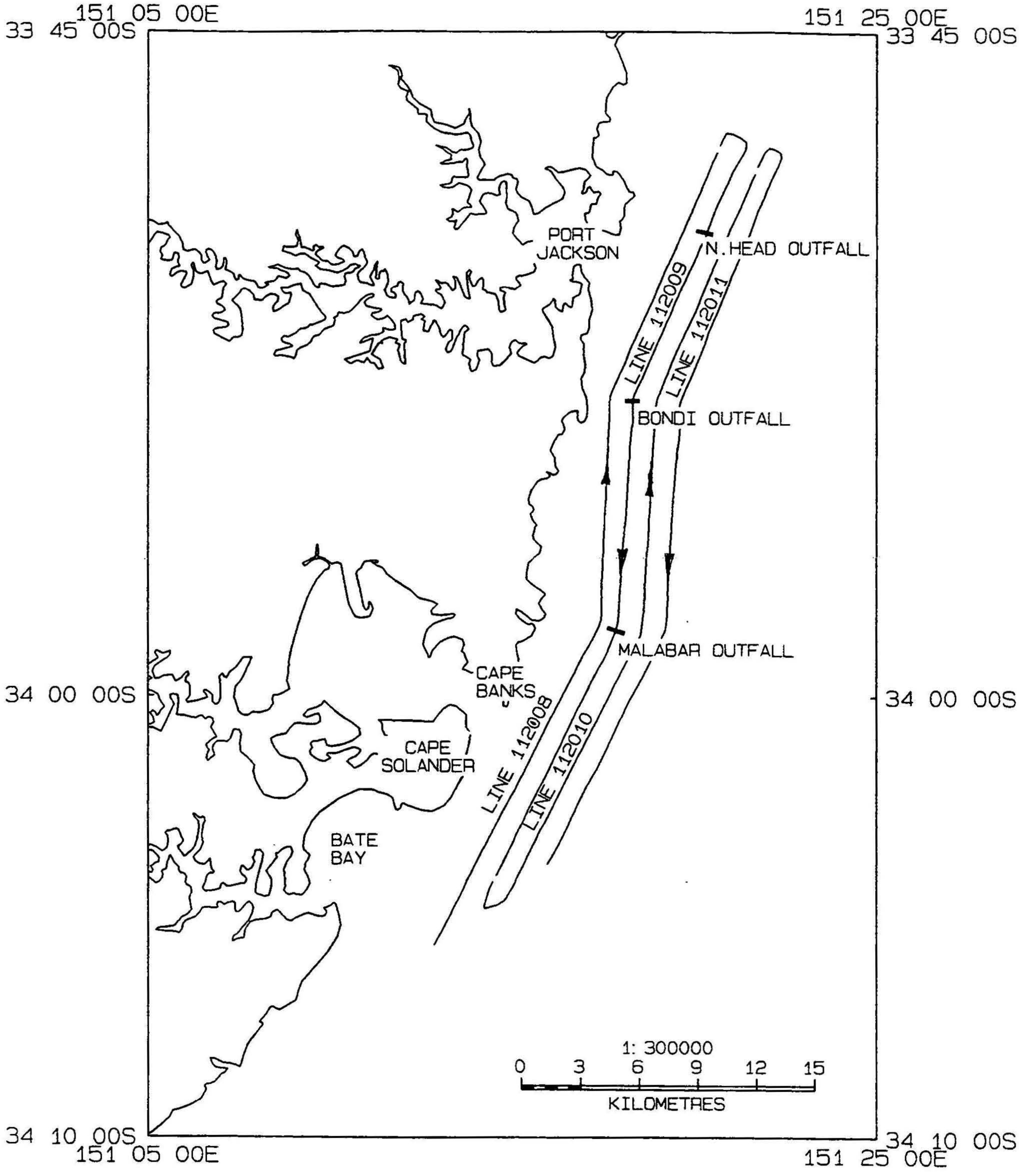


Figure .6. Survey track of the CGT the tow-fish at 25 metres water depth.

C. G. T. at 45 m WATER DEPTH.
Lines 112012 - 112015

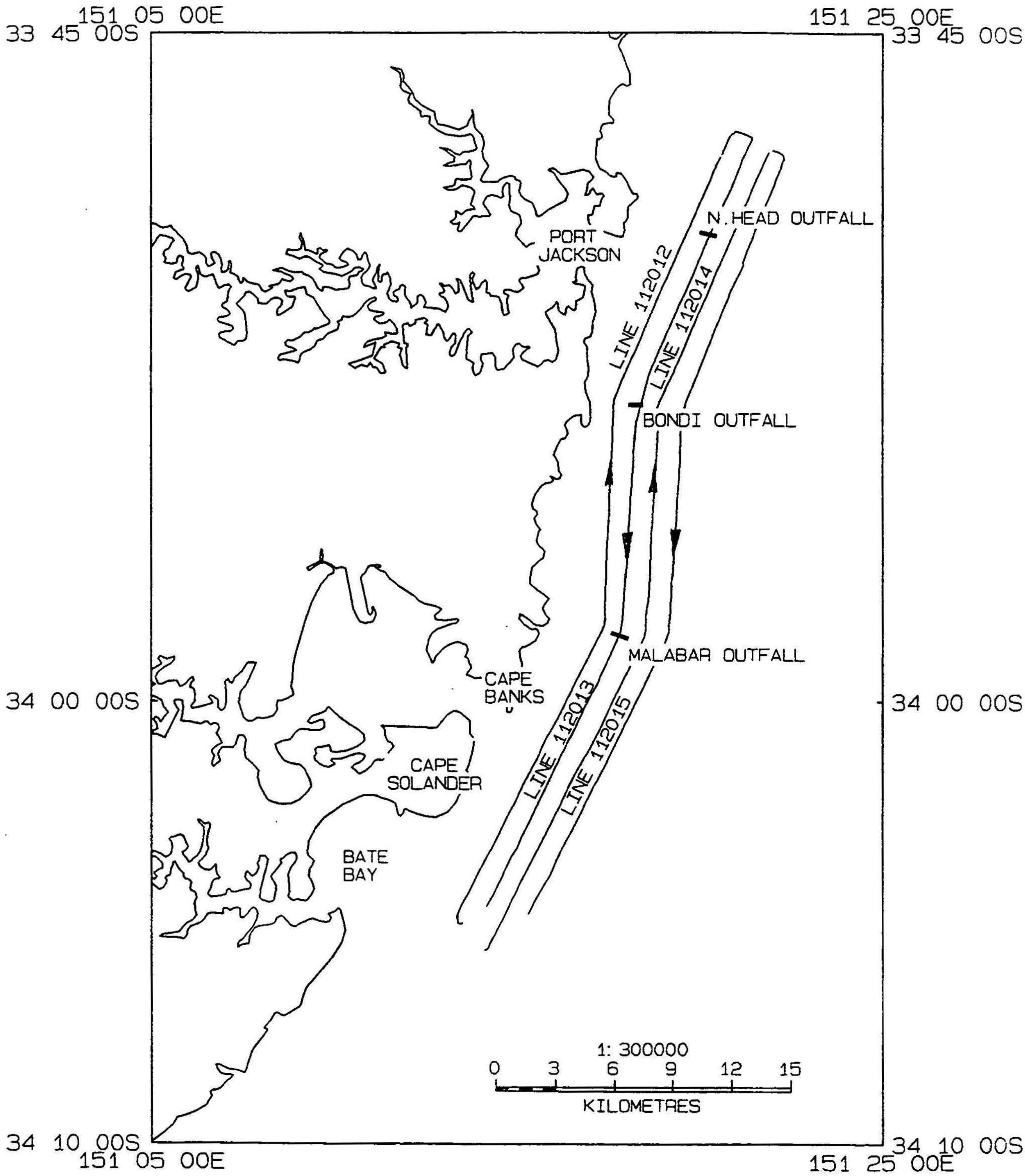


Figure . 7. Survey track of the CGT the tow-fish at 45 metres water depth.

C. G. T. at 15 m ABOVE the SEA FLOOR.
Lines 112016 and 112017

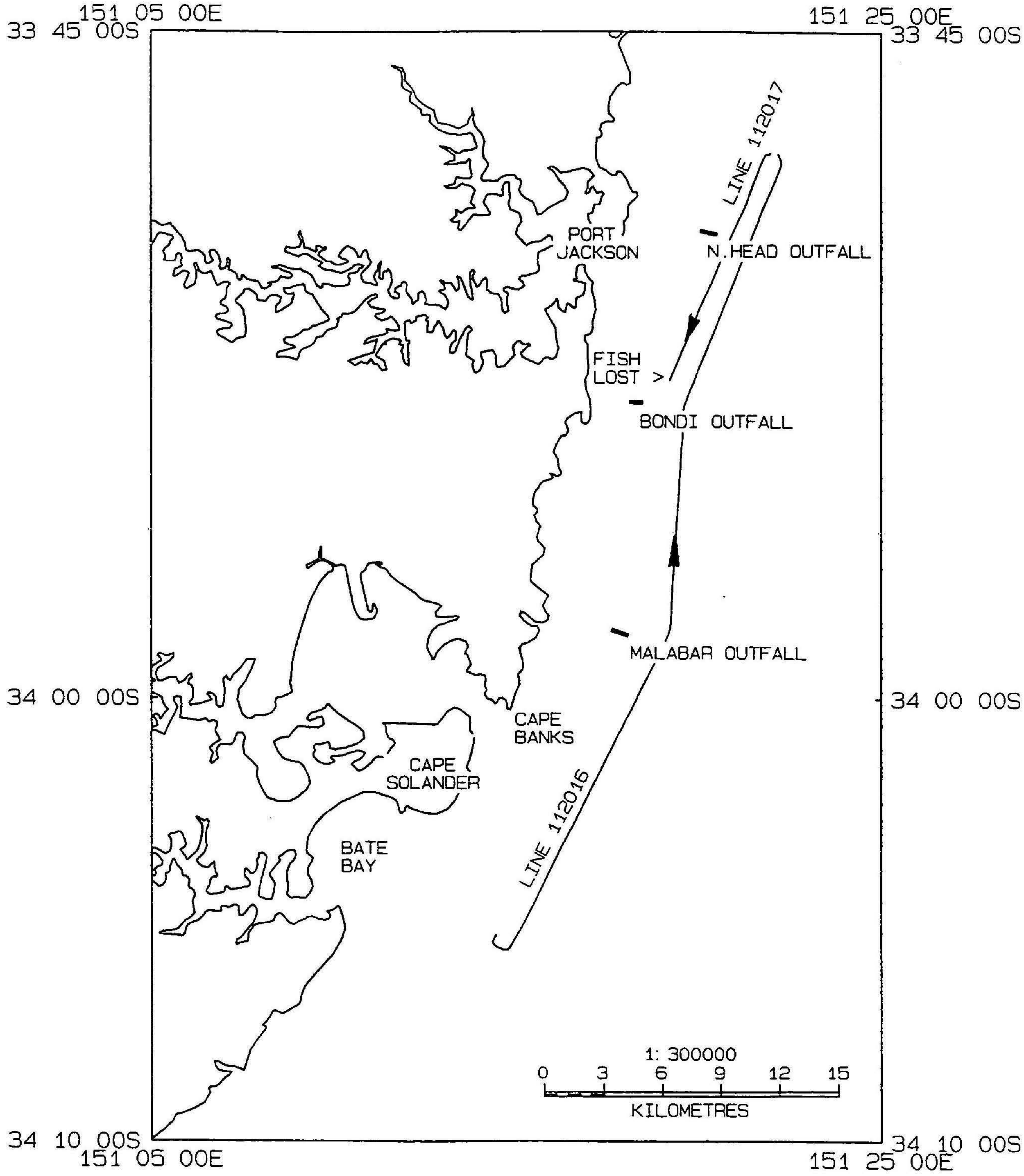


Figure 8. Survey track of the CGT the tow-fish at 15 metres above the sea floor.

C. G. T. Lines Bate Bay, 112001, 112018 and 112019

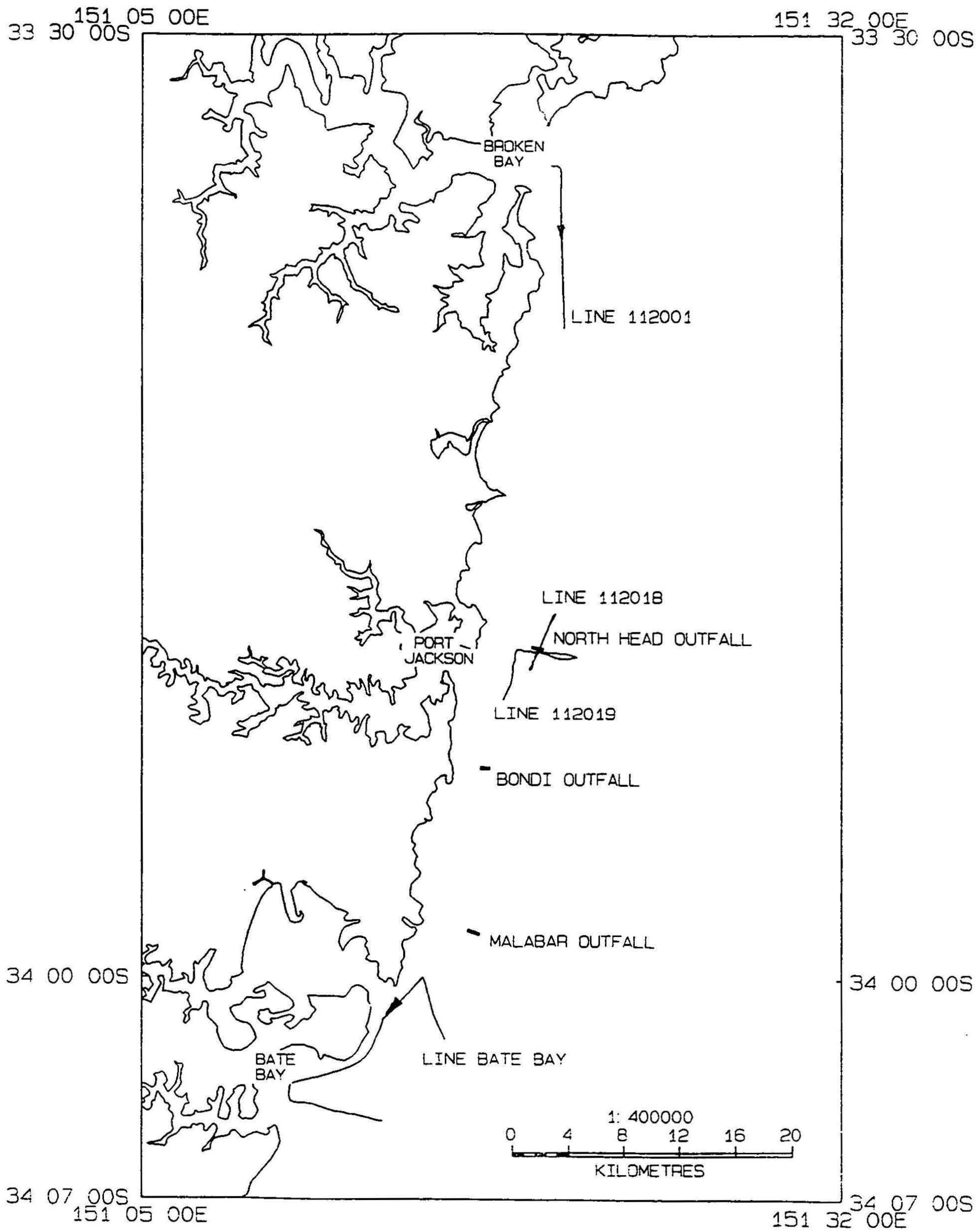


Figure .9. Survey track of the CGT lines Bate Bay,112001, 112018 and 11219.

Table 4 Summary of data for the longitudinal profiles of CGT data collected from the coastal survey between Broken Bay and Port Hacking

Line Number	DHD	SDL	Comments
112001	Yes	No	Offshore Broken Bay
112003	Yes	Yes	Cape Solander via Bate Bay to offshore Port Hacking.
112004	Yes	Yes	tow fish @ 5 metres depth
112005	Yes	Yes	tow fish @ 5 metres depth
112006	Yes	Yes	tow fish @ 5 metres depth
112007	Yes	Yes	tow fish @ 5 metres depth
112008	Yes	Yes	tow fish @ 25 metres depth
112009	Yes	Yes	tow fish @ 25 metres depth
112010	Yes	Yes	tow fish @ 25 metres depth
112011	Yes	Yes	tow fish @ 25 metres depth
112012	Yes	Yes	tow fish @ 45 metres depth
112013	Yes	Yes	tow fish @ 45 metres depth
112014	Yes	Yes	tow fish @ 45 metres depth
112015	Yes	Yes	tow fish @ 45 metres depth
112016	Yes	No	tow fish @ 15 metres altitude
112017	Yes	No	tow-fish was lost
112018	Yes	No	Near North Head outfall
112019	Yes	No	Line abandoned.
Bate Bay line	Yes	Yes	Composite of 112003 and other data

7. Vertical profiles of hydrocarbons in the coastal zone: Results

The following is a brief description of the vertical distributions of hydrocarbons in the water column.

Typical background levels of hydrocarbons are: THC (total hydrocarbons) = 14 ppm; methane = 3ppm, ethane and propane = 0.02 ppm, ethylene = 0.1 ppm, propylene = 0.07 ppm and butanes < 0.01 ppm). Throughout the survey apparent *n*-C_5 (*n*-pentane) concentrations are high and it is believed that they do not represent true seawater concentrations. Persistent problems with this analysis suggest a systematic interference from another compound(s) eluting from the chromatographic column with a retention time identical to that of *n*-pentane and consequently pentane has not been used in the interpretations and statistical analyses. There are no other known artefacts for the other hydrocarbons reported here.

7.1 Broken Bay

Vertical profile (VP112001) was conducted in Broken Bay near the entrance to Pittwater and the DHD data are summarised in Figure 10 and 11. Methane, C_2 and C_3 hydrocarbons were typical of background levels in ocean waters but wetness index was elevated (2-4 %), mainly as a result of increased butane concentrations.

7.2 Port Jackson

Three vertical profiles were conducted directly offshore of the entrance to Port Jackson (Figure 4) as follows.

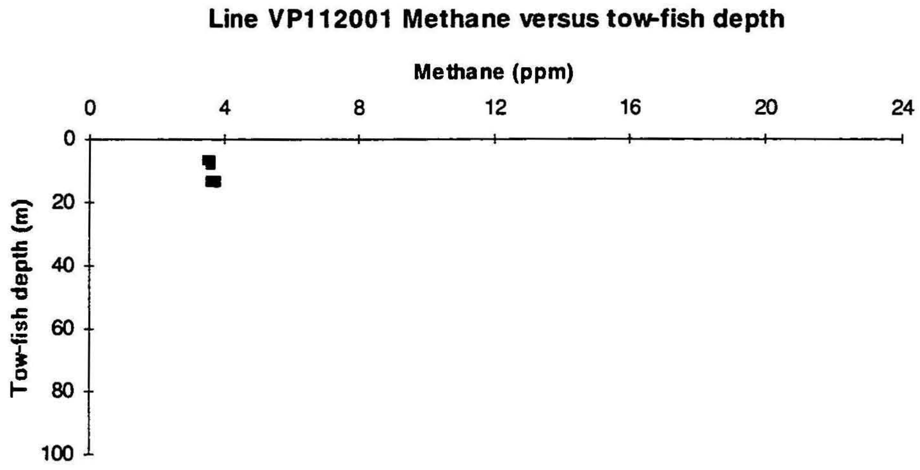
1. VP112004 was located between North and South Head.
2. VP112005 was located 1.3 nautical miles SSE of the entrance to Port Jackson.
3. VP112003 was located 2.8 nautical miles SSE of the entrance.

The DHD data from these profiles are summarised in Figure 12 to 17. The highest concentrations of light hydrocarbons were found at the station between North and South Heads (VP 112004) and generally decrease with increasing distance offshore, particularly the unsaturated hydrocarbons (ethylene and propylene). The elevated concentrations of saturated C_2-C_4 hydrocarbons in the vicinity of Port Jackson result in a wetness index of 3-5 % nearshore decreasing to 1-2 % offshore.

At Site VP112004 (between North and South Heads) slightly elevated concentrations of methane (5 ppm) were found with somewhat higher values occurring at the surface (Figure 12). Concentrations of C_{2+} hydrocarbons, notably butane, were also above background levels but, in contrast to methane, concentrations increased with increasing water depth (Figure 13) and, as a result, so did percent wetness.

At site VP112005 (1.3 nautical miles to the southeast), somewhat elevated levels of hydrocarbons were detected and these generally decreased with increasing water depth (Figure 14 and 15), percent wetness remaining approximately constant.

At site VP112003, 2.8 nautical miles to the southeast of the entrance, hydrocarbon concentrations were typical of background levels (Figure 16 and 17).



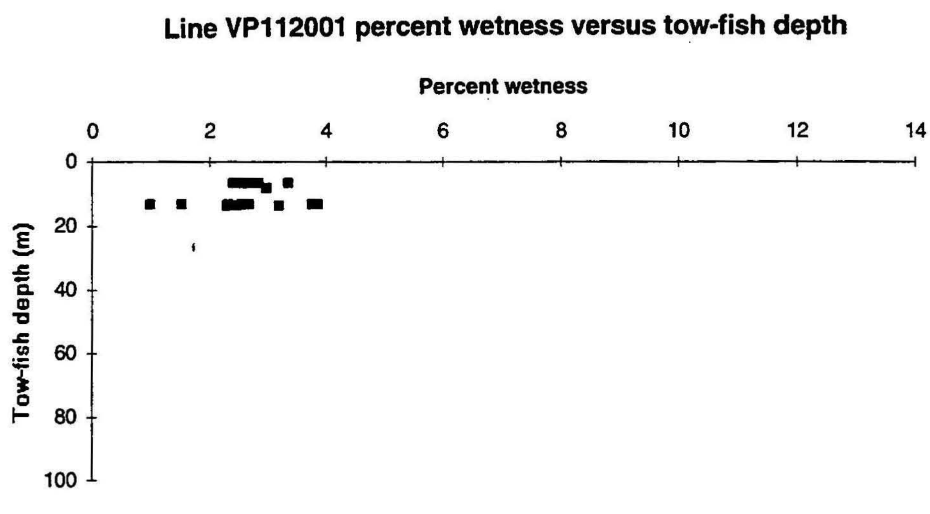
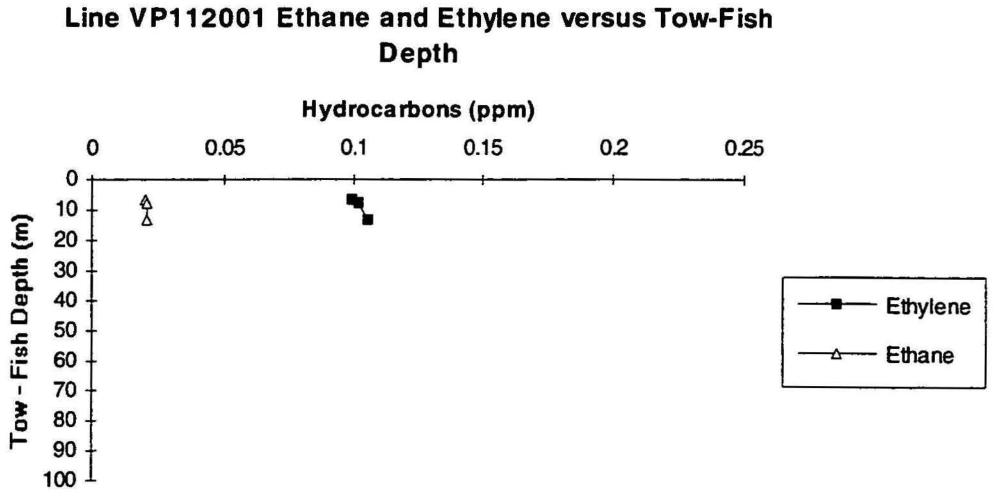


Figure 10 Vertical profiles of methane and percent wetness near Broken Bay.



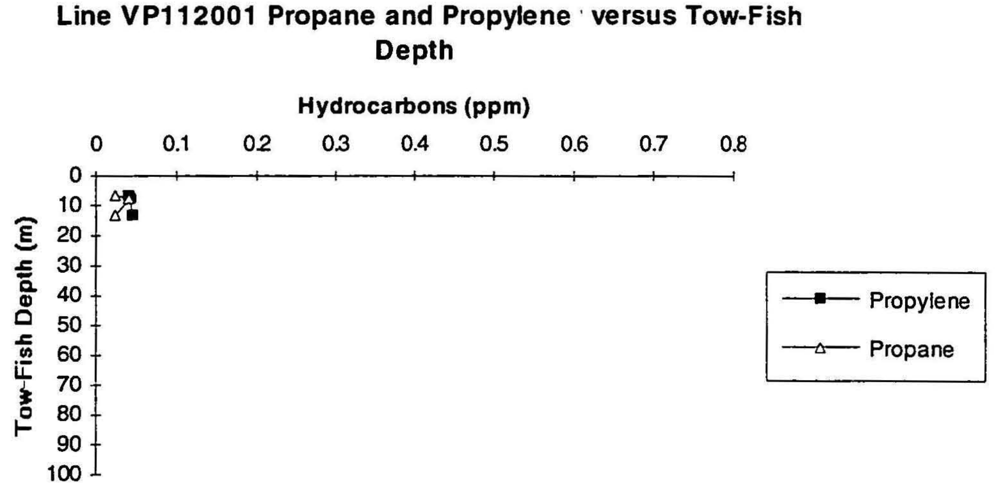
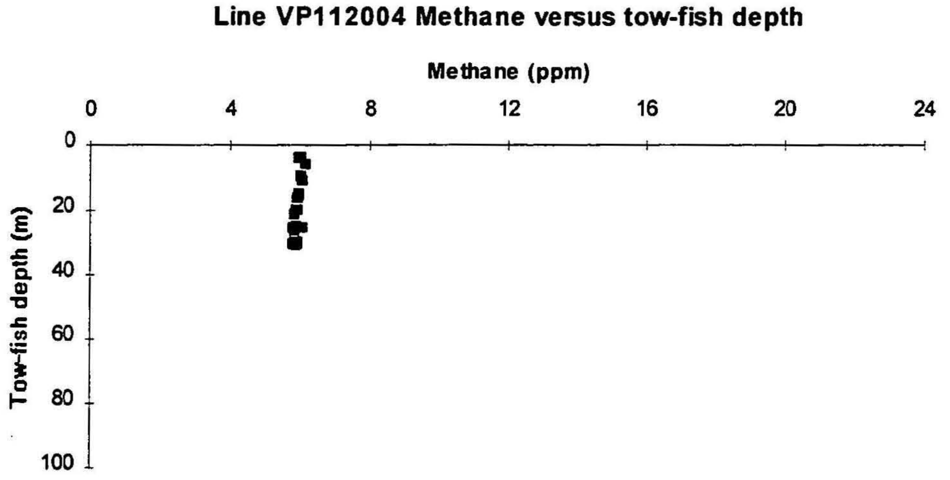


Figure 11. Vertical distribution of light hydrocarbons near Broken Bay.



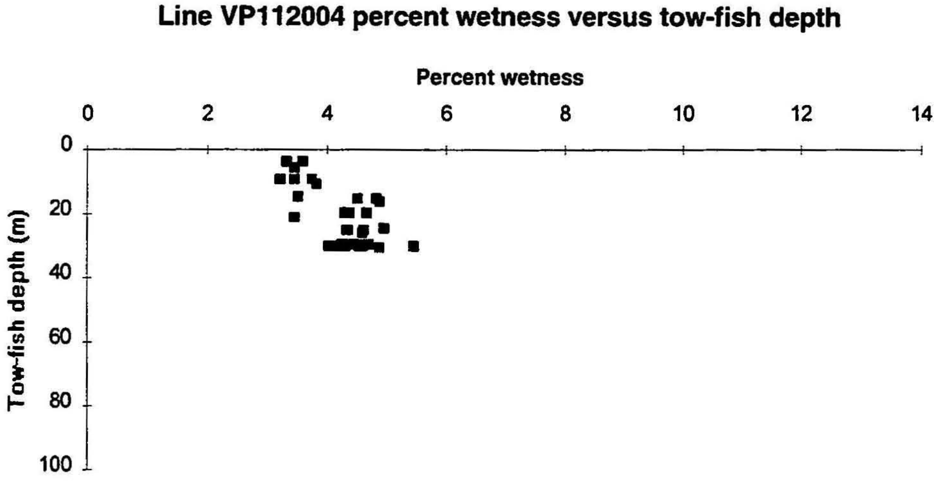
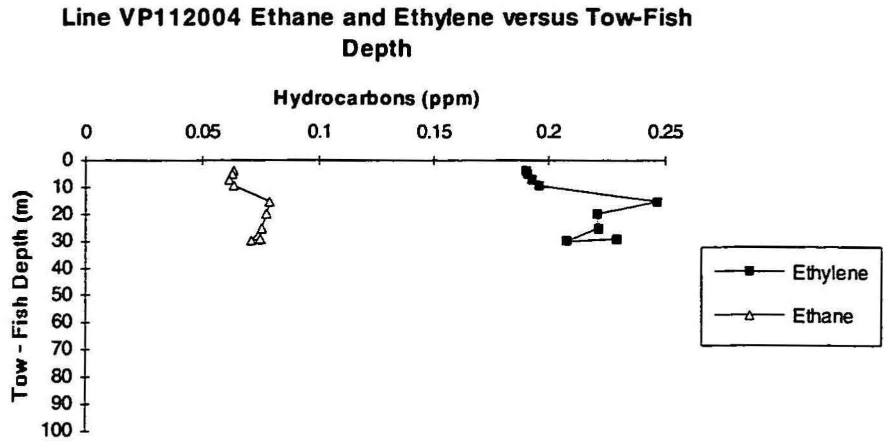
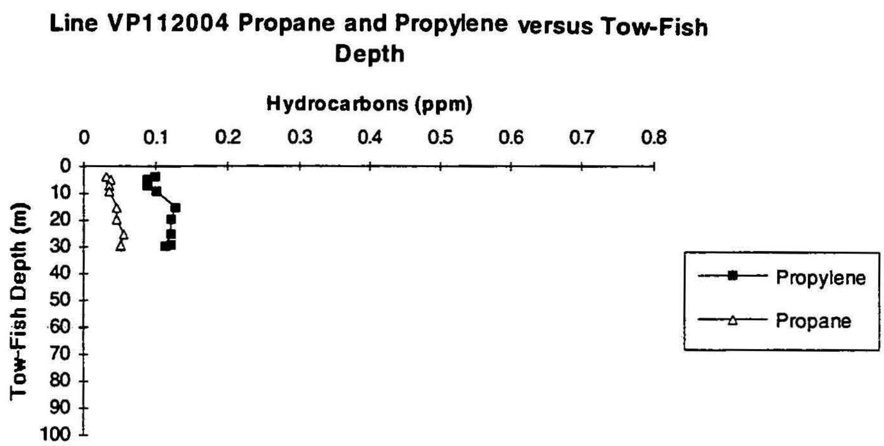


Figure 12 Vertical profiles of methane and percent wetness between North and South Heads, Port Jackson.





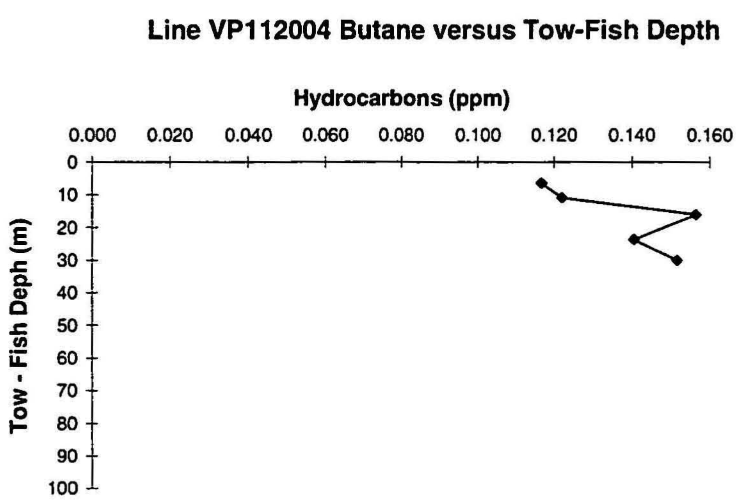
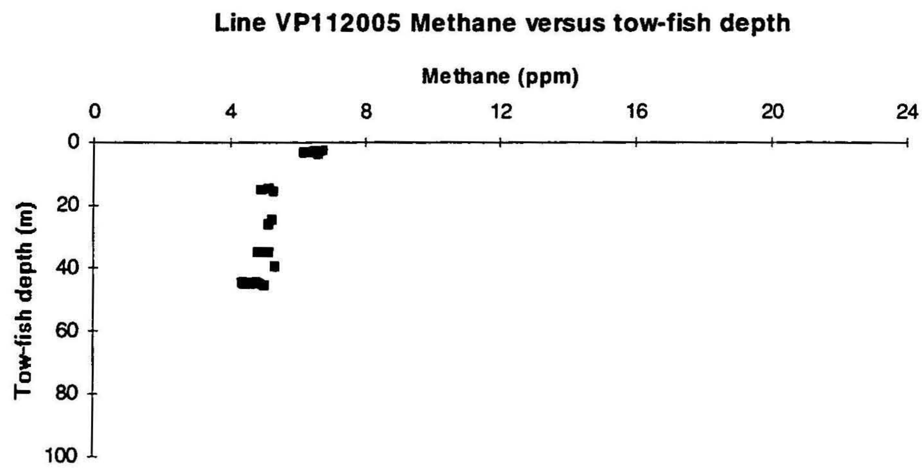


Figure 13. Vertical distribution of light hydrocarbon concentrations between North and South Head



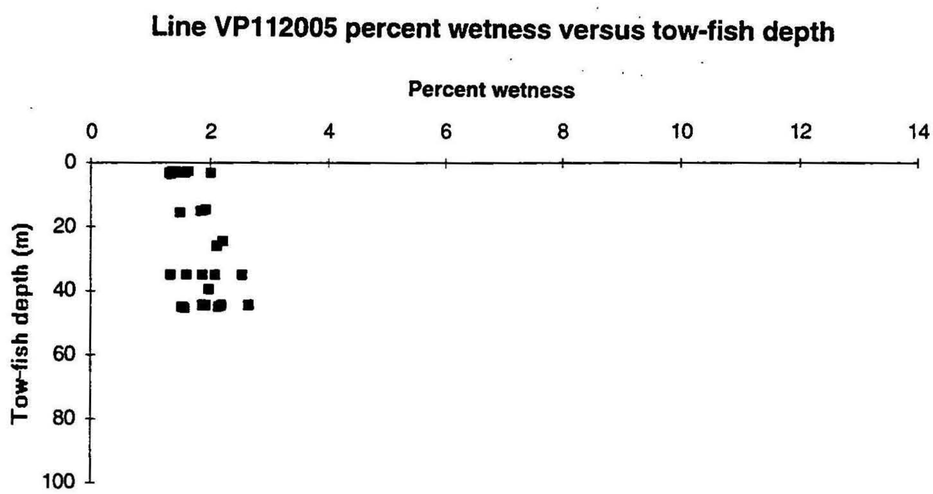
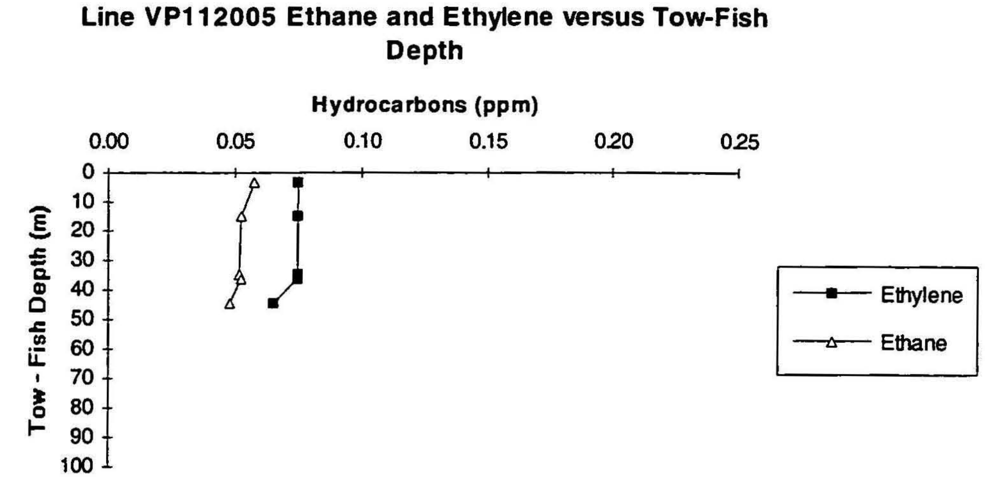


Figure 14 Vertical profiles of methane and percent wetness 1.3 nautical miles SSE of the entrance to Port Jackson.



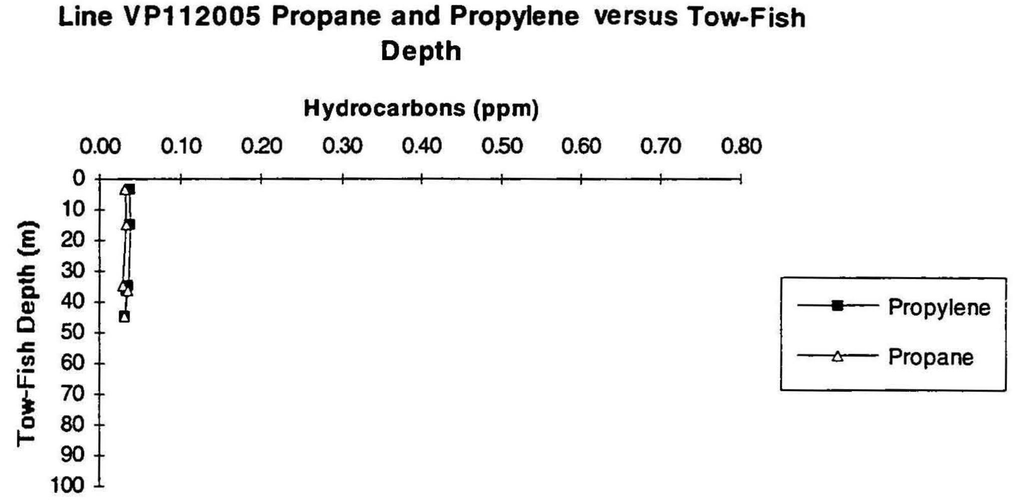
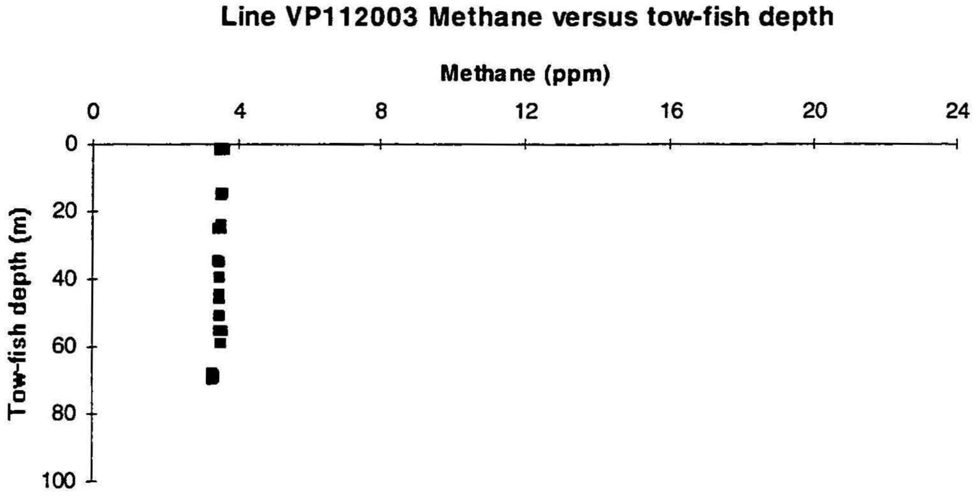


Figure 15. Vertical distribution of light hydrocarbons 1.3 nautical miles SSE of the entrance to Port Jackson VP112005



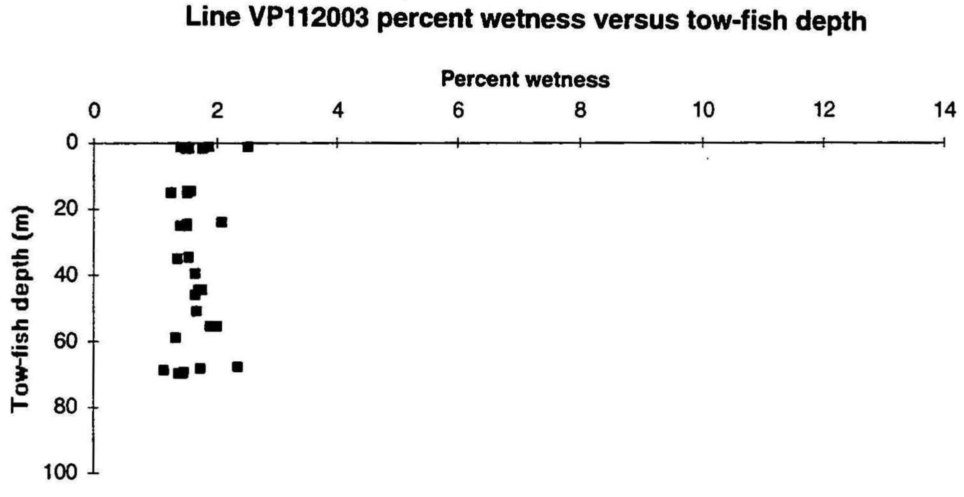
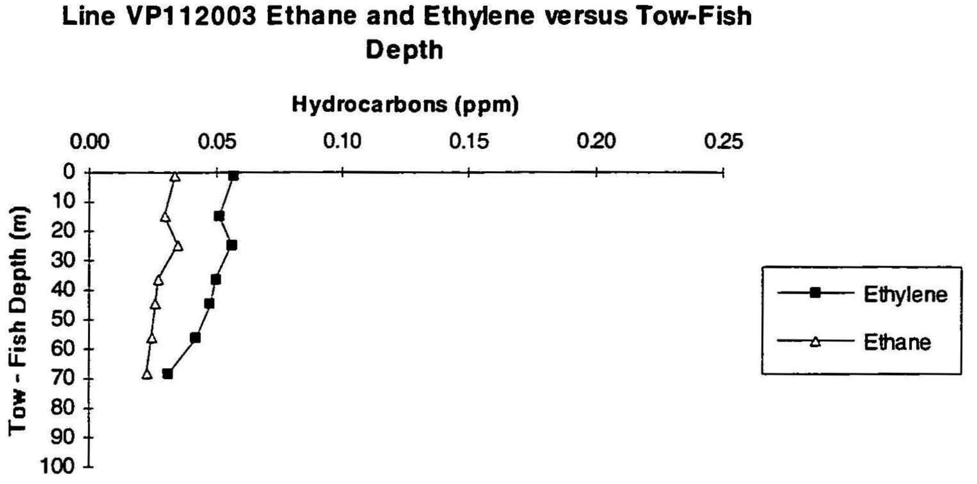


Figure 16 Vertical profiles of methane and percent wetness 2.8 nautical miles SSE of the entrance to Port Jackson.



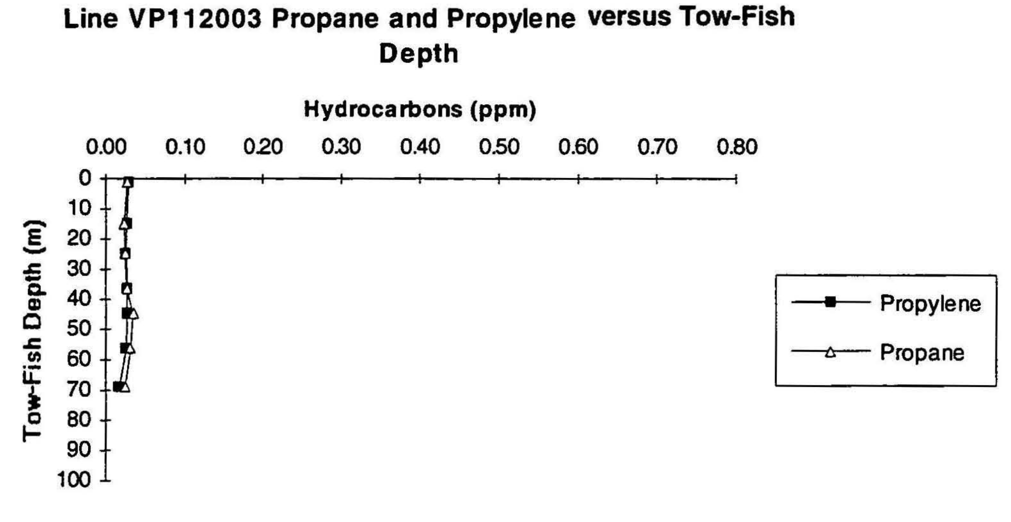


Figure 17. Vertical distribution of light hydrocarbons 2.8 nautical miles SSE of the entrance to Port Jackson VP112003.

7.3 North Head Outfall

Five vertical profiles were conducted in the vicinity of the North Head Outfall (refer Figure 4 for location) as follows:

1. VP112002 - 1 nautical mile to the north of the outfall;
2. VP112014 - directly over the outfall;
3. VP112019 - directly over the outfall and undertaken five days after VP112014.
4. VP112013 -; 0.5 nautical mile to the south of the outfall; and
5. VP112020 - 0.5 nautical mile to the south of the outfall, but occupied about 5 days after VP112013.

The location of the first profile (Site VP112002) was chosen because the plume was detected to the north of the outfall in the previous pilot study (Survey 104). However, there were no persistent anomalous hydrocarbons detected to the north of the outfall during this survey (Site VP112002, refer to Figure 18 and Figure 19).

At Site VP112014 (directly over the outfall) methane concentrations were higher than background values in surface waters and generally increased with depth (Figure 20), the highest concentrations were found in bottom-waters (14 ppm). Ethane was slightly above background, while other C_{2+} hydrocarbons remained at approximately background levels (Figure 21). Percent wetness decreased from 1 % at the surface to <0.5 % at depth reflecting primarily the trace changes in C_2-C_4 concentrations compared to the large changes in methane concentration.

Site VP112019 was located near to Site VP 112014, but occupied five days later. Methane concentrations were near background in surface waters but reached a maximum concentration of 12 ppm in a sub-surface plume located at about 40 m (Figure 22). Percent wetness was generally low, <2 % with the minimum value occurring at maximum methane concentrations. Minor amounts of ethane (about two-fold background) were evident in this plume (Figure 23).

At Site VP112013 (0.5 nautical mile south of the outfall), elevated levels of methane (12 ppm) were found in a near-surface plume (Figure 24). Percent wetness values were <2 % but increased from <0.5 % at the surface to 2 % at depth. No anomalous concentrations of the other light hydrocarbons were detected (Figure 25). In contrast, VP112020 (occupied about 5 days after VP112013 and in the same location) shows generally near background levels of methane in the surface waters (Figure 26), with methane systematically increasing with depth to reach maximum concentrations in bottom waters of 6 ppm (about two-fold background levels). No anomalous concentrations of the other light hydrocarbons were detected (Figure 27).

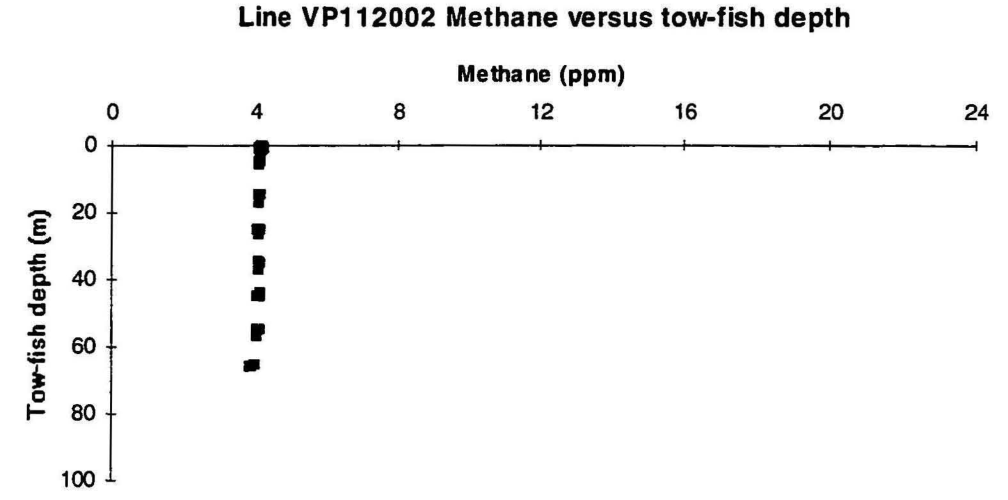
7.4 Bondi Outfall

Two vertical profiles were conducted south of the Bondi Outfall (refer to Figure 4):

1. VP112006 collected 0.5 nautical mile south of the outfall; and
2. VP112007 collected 1 nautical mile to the east-southeast of the outfall.

At Site VP112006 elevated levels of methane (8 ppm) were measured at the surface and increased to a maximum of (24 ppm) in a large subsurface plume, which extended to a depth of about 50 m (Figure 28). Percent wetness in the plume was low, generally being <1 %, indicative of elevated methane and background concentrations of C_2-C_4 hydrocarbons (Figure 29).

At Site VP112007, further from the outfalls, methane concentrations in surface waters were close to background but elevated levels of methane were found in a well defined mid-water plume with maximum methane concentrations about two-fold background (8 ppm) from 15 m to 40 m (Figure 30) The percent wetness index was low (<2 %) and variable and did not clearly define a plume. Minor increases in ethane were detected (Figure 31), but other saturated hydrocarbons were near background levels.



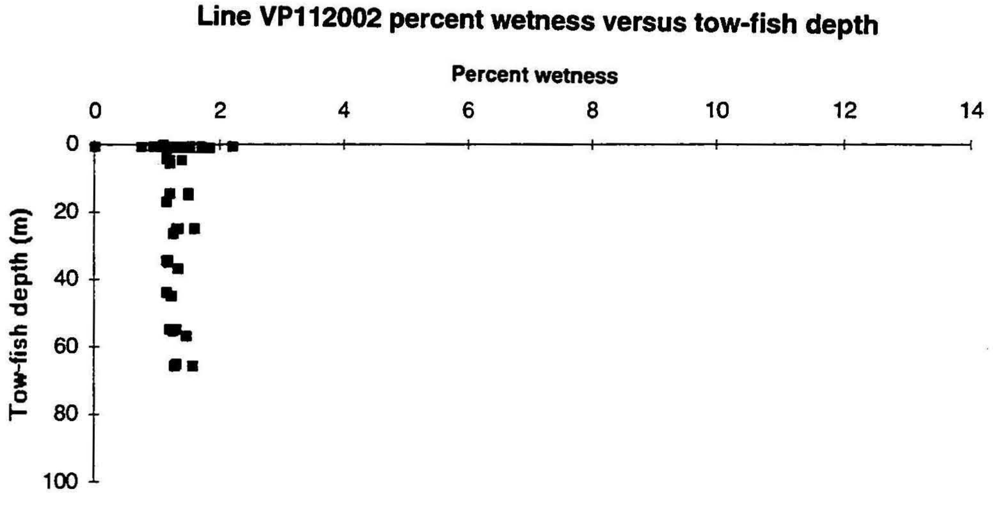
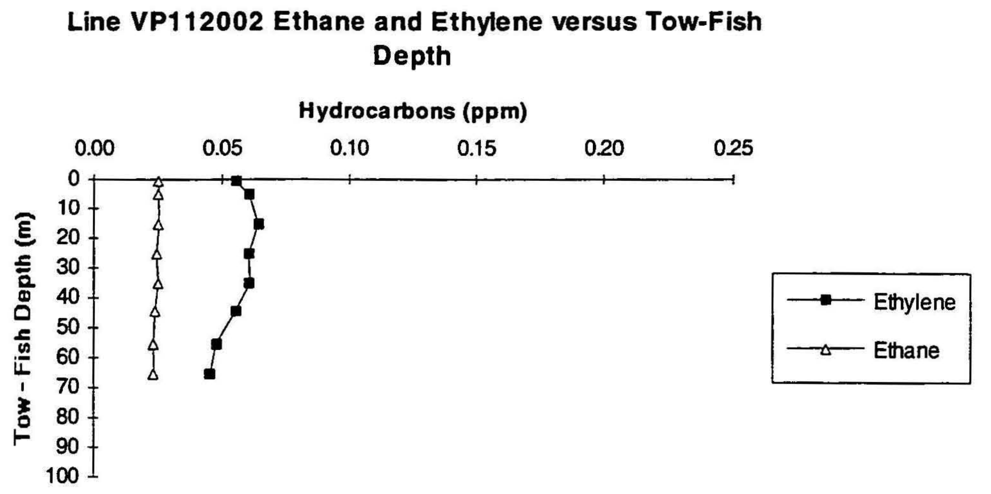


Figure 18 Vertical profiles of methane and percent wetness one nautical mile to the north of the North Head outfall.



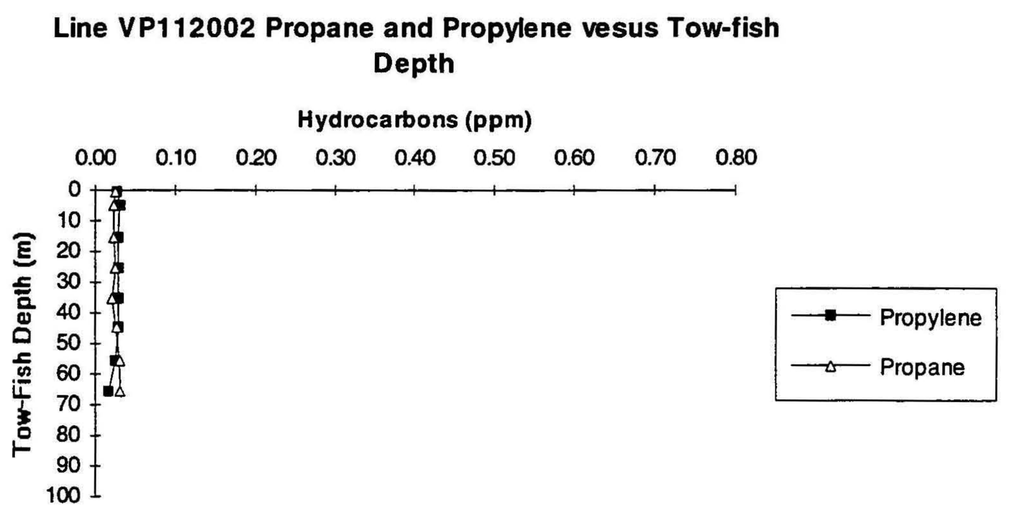


Figure 19. Vertical distribution of light hydrocarbons one nautical mile to the north of North Head outfall VP112002.

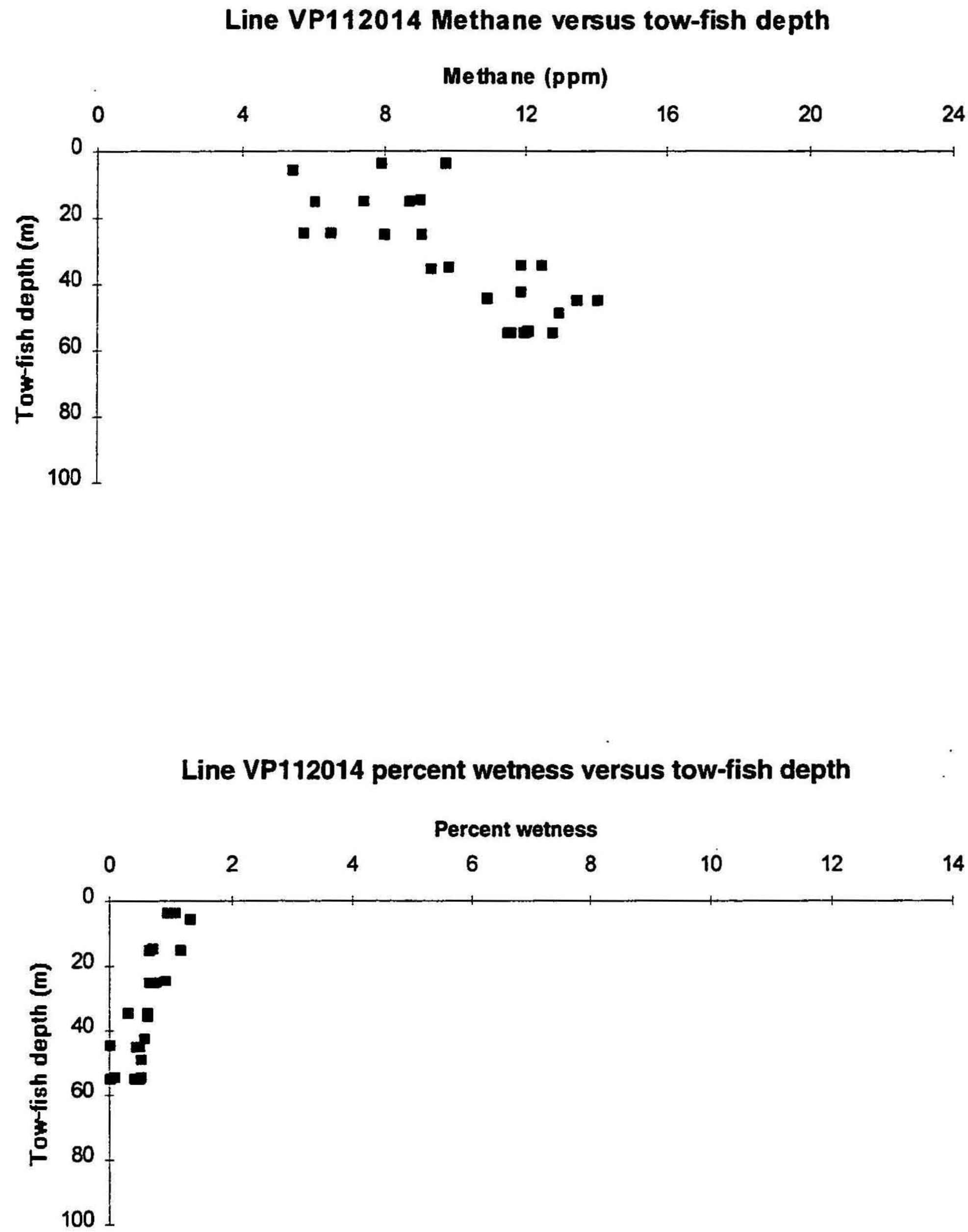
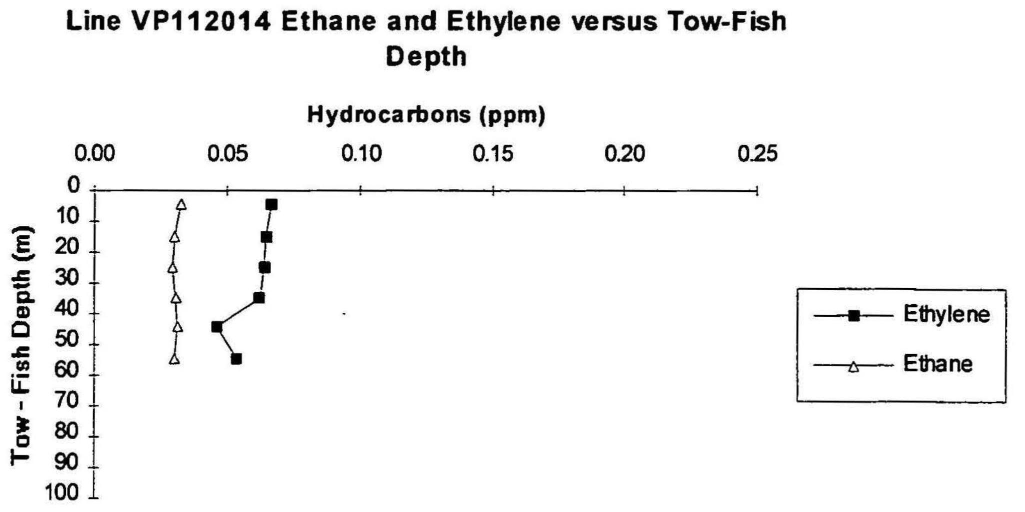


Figure 20 Vertical profiles of methane and percent wetness located directly over the North Head outfall.



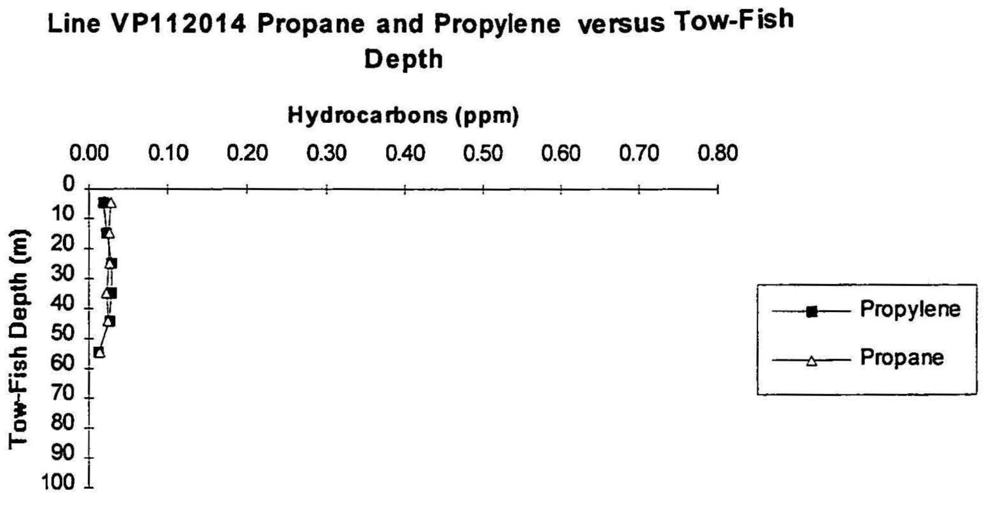
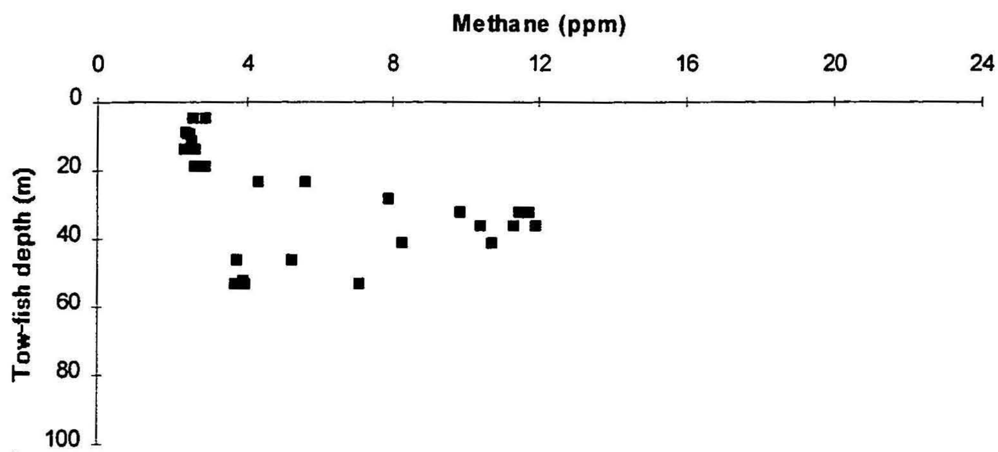


Figure 21. Vertical distribution of light hydrocarbons located directly over the North Head outfall, VP112014.

Line VP112019 Methane versus tow-fish depth



Line VP112019 percent wetness versus tow-fish depth

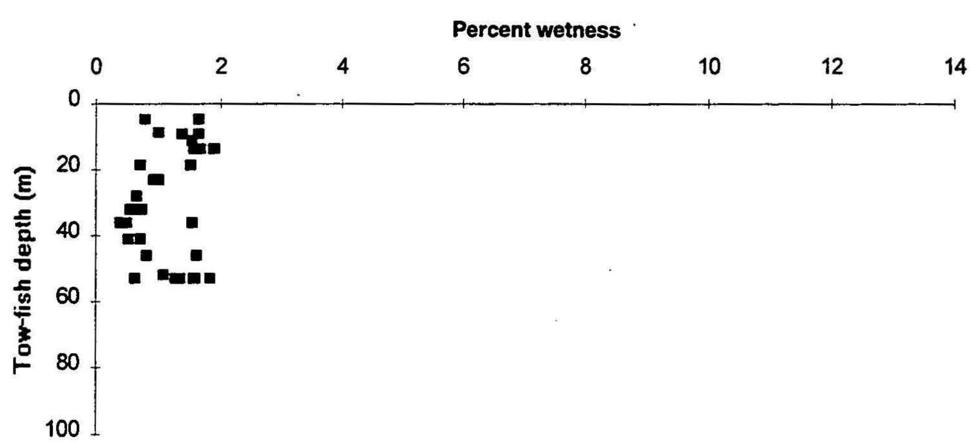
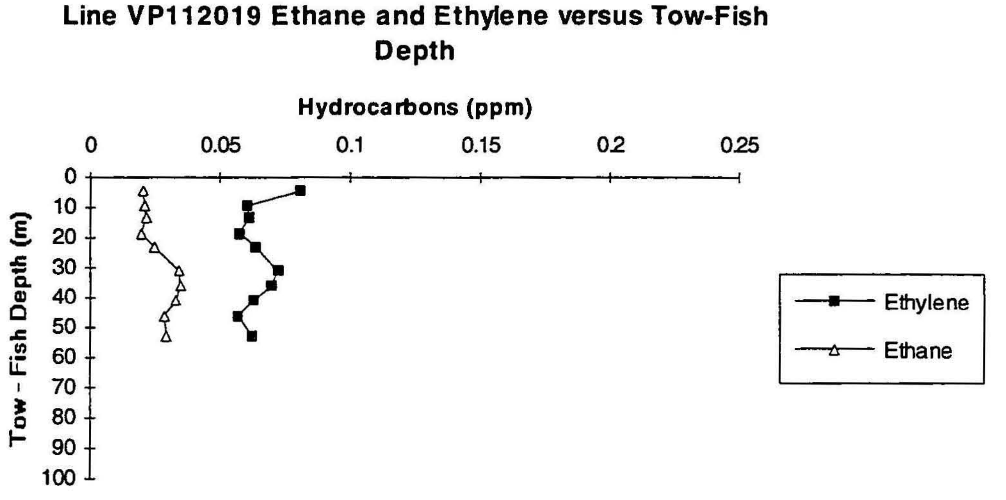


Figure 22 Vertical profiles of methane and percent wetness located directly over the North head outfall and undertaked five days after VP112014.



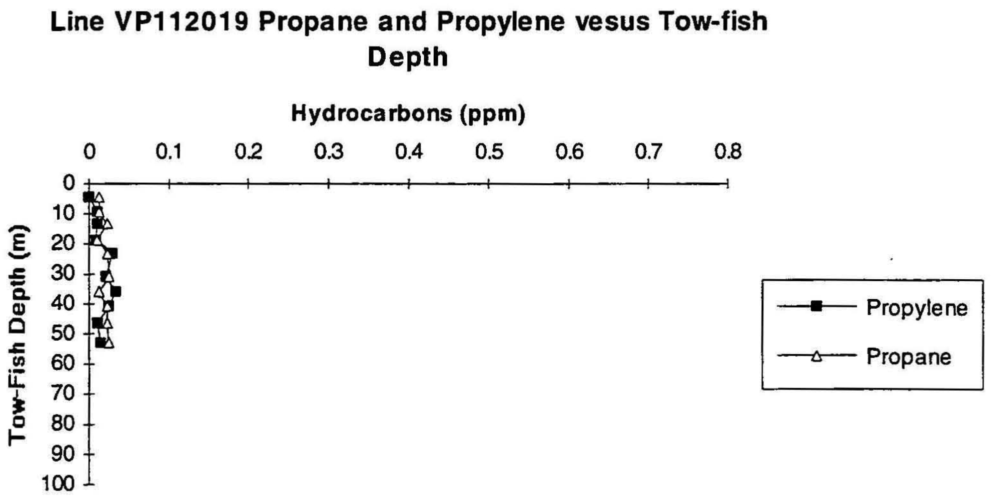
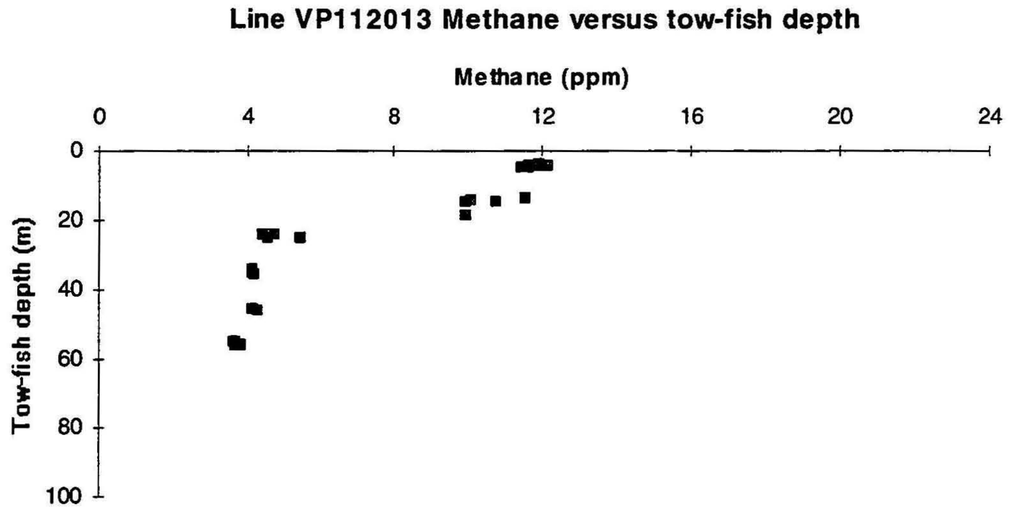


Figure 23. Vertical distribution of light hydrocarbons located directly over the North Head outfall and undertaken 5 days after VP112014



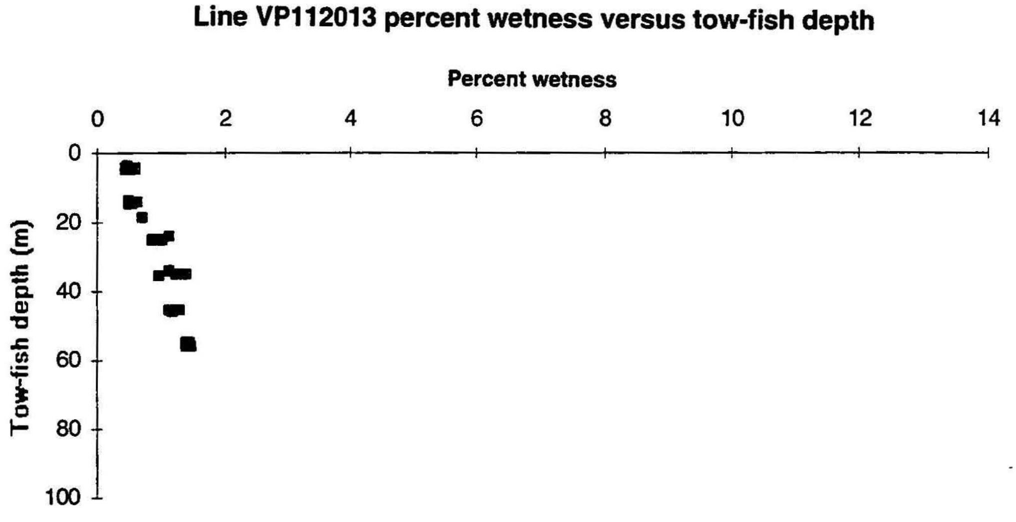
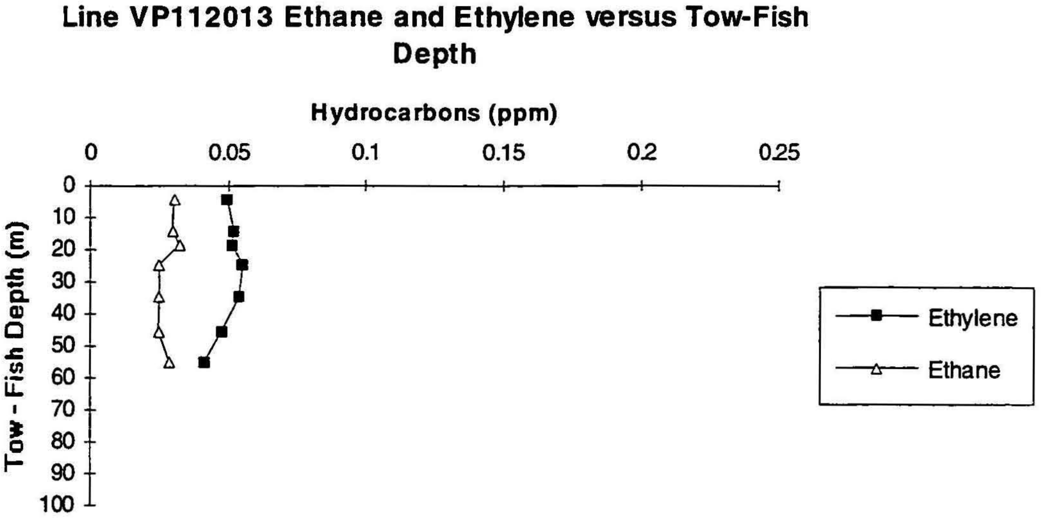


Figure 24 Vertical profiles of methane and percent wetness 0.5 nautical mile to the south of the North Head outfall.



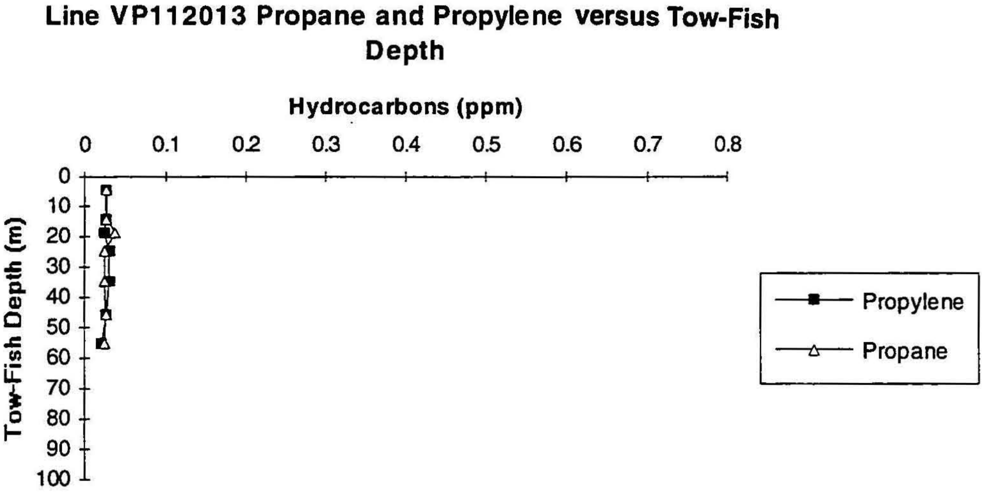
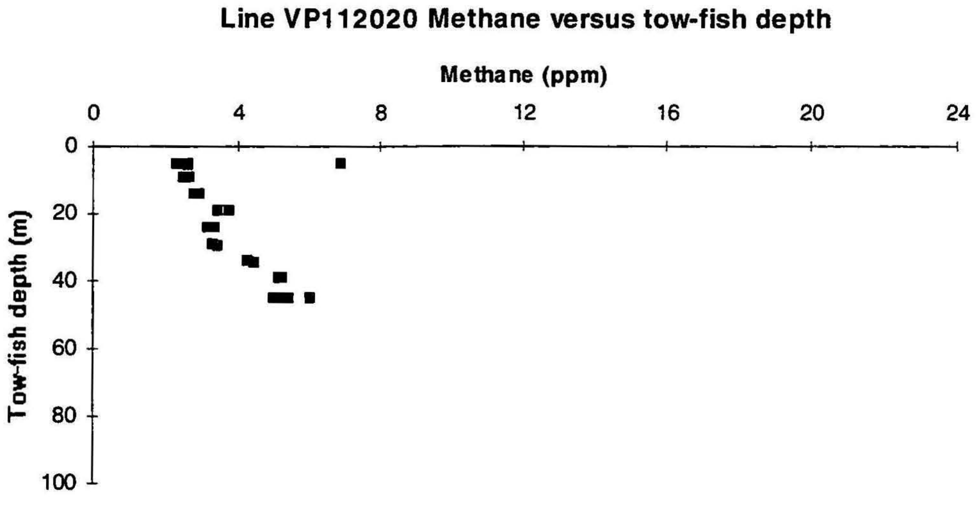


Figure 25. Vertical distribution of light hydrocarbons 0.5 nautical mile to the south of the North Head outfall, VP112013.



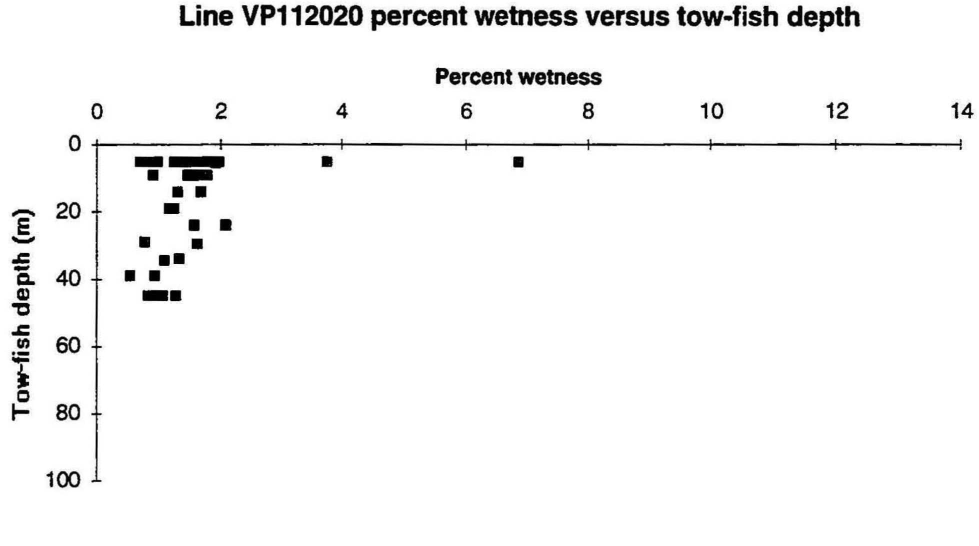
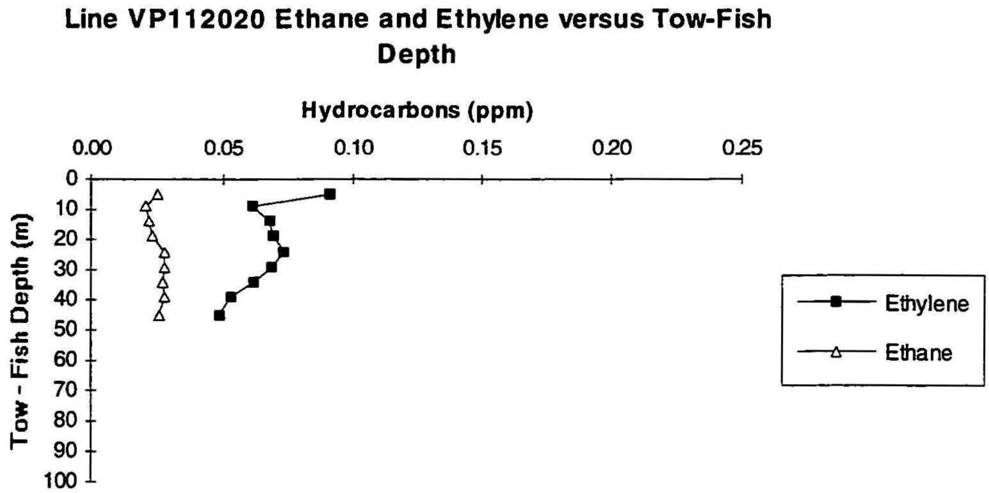


Figure 26 Vertical profiles of methane and percent wetness 0.5 nautical mile to the south of the North Head outfall, but occupied about 5 days after VP112013.



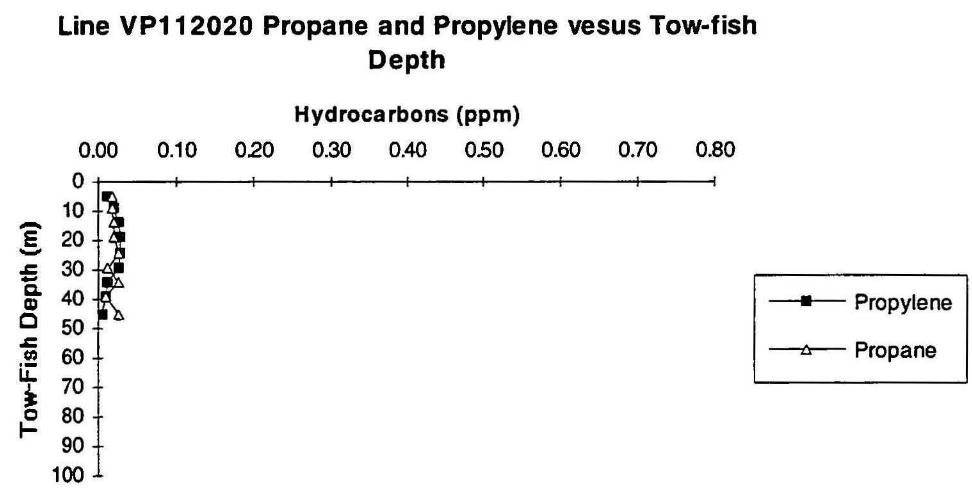
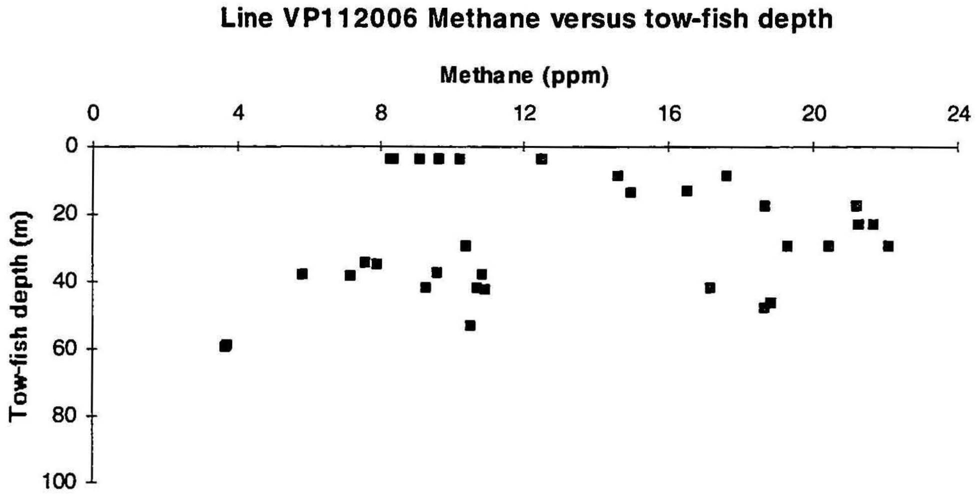


Figure 27. Vertical distribution of light hydrocarbons 0.5 miles to the south of the North Head outfall, but occupied about 5 days after VP112013.



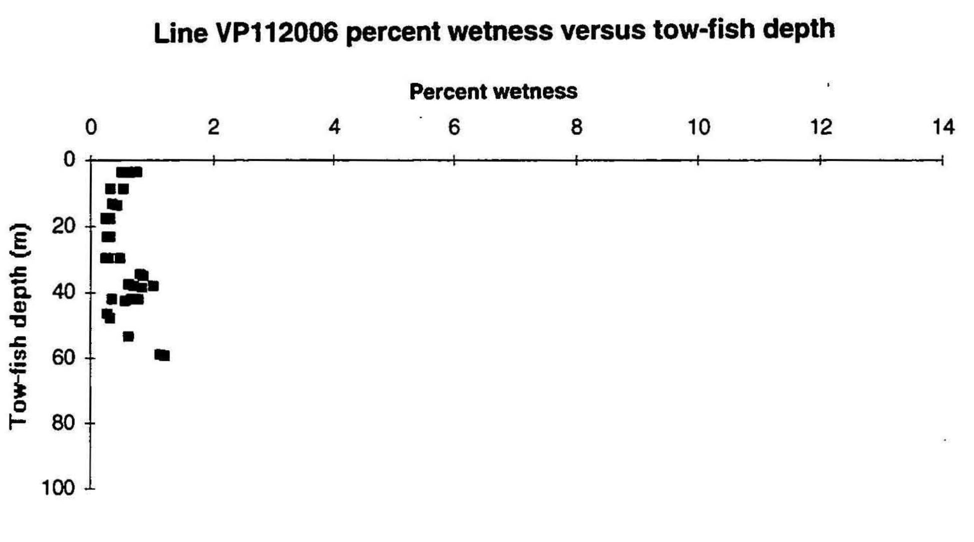
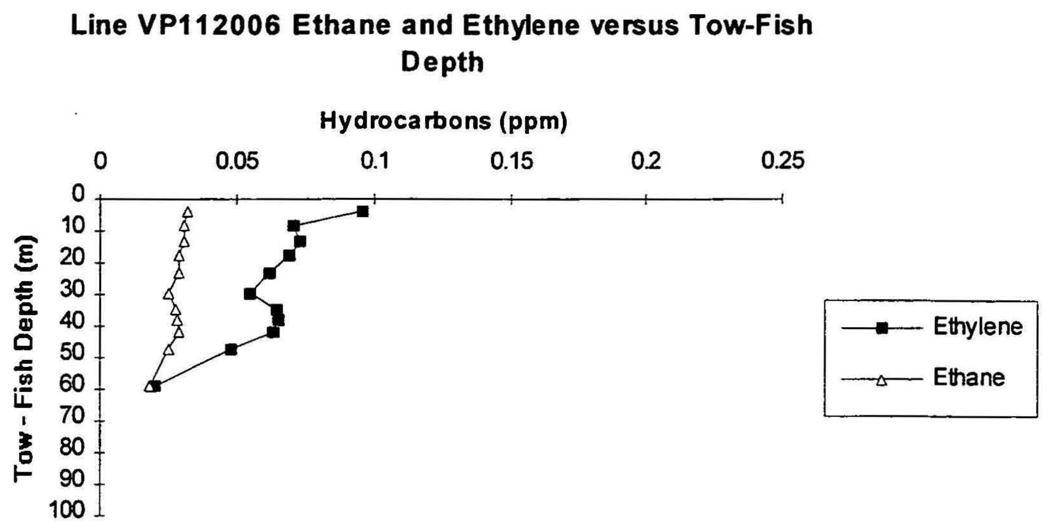


Figure 28 Vertical profiles of methane and percent wetness 0.5 nautical mile to the south of Bondi outfall.



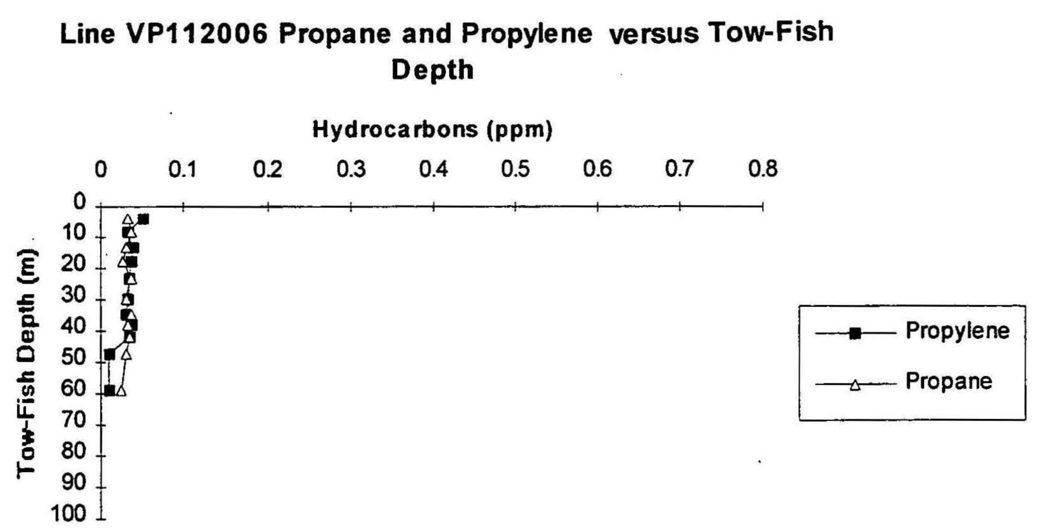
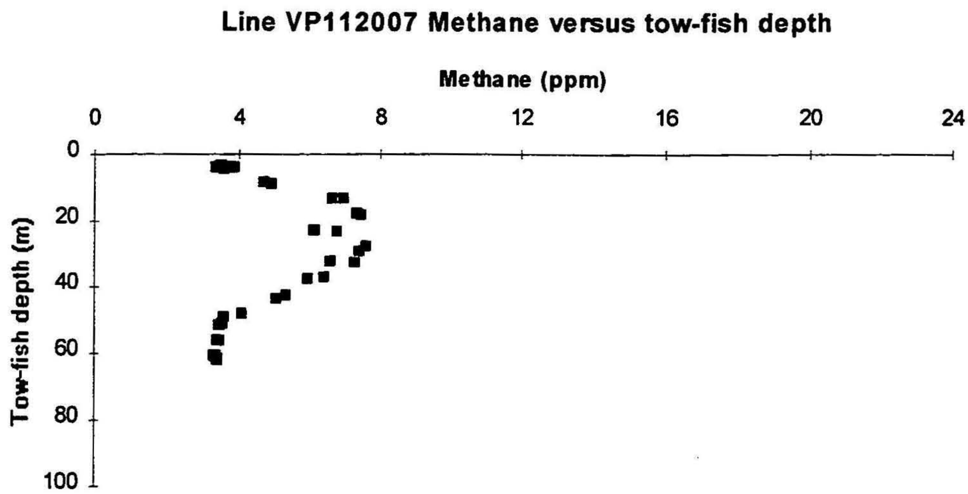


Figure 29. Vertical distribution of light hydrocarbons 0.5 mile to the south of the Bondi outfall.



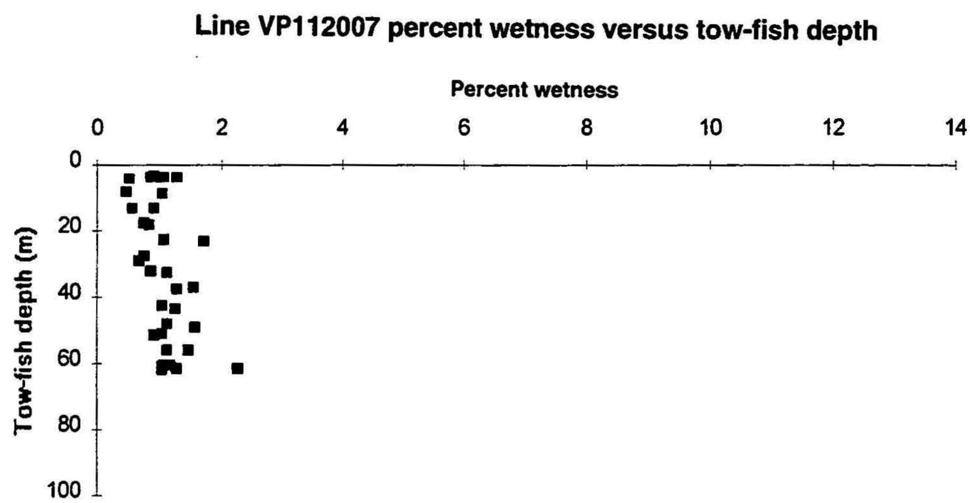
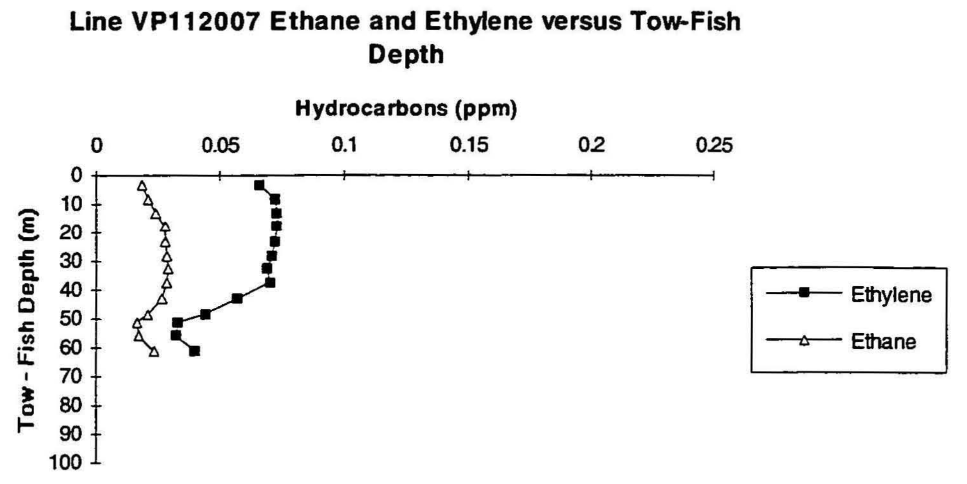


Figure 30. Vertical profiles of methane and percent wetness one nautical mile to the east south east of Bondi outfall.



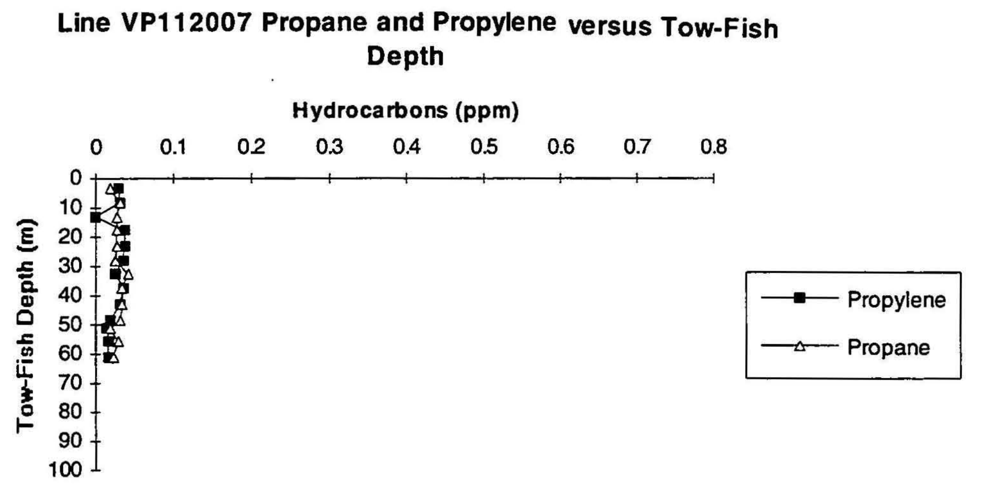


Figure 31. Vertical distribution of light hydrocarbons 1 nautical mile to the south east of the Bondi outfall.

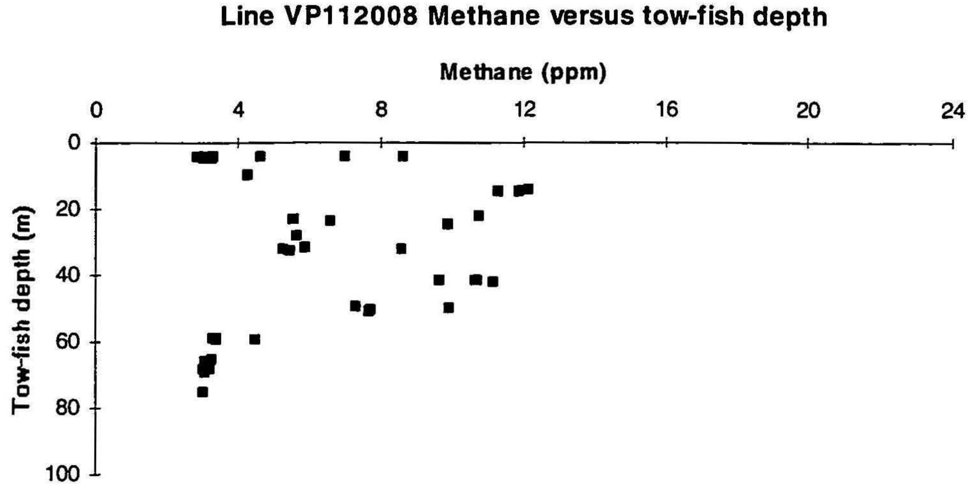
7.5 Malabar Outfall

Three vertical profiles were conducted to the south of the Malabar outfall (Figure 4):

1. VP112008 located 1 nautical mile to the south of the outfall (Figure 32 and Figure 33)
2. VP112015 located 1 nautical mile to the southwest of the outfall (Figure 34 and Figure 35).
3. VP112009 located 1.5 nautical miles to the south of the outfall (Figure 36 and Figure 37).

Elevated levels of methane (about three-fold background) and low percent wetness values were found throughout the water column at VP 112008 (Figure 32). Minor increases in ethane (about two-fold background) were also found with other hydrocarbon concentrations more typical of background (Figure 33). A similar pattern of hydrocarbon distributions were found at site at VP112015, located directly south and southwest of the outfall and Figure 34 and Figure 35).

Hydrocarbon concentrations at the other site (VP112009), located to the southeast of the outfall and the most offshore site, were typical of background concentrations (Figure 36 and Figure 37) and hence, indicate that the outfall plume (at least under the prevailing weather conditions) did not extend any significant distance (< 0.5 nautical mile) to the east of the outfall at this time.



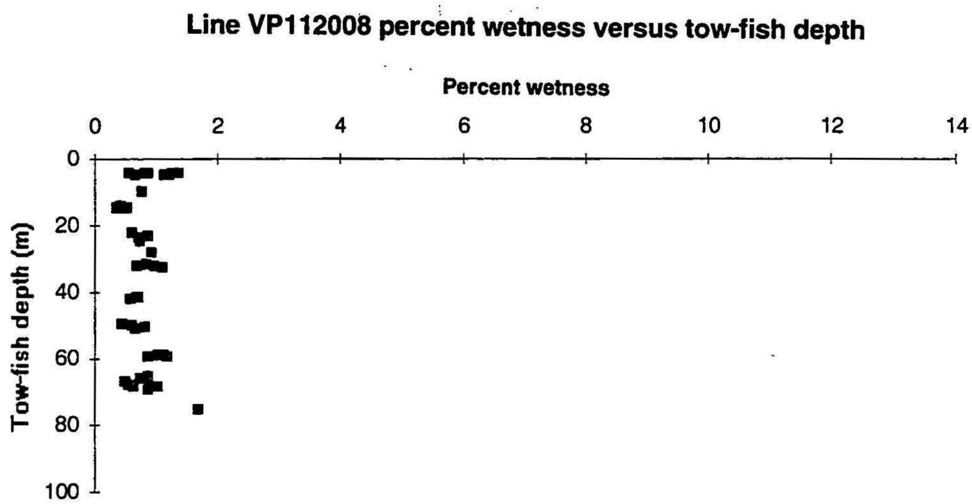
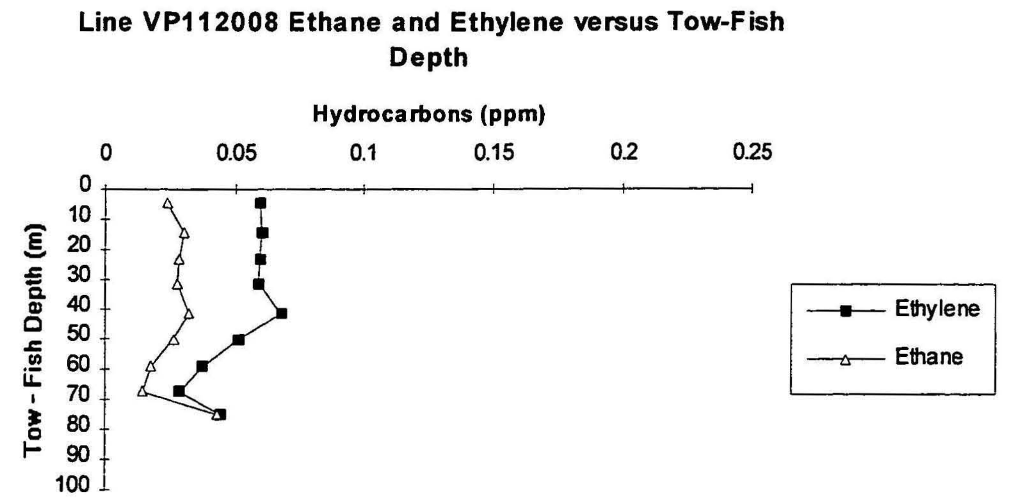


Figure 32 Vertical profiles of methane and percent wetness one nautical mile to the south of the Malabar outfall.



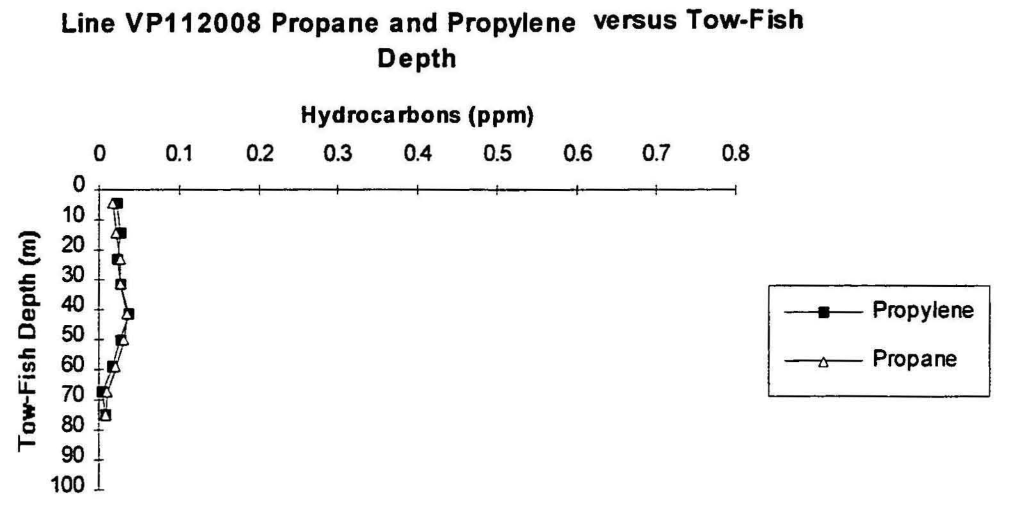
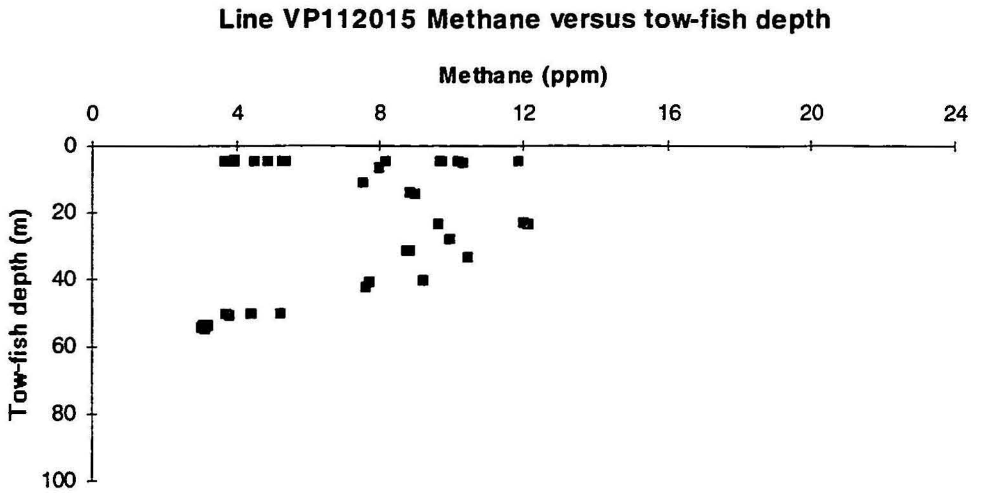


Figure 33. Vertical distribution of light hydrocarbons one nautical mile to the southwest of the Malabar Outfall.



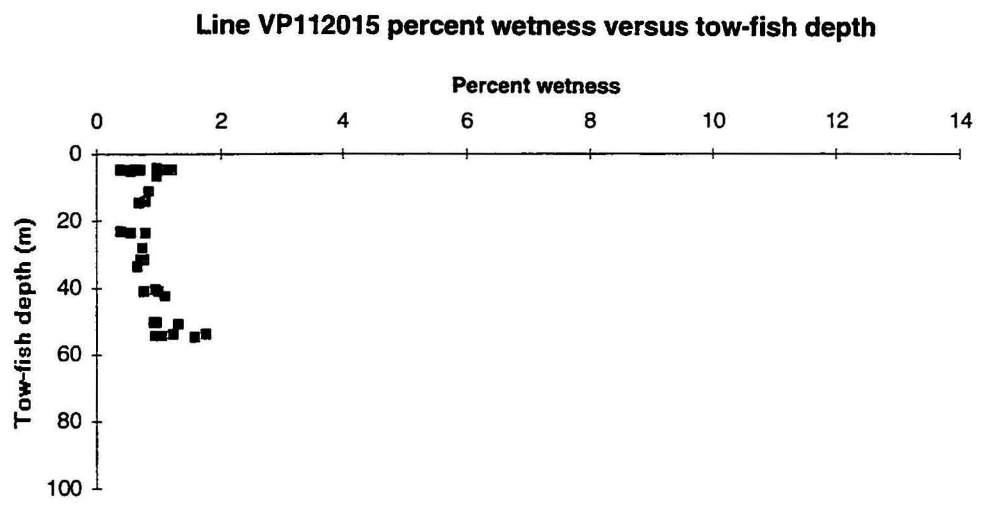
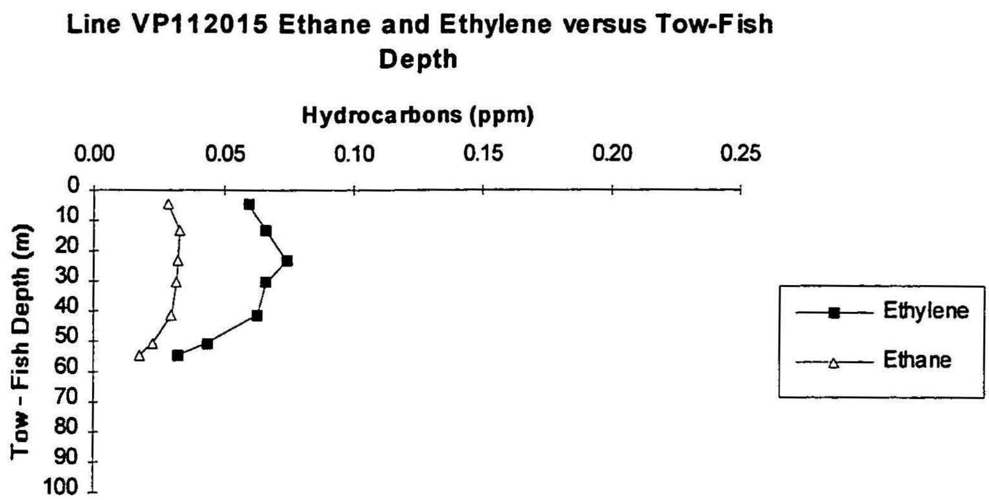


Figure 34 Vertical profiles of methane and percent wetness one nautical mile to the south west of the Malabar outfall.



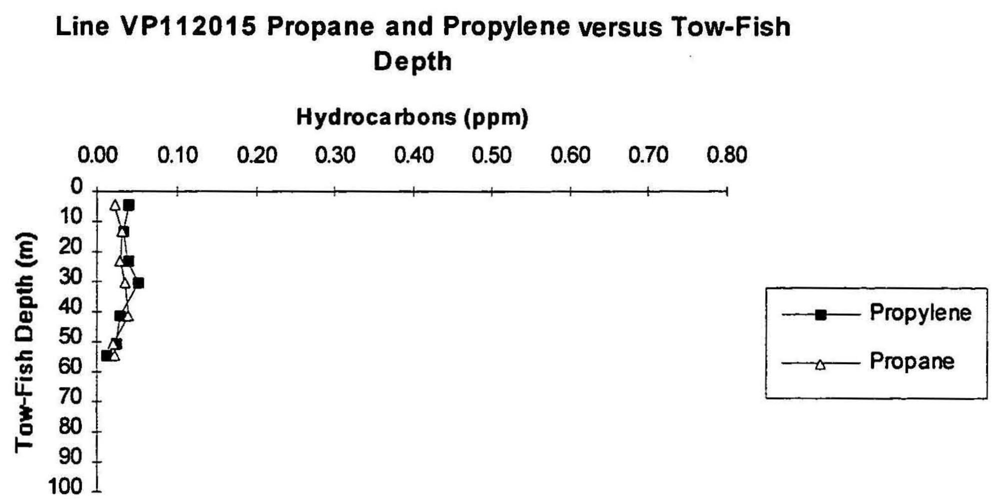
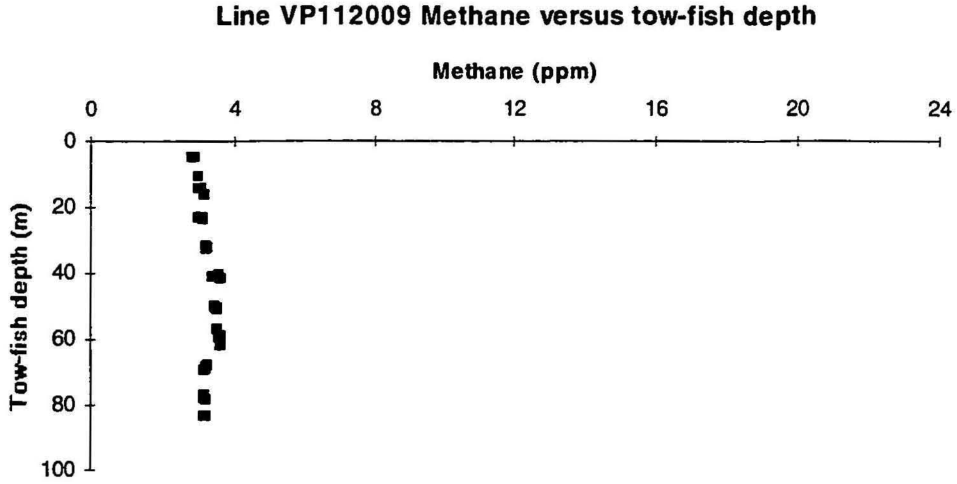


Figure 35. Vertical distribution of light hydrocarbons one nautical mile to the south west of the Malabar Outfall.



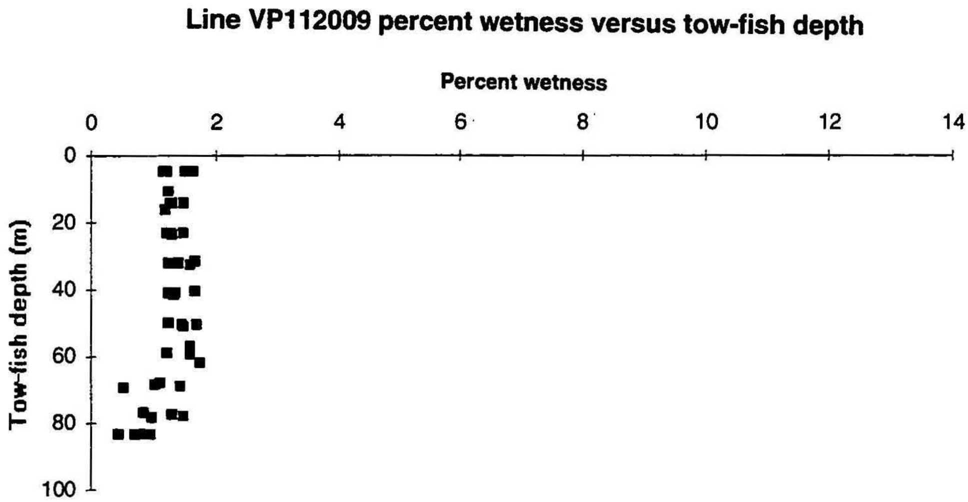
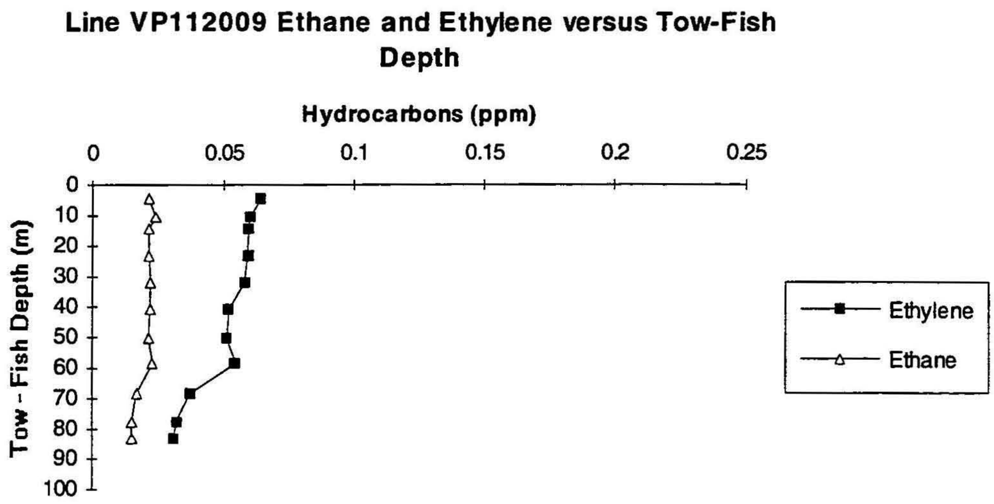


Figure 36 Vertical profiles of methane and percent wetness 1.5 nautical miles to the south of the Malabar outfall.



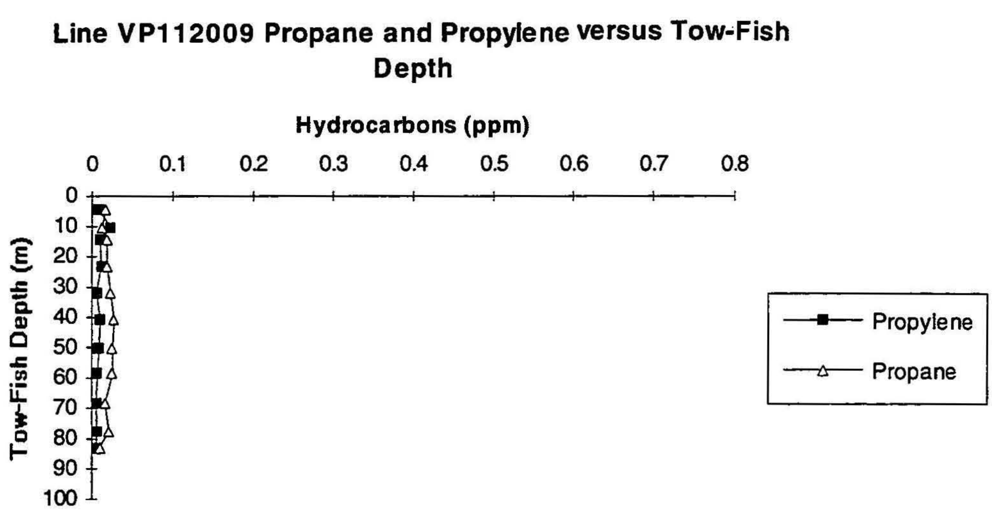


Figure 37. Vertical distribution of light hydrocarbons 1.5 nautical miles to the south of the Malabar outfall.

7.6 Entrance to Botany Bay

Three vertical profiles were conducted in the vicinity of Botany Bay (refer to Figure 4 for locations) :

1. VP112017 was located within the southern entrance to Botany Bay (Figure 38 and Figure 39).
2. VP112010 was conducted in 100 m of water 3 nautical miles southeast of the entrance to Botany Bay (Figure 40 and Figure 41); and
3. VP112016 was conducted in about 50 m water approximately 1 nautical mile to the northeast of Botany Bay off Cape Banks and about 2.5 nautical miles southwest of the Malabar Outfall, (Figure 42 and Figure 43)

A further two vertical profiles were proposed at the entrance to Botany Bay but these were not able to be conducted due to shipping movements in the area. Vertical profiles were conducted on a run-out tide and some measurements of ocean currents were made by the Water Board during this period.

Within the entrance to Botany Bay (VP112017) increases in methane (to 11 ppm), ethane (to 0.13 ppm), ethylene (to 0.17 ppm), propane (to 0.8 ppm), propylene (to 0.8 ppm) and butanes were detected with concentrations of all hydrocarbons systematically increasing with depth and occurring at water depths of 10 to 30 m (Figure 38 and Figure 39). The molecular compositions of this suite of hydrocarbons is clearly different to those detected at the ocean outfalls and at the entrance to Port Jackson. Here, wetness coefficients (maximum of 14 %) were significantly higher than background reflecting the very large increases in saturated C_{2+} hydrocarbon concentrations (Figure 39) which increase systematically with depth. In contrast, C_{2+} hydrocarbons and percent wetness (0- 2 %) was generally lower than background (2 - 2.5 %) near the ocean outfalls.

The hydrocarbon signature for VP112017 is also substantially different to that found in VP112004, located at the entrance to Port Jackson, which was the only other vertical profile to show substantially elevated wetness coefficients (5 %). The vertical profile conducted at entrance to Port Jackson showed elevated concentrations (3-14 times background) of C_{2+} hydrocarbons (Table 5), whereas the vertical profile conducted in the entrance to Botany Bay showed similar concentrations of ethane, ethylene and butane (3-13 times background) but extremely high propane and propylene (40-75 times background - refer to Table 5).

Table 5 Hydrocarbon signature for waters in the entrance to Port Jackson and Botany Bay.

	Botany Bay (VP112017)		Port Jackson (VP112004)	
	Max. Conc. (ppm)	Peak/ Background	Max. Conc. (ppm)	Peak/ Background
Methane	12	4	6	2
Ethane	0.12	6	0.08	4
Ethylene	0.15	3	0.25	5
Propane	0.8	40	0.005	3
Propylene	0.75	75	0.14	14
Butane	0.20	10	0.15	10

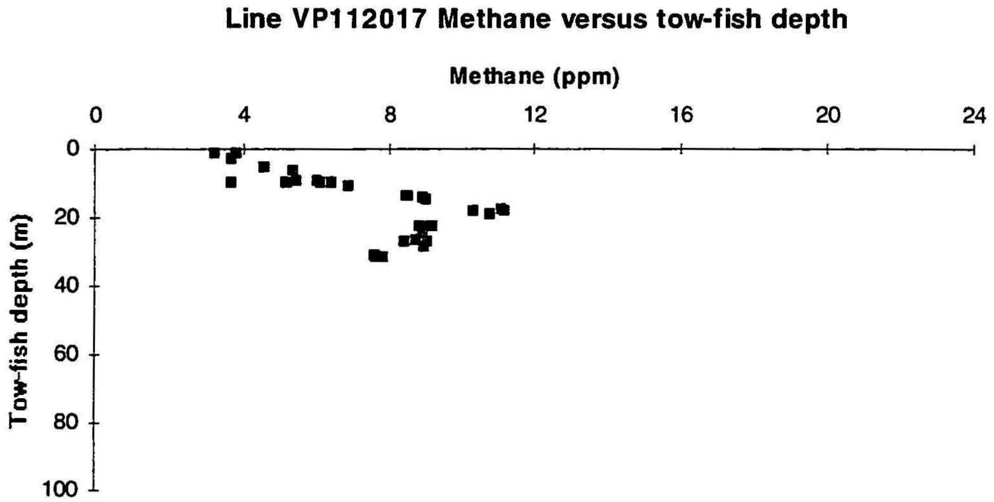
To the southeast of Botany Bay (VP112010) levels of hydrocarbons were generally close to background but slightly elevated concentrations of methane (4.5 ppm), ethane (0.035 ppm), propane (0.05 ppm) were found from 40 to 80 metres water depth in a broad mid-water plume (Figure 40 and Figure 41). Percent wetness values also increased in this plume (maximum of 3 %).

Vertical profile VP112016 was collected to the northeast of Botany Bay but about 2.5 nautical miles southwest of the Malabar Outfall. A sub-surface plume of methane with concentrations three to four fold background associated with low percent wetness (<1.5 %) were measured at about 20 m water depth (Figure 42). Minor increases in ethane, propane and butane were also detected (Figure 43).

7.7 Offshore Bate Bay

The southern most vertical profile (VP112018) was conducted 3.5 nautical miles offshore of Bate Bay, 3.8 nautical miles south of Botany Bay, and 7 nautical miles southwest of the Malabar Outfall (Figure 4) in an area potentially affected by discharges from Malabar Outfalls, Botany Bay and Port Hacking.

Small increases in methane, about double background concentrations, with an associated increase in percent wetness were detected in a mid-water plume at a depth of about 40 metres (Figure 44 Vertical profiles of methane and percent wetness 3.5 nautical miles offshore from Bate Bay). Elevated levels of ethane and propane and occasional or more erratic increases in concentration of butane were detected within the mid-water plume (Figure 45).



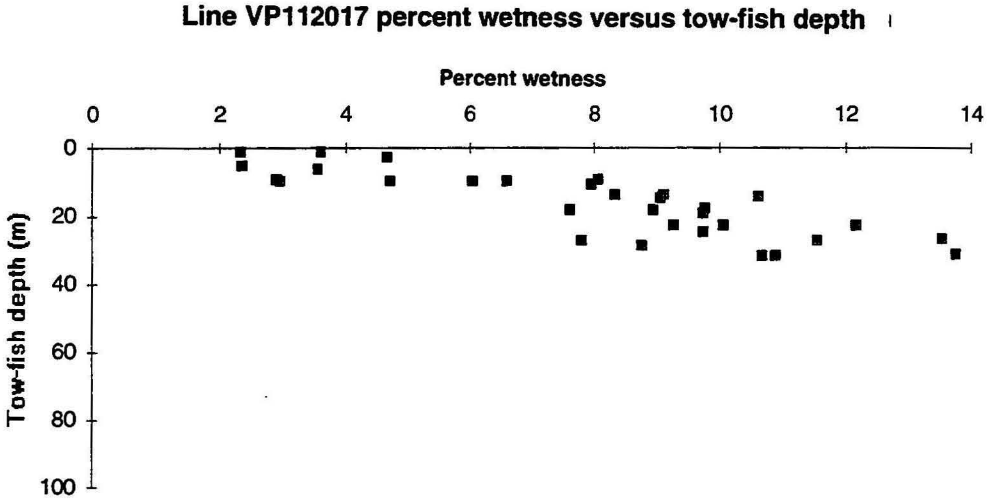
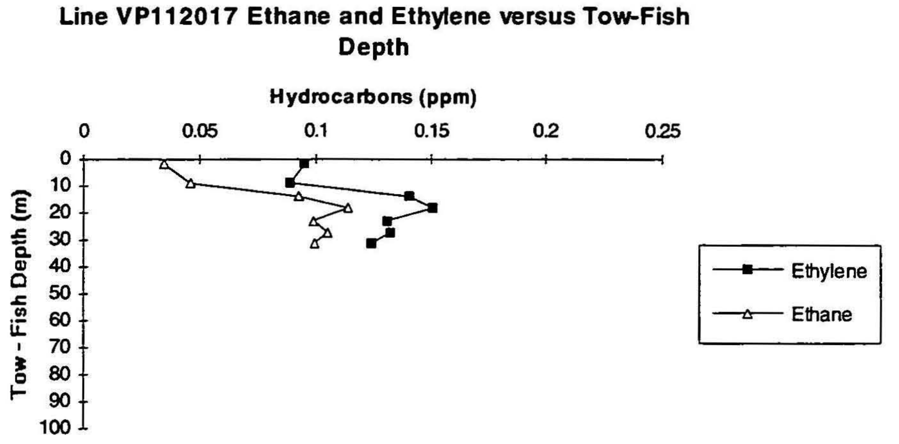
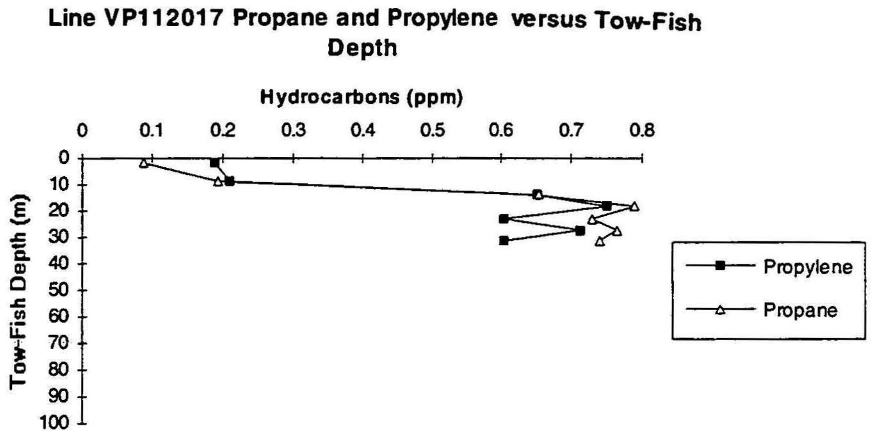


Figure 38 Vertical profiles of methane and percent wetness at the entrance to Botany Bay.





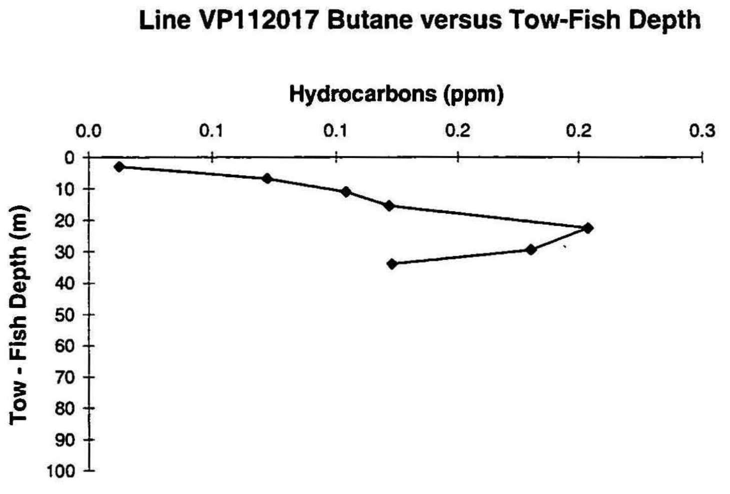
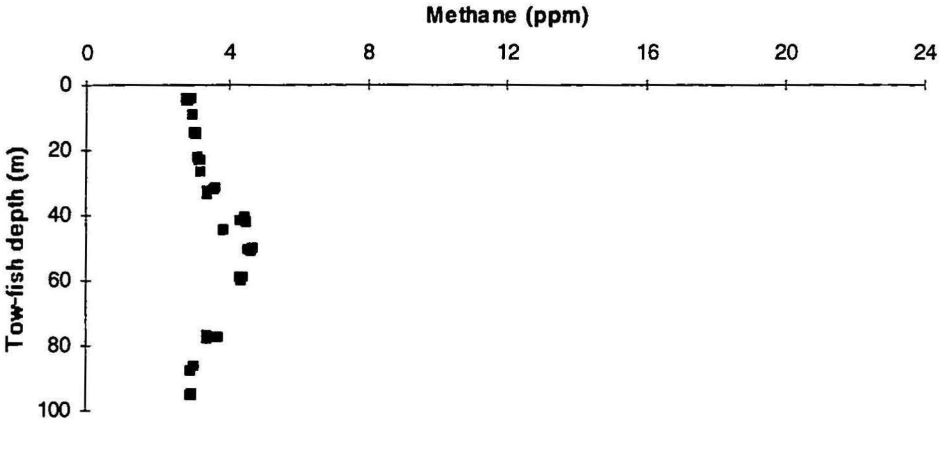


Figure 39. Vertical distribution of light hydrocarbons near the entrance to Botany Bay.

Line VP112010 Methane versus tow-fish depth



Line VP112010 percent wetness versus tow-fish depth

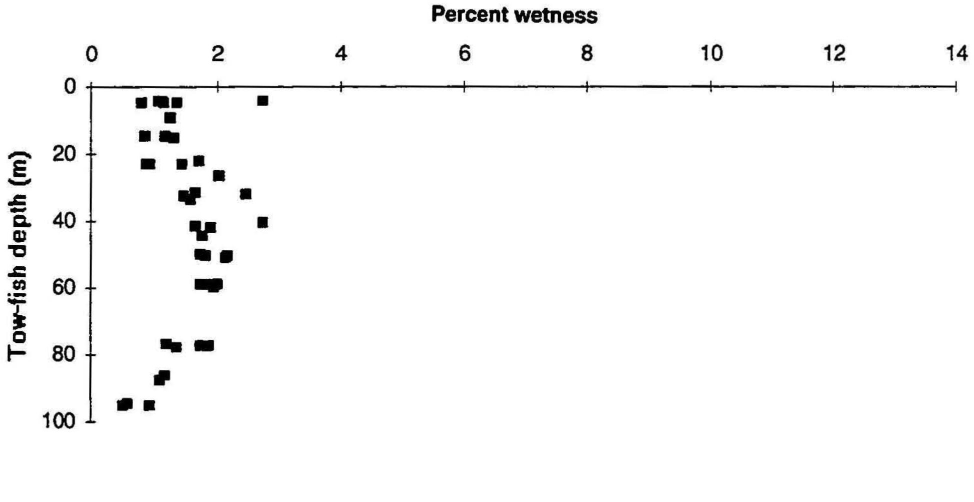
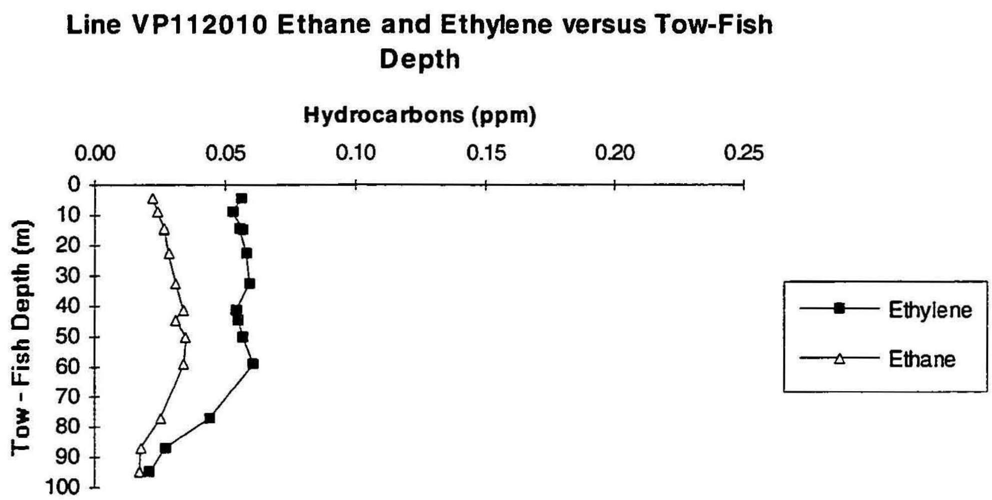


Figure 40. Vertical profiles of methane and percent wetness conducted in 100m of water 3 nautical miles south east of the entrance to Botany Bay.



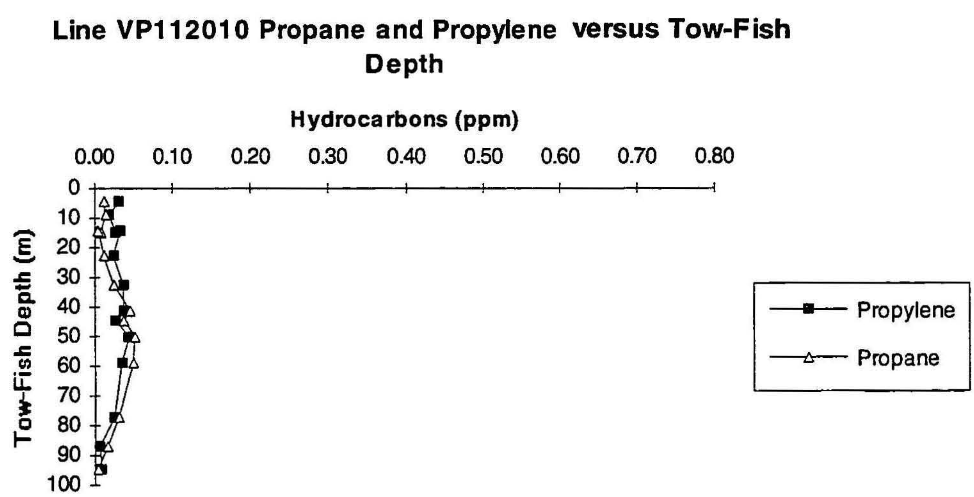
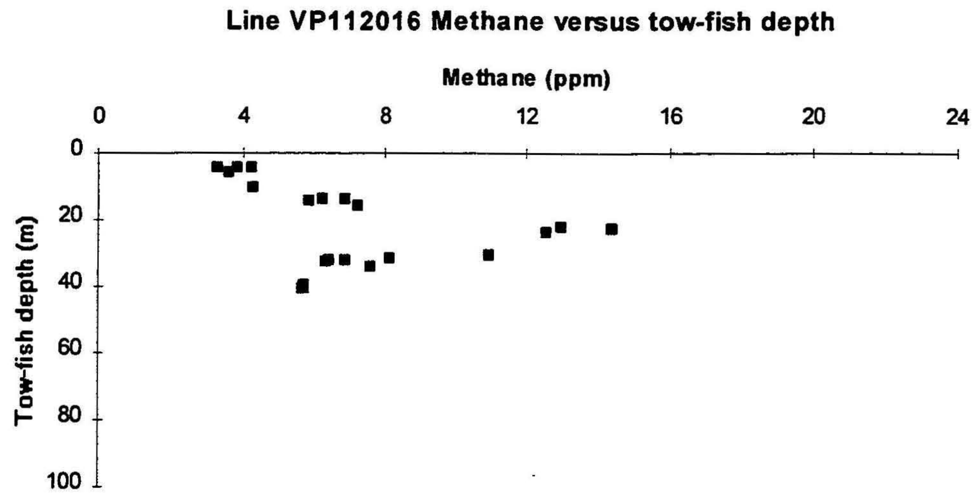


Figure 41. Vertical distribution of light hydrocarbons conducted in 100m of water 3 nautical miles south east of the entrance to Botany Bay.



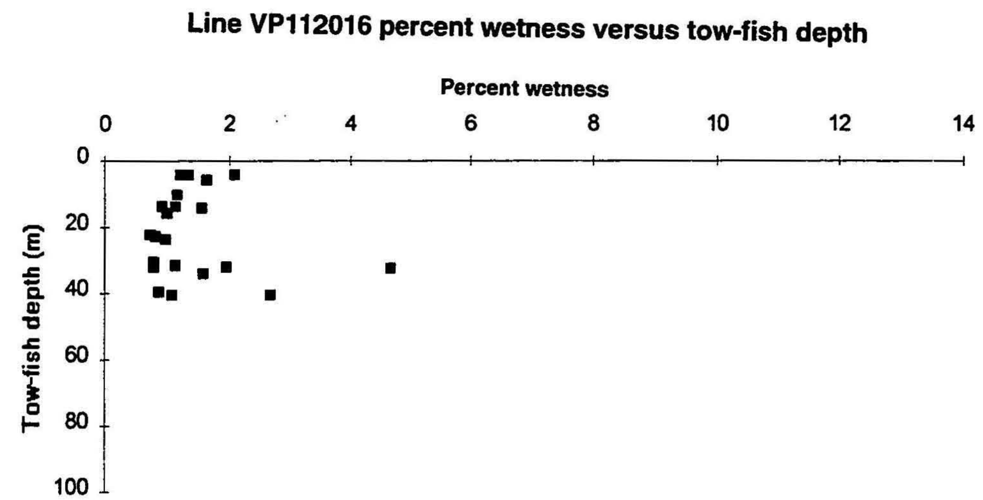
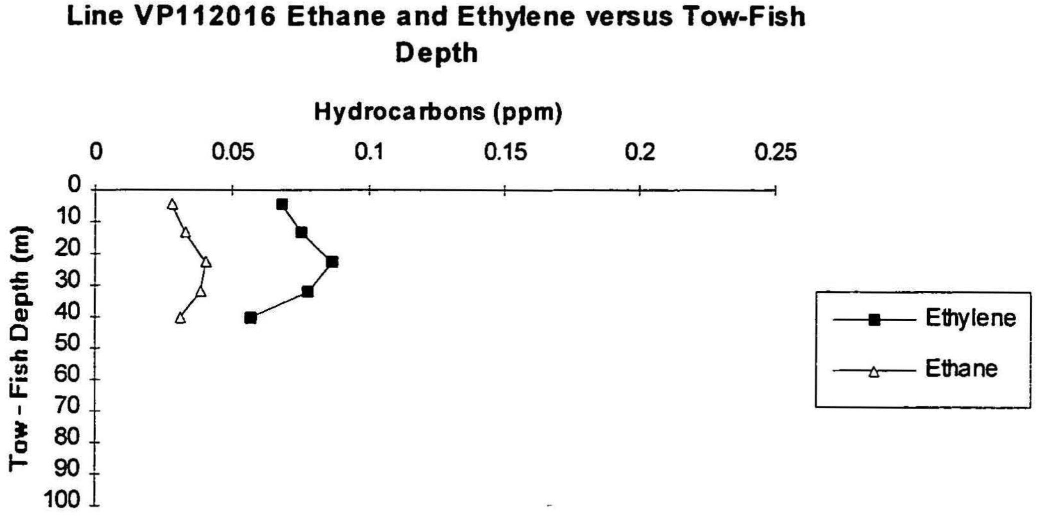


Figure 42. Vertical profiles of methane and percent wetness one nautical mile to the north east of Botany Bay off Cape Banks, in about 50 m of water.



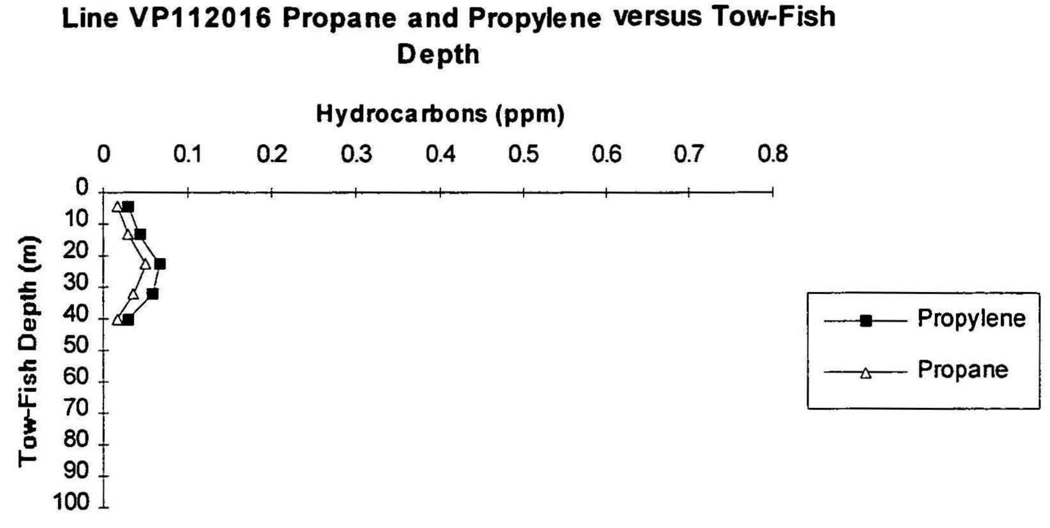
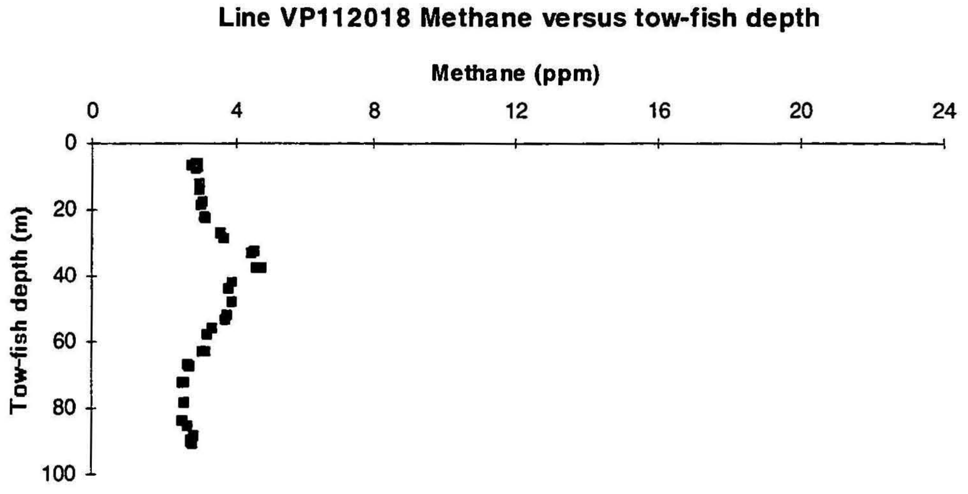


Figure 43. Vertical distribution of light hydrocarbons 1 nautical mile to the north east of Botany Bay off Cape Banks, in about 50m of water.



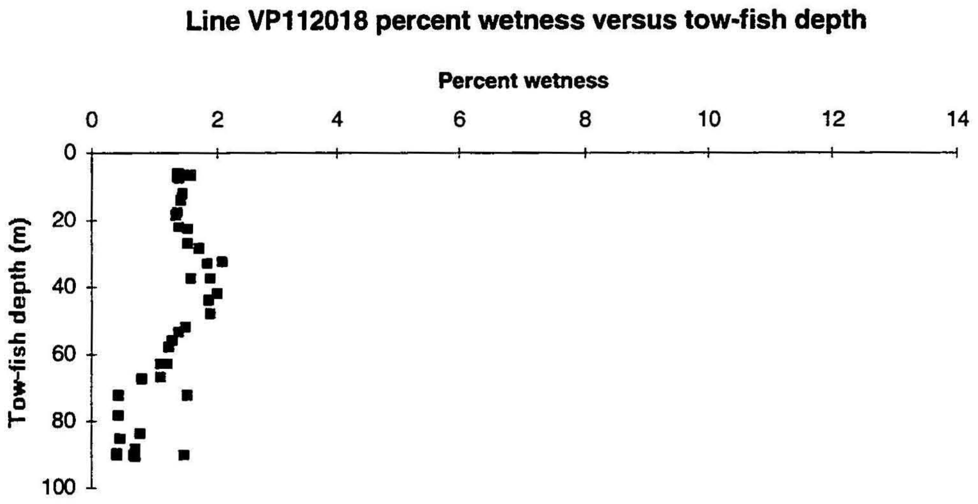
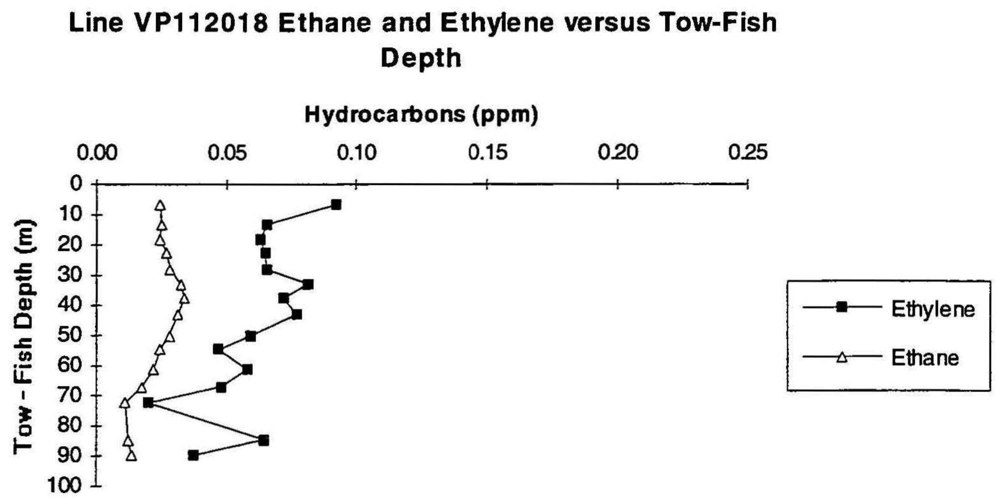


Figure 44. Vertical profiles of methane and percent wetness 3.5 nautical miles offshore from Bate Bay.



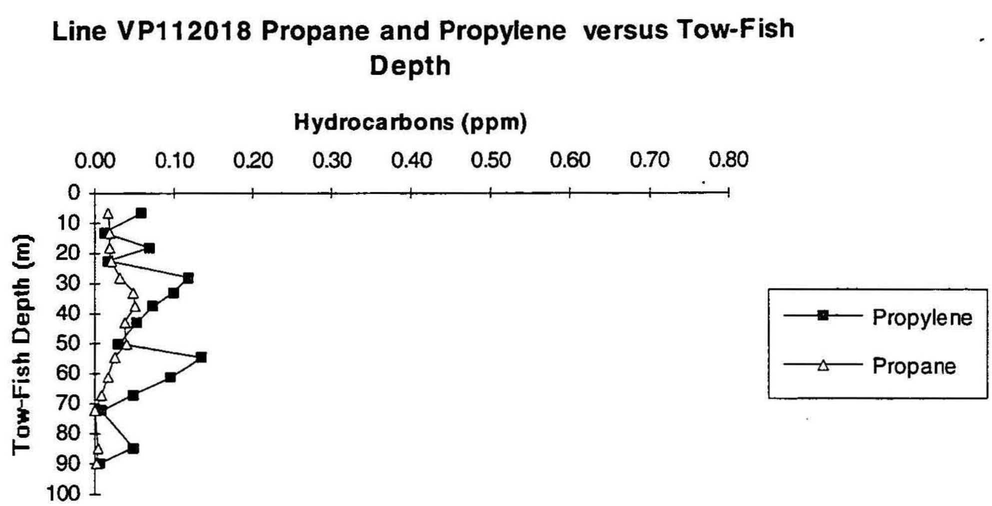


Figure 45. Vertical distribution of light hydrocarbons 3.5 nautical miles offshore from Bate Bay.

8. Vertical profiles of hydrocarbons in the coastal zone: Discussion

One of the objectives of this survey was to test if the potential locations of hydrocarbon inputs (Port Jackson, Botany Bay, Broken Bay and the various deep ocean outfalls) discharging to the coastal zone near Sydney could be distinguished from each other on the basis of both molecular and isotopic compositions. If these sources can be distinguished then the distribution and dilution of individual sources may be determined.

In the petroleum exploration industry the percent wetness of hydrocarbons seeps has traditionally been used to distinguish between hydrocarbons derived from petrogenic 'wet sources' and 'dry' biogenic gas. To test whether the wetness index was capable of distinguishing between potential sources (individual outfalls and estuaries) the relative abundances of methane and the saturated C_{2+} hydrocarbons from vertical profiles from each of the ocean outfalls and those from the entrances to the estuaries were compared.

Figure 46 plots methane concentration versus percent hydrocarbon wetness for all data collected from near the ocean outfalls. In this plot there is a cluster of data with concentrations of methane about 3 ppm and percent wetness (1.0 % to 2.5 %), background levels for near-surface seawater. Data from near the ocean outfalls plot on a trend-line of decreasing percent wetness with increasing methane concentration. All ocean outfall data plot on the same trend line irrespective of individual outfall source and therefore inputs from Bondi, North Head and Malabar cannot be differentiated on the basis of percent wetness alone.

The cross-plot of methane versus percent hydrocarbon wetness for the vertical profiles conducted near the entrances to the estuaries is shown in Figure 47. In this plot there is also a cluster of data points about 'background' values (methane < 3 ppm and wetness values 1-2.5 %). However, in this plot there is a general trend of increasing wetness with increasing methane content. For example, data from profile VP112017 (from south of the entrance to Botany Bay - closed squares) has wetness values of up to 14 % at methane concentration of about 10 ppm. Data from the entrance to Port Jackson (VP112004) fall on this trend-line although at lower methane values compared to the Botany Bay data. Vertical profile VP112005 (open squares) collected 1.3 nm SSE of the entrance to Port Jackson shows a trend of slightly decreasing wetness with increasing methane, probably reflecting the influence of the North Head Outfall.

The contrasts between the estuarine data and the outfall data are shown more clearly in Figure 48. All of the ocean outfall data (including the VP 112016 near the entrance to Botany bay) plot on the trend-line of decreasing wetness with increasing methane. In contrast, those vertical profiles occupied near the entrances to major estuaries with elevated hydrocarbon concentrations (most notably VP112017 and VP112004) plot on a trend line of increasing wetness (increasing C_{2+} abundance) with increasing methane content. It should be noted that sources only become separable at elevated hydrocarbon levels and much of the data cluster about background (methane 3-5 ppm and percent wetness 1-2 %).

These data clearly show differences in the molecular composition of ocean outfall and estuarine hydrocarbon mixtures and that percent wetness is a useful parameter for distinguishing between these sources. Percent wetness is not, however, useful for distinguishing between individual outfalls or between individual estuaries.

To test whether there were any significant differences between individual estuaries and outfalls a multivariate analysis was undertaken in which all of the hydrocarbon data collected was analysed. Canonical analysis of variance is a multi-variate statistical technique which is used to highlight the differences between groups, identify parameters which differentiate between these groups and illustrate these differences graphically using a reduced set of variables (canonical variates) usually as cross plots (Krzanowski, 1988 and StatSoft, 1994). To determine whether there were any significant differences in hydrocarbon signature between individual ocean outfalls and estuaries the vertical profile data were classified into the groups in Table 6.

Table 6 Allocation of vertical profiles to individual sources

Source	Vertical Profile
Malabar Outfall	VP112008 VP112015
Bondi Outfall	VP112006
North Head Outfall	VP112014 VP112013 VP112019
Port Jackson	VP112004
Botany Bay	VP112017
Background Ocean Water	VP112002

Only those vertical profiles located directly in the mouth of the estuary were used to minimise the possibility of contamination from other sources such as deep ocean outfalls. In addition, vertical profiles that did not show any significant enhancement in hydrocarbon concentration were not used in the analysis, thus Broken Bay is not represented as it did not show a significant increase in the concentration of any of the measured hydrocarbons. The analysis was also restricted to those variables that were significantly above detection limit (*ie* had a non-zero variance).

To determine whether there was any significant difference between the groups the first and second canonical variate scores for the data set are plotted in Figure 49. It can be seen from this diagram that data fall into three clear groups:

1. Port Jackson (closed squares);

2. Botany Bay (closed circles); and
3. Ocean Outfalls/Background Ocean Water (remaining symbols).

Port Jackson samples are characterised by high values of the first canonical variate. The correlation coefficients in Table 7 show that this variate is strongly correlated to ethylene and moderately correlated to ethane suggesting a distinctive ethylene and ethane signature for Port Jackson. Botany Bay samples are characterised by negative values of the second canonical variate. The correlation coefficients (Table 7) show that this root is strongly correlated (negatively) to propylene, propane, ethane, butane and ethylene suggesting that Botany Bay waters have high concentrations of a wide range of saturated and unsaturated hydrocarbons.

The eigenvalues for this analysis (Table 7) show that the first and second canonical variates account for 94 % of the variance in the original data. The third canonical variate only explains an additional 5 % of the variance and is therefore unlikely to be of any utility in differentiating between sources. Cross-plots using the third variate (not reproduced here) confirmed this assessment.

It is noteworthy that the ocean outfalls cannot be distinguished from background ocean waters in this analysis. The reason for this is related to the following

- each vertical profile includes both relatively clean ocean water and diluted plume and so are not pure end-members; and
- the analysis may have included too many sources to effectively differentiate.

In an effort to discriminate between individual outfalls and ocean waters a further canonical analysis was undertaken with the data from the vertical profiles split into three major groups: outfalls, estuaries and background ocean waters as shown in Table 8.

Table 7 Raw coefficients for canonical variables used to discriminate between individual outfalls and estuaries.

Variables	Raw coefficients for discriminant functions		Canonical variate correlation matrix	
	Variate 1	Variate 2	Variate 1	Variate 2
THC	0.404	0.072	-0.023	0.089
METHANE	-0.180	-0.062	-0.020	0.010
ETHANE	57.997	9.542	0.295	-0.708
ETHYLENE	53.402	1.8065`	0.739	-0.479
PROPANE	-12.611	-0.284	0.014	-0.874
PROPYLENE	-2.019	-14.385	0.076	-0.930
BUTANE	20.892	4.396	0.342	-0.584
HEXANE	-0.998	1.161	0.016	-0.034
Eigenvalue	17.99	3.05		
Cumulative Proportion	0.799	0.935		

Table 8 VP data allocated to three supergroups - estuaries, outfalls and ocean waters.

Source	Vertical Profiles
Outfalls	VP112008
	VP112015
	VP112006
	VP112014
	VP112013
	VP112019
Estuaries	VP112004
	VP112017
Background Ocean Water	VP112002

A bivariate plot of the first and second canonical variates (Figure 50) shows that each of these three groups plot in separate clusters. Importantly this analysis is able to distinguish background ocean water from both outfalls and estuaries. Furthermore the structure of the data is consistent with Vertical Profiles from each of the sources containing a mixture of clean ocean water and outfalls or estuarine sourced waters.

In Figure 50 data from the Vertical Profiles collected in the mouth of the two estuaries (Port Jackson and Botany Bay) are characterised by increasing values of the first canonical variate. The correlation coefficients given in Table 9 show that first canonical variate is correlated most strongly with ethane, butane and ethylene. In contrast the ocean outfalls are characterised by increasing scores on the second canonical variate. The correlation coefficients in Table 9 indicate that second canonical variate correlates most strongly with THC, methane and ethane. This is consistent with earlier observations that effluent discharged from the outfalls has high concentrations of methane and minor ethane.

In this analysis both estuarine and outfall data overlap with the clean ocean water data and samples with higher concentrations of hydrocarbons plotting with higher scores on each axis. The discriminant functions (equation for each variate) found in this analysis could therefore be used to quantify both source and concentration of each source and to map the distribution and concentration of both effluent and estuarine waters in the coastal zone. Comparison of Figure 50 with a bivariate plot of methane and percent wetness (Figure 48) shows that discriminatory power provided using canonical variate scores is not significantly higher than the cross-plot approach. Where hydrocarbons associated with effluent from the deep ocean outfalls needs to be distinguished from estuarine hydrocarbons then a simple bivariate plot of methane and percent wetness is suitable.

The earlier analysis also indicated the possibility of distinguishing between individual outfall plumes on the basis of hydrocarbon signature. To investigate whether effluent discharged from individual outfalls have different light hydrocarbon signatures the analysis was repeated with only three sources: North Head, Malabar and Bondi.

Table 9 Raw coefficients for canonical variables used to discriminate between outfalls, estuaries and clean ocean waters.

Variables	Raw coefficients for discriminant functions		Canonical Variates correlation matrix	
	Root 1	Root 2	Root 1	Root 2
THC	-0.009	0.142	-0.033	0.938
METHANE	-0.072	-0.068	-0.012	-0.684
ETHANE	15.547	3.384	0.708	0.319
ETHYLENE	26.277	0.315	0.671	0.170
PROPANE	-4.933	-0.667	0.288	0.063
PROPYLENE	10.370	-0.770	0.375	0.074
BUTANE	6.268	2.598	0.704	0.137
HEXANE	-1.224	3.804	0.039	0.154
Eigenvalue	6.15	0.31		
Cumulative Proportion	0.95	1.00		

Plotting the first and second canonical variates in Figure 51 shows significant overlap between each group. Data from Malabar and North Head plot as relatively distinct groups, North Head having relatively high values of the first canonical variate whereas Malabar tends to have relatively low values. The data for the Bondi outfall showed greatest variability and overlapped with both the other groups. Refer to Table 10 for details of the analysis.

Table 10 **Raw coefficients for canonical variables used to discriminate between individual outfalls.**

Variables	Raw coefficients for discriminant functions		Canonical variates correlation matrix	
	Root 1	Root 2	Root 1	Root 2
THC	0.217	0.015	0.493	0.657
METHANE	-0.409	0.291	0.085	0.761
ETHANE	59.40	-178.1	0.199	0.150
ETHYLENE	26.01	32.80	0.116	0.269
PROPANE	-11.52	20.33	-0.044	0.304
PROPYLENE	-43.10	4.00	-0.176	0.271
BUTANE	22.53	44.20	0.041	0.187
HEXANE	1.12	0.367	0.002	-0.050
Eigenvalue	1.21	0.31		
Cumulative Proportion	0.80	1.00		

In summary the vertical profile data indicate the following.

1. Bivariate plots of methane and wetness were capable of distinguishing between effluent discharged from the deep ocean outfalls and waters discharged from estuaries. Discharged effluent was characterised by high methane concentrations and a 'dry' molecular signature (decreasing wetness values <2 % with increasing methane). Waters outflowing from nearby estuaries were characterised by low concentrations of methane (<10 ppm) and a 'wet' molecular signature (increasing wetness values >2 % with increasing methane) as a result of elevated concentrations of saturated C_{2+} hydrocarbons, notably ethane, propane and butane. Methane/wetness signatures could not be used to differentiate between individual estuaries
2. Multivariate analysis of the all hydrocarbon data showed that waters from Port Jackson and Botany Bay had different light hydrocarbon characteristics which could be further distinguished from outfall hydrocarbons
3. A vertical profile measured in the entrance to Botany Bay recorded the highest concentration of C_{2+} hydrocarbons (including the saturated and unsaturated hydrocarbons), and Botany Bay is potentially a significant contributor of hydrocarbons to coastal waters. We cannot report that the hydrocarbon exports from Botany Bay are naturally occurring or anthropogenic but elevated levels of the unsaturated hydrocarbons (ethylene and propylene) which accompany the elevated ethane and propane suggest a naturally occurring input as the unsaturated hydrocarbons may be produced biogenically in surface waters. Modest increases in hydrocarbon concentration were recorded at the entrance to Port Jackson and generally no increase in hydrocarbon concentration occurred at the entrance to Broken Bay (although some elevated butane were found).
4. There were no clear differences in the light hydrocarbon composition of effluent discharged from individual outfalls.

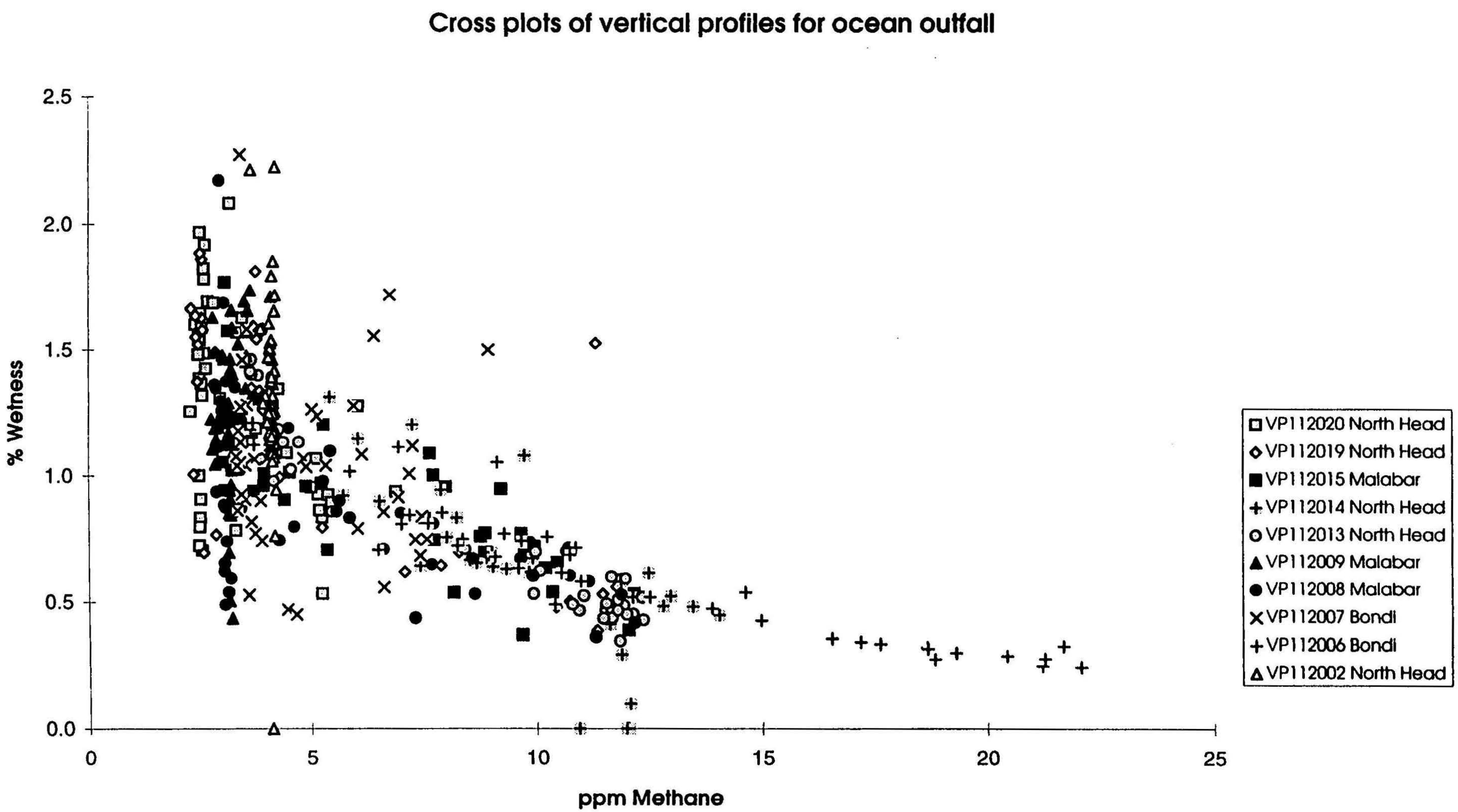


Figure 46. Methane versus percent hydrocarbon wetness of all vertical profile data collected near ocean outfalls.

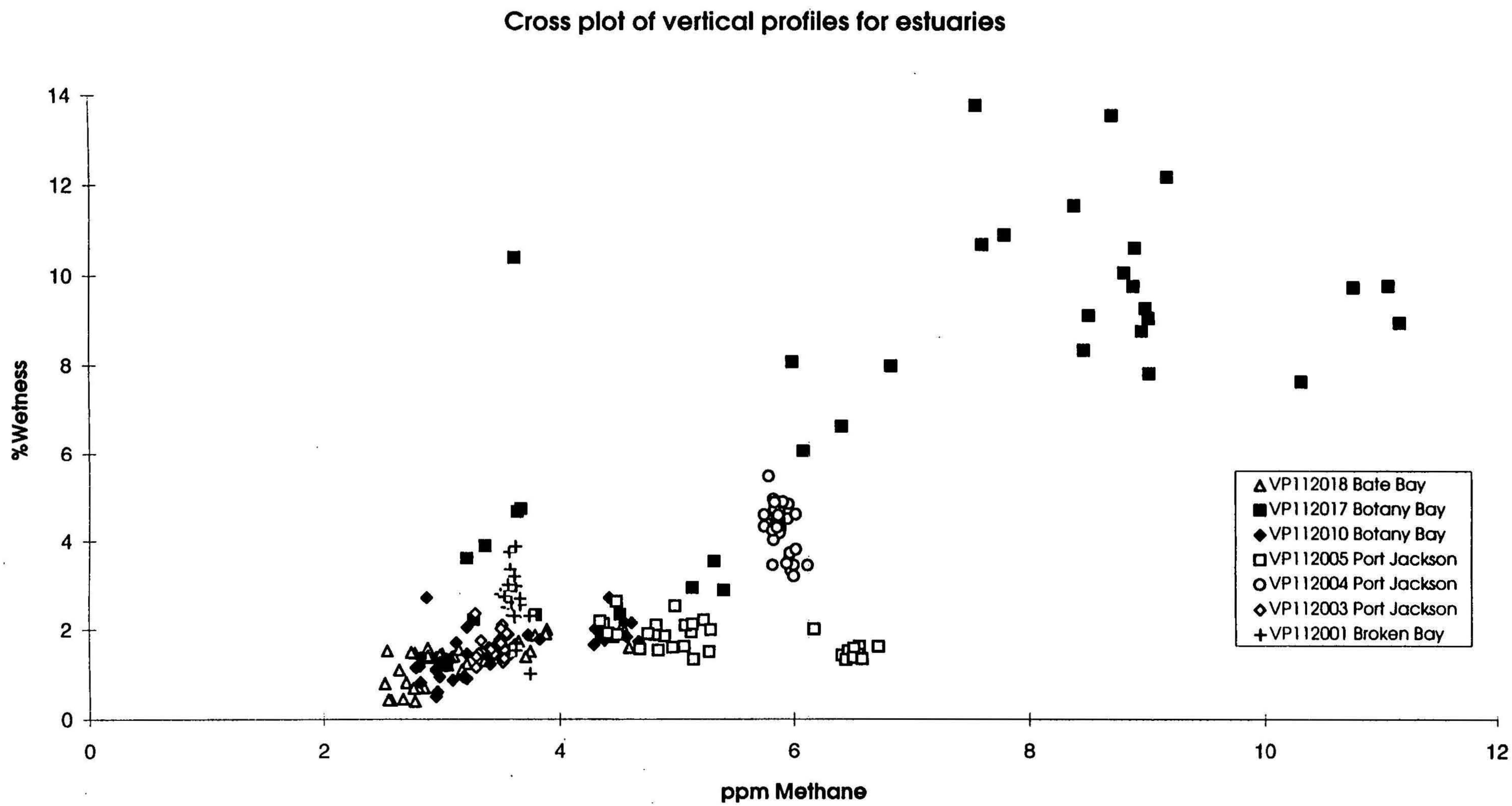


Figure 47. Methane versus percent hydrocarbon wetness of all vertical profile data collected near the entrance to estuaries.

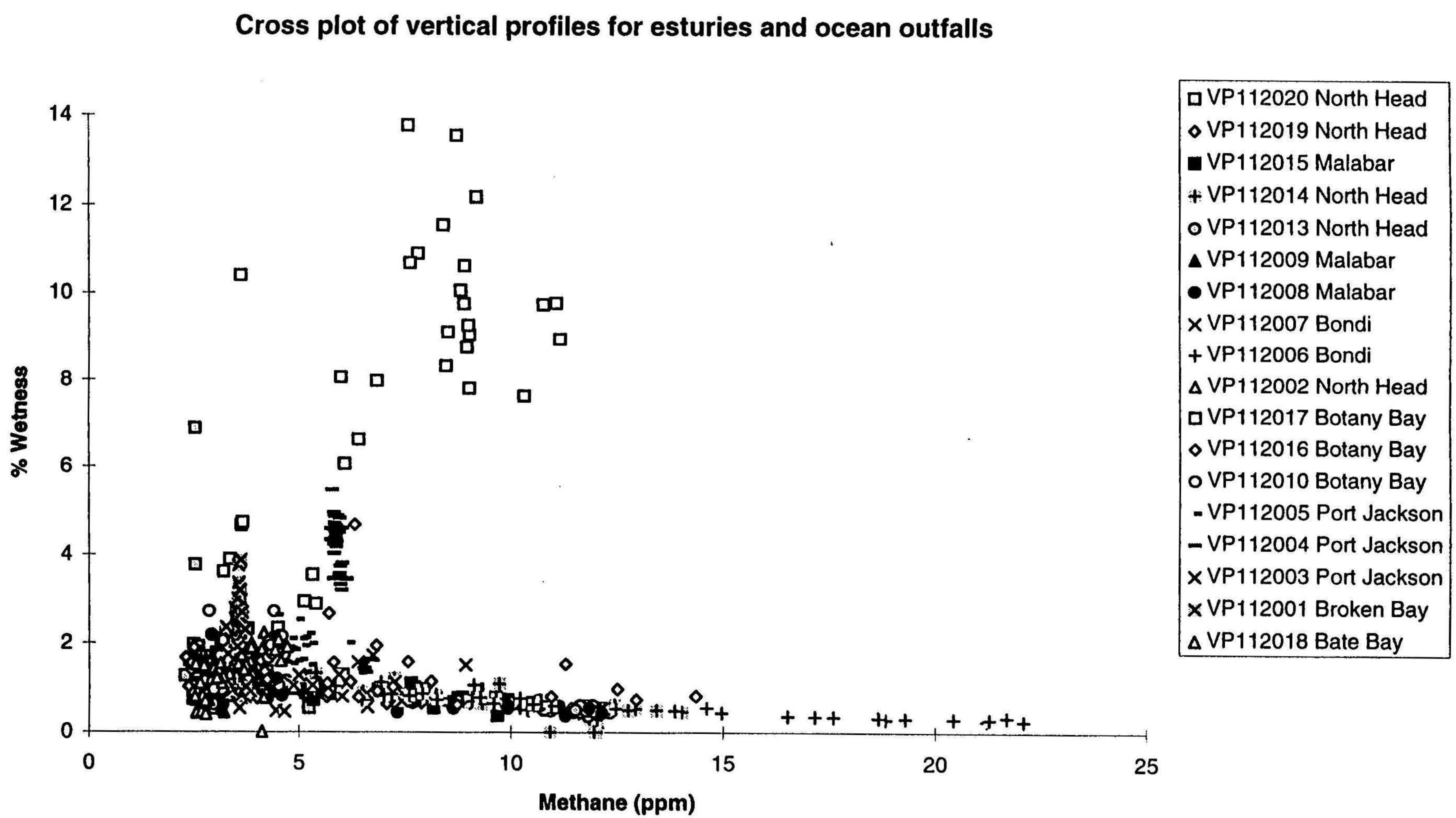


Figure 48.Composite plot of methane versus percent hydrocarbon wetness of all vertical profile data.

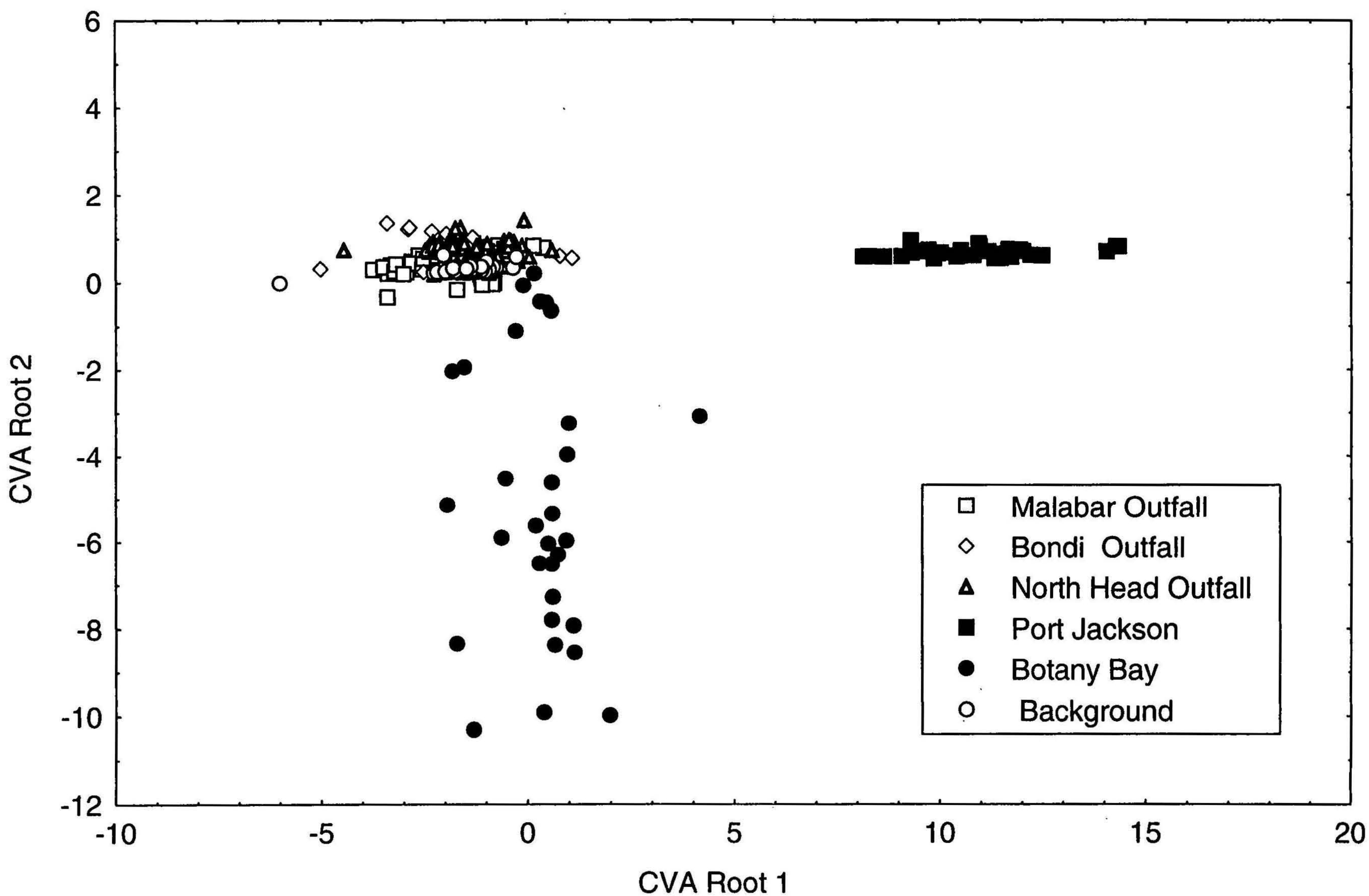


Figure 49. Cross plot of first and second canonical variates calculated using vertical profile data classified into five groups: North Head Outfall, Bondi Outfall, Malabar Outfall, Botany Bay, Port Jackson and Background Ocean Water.

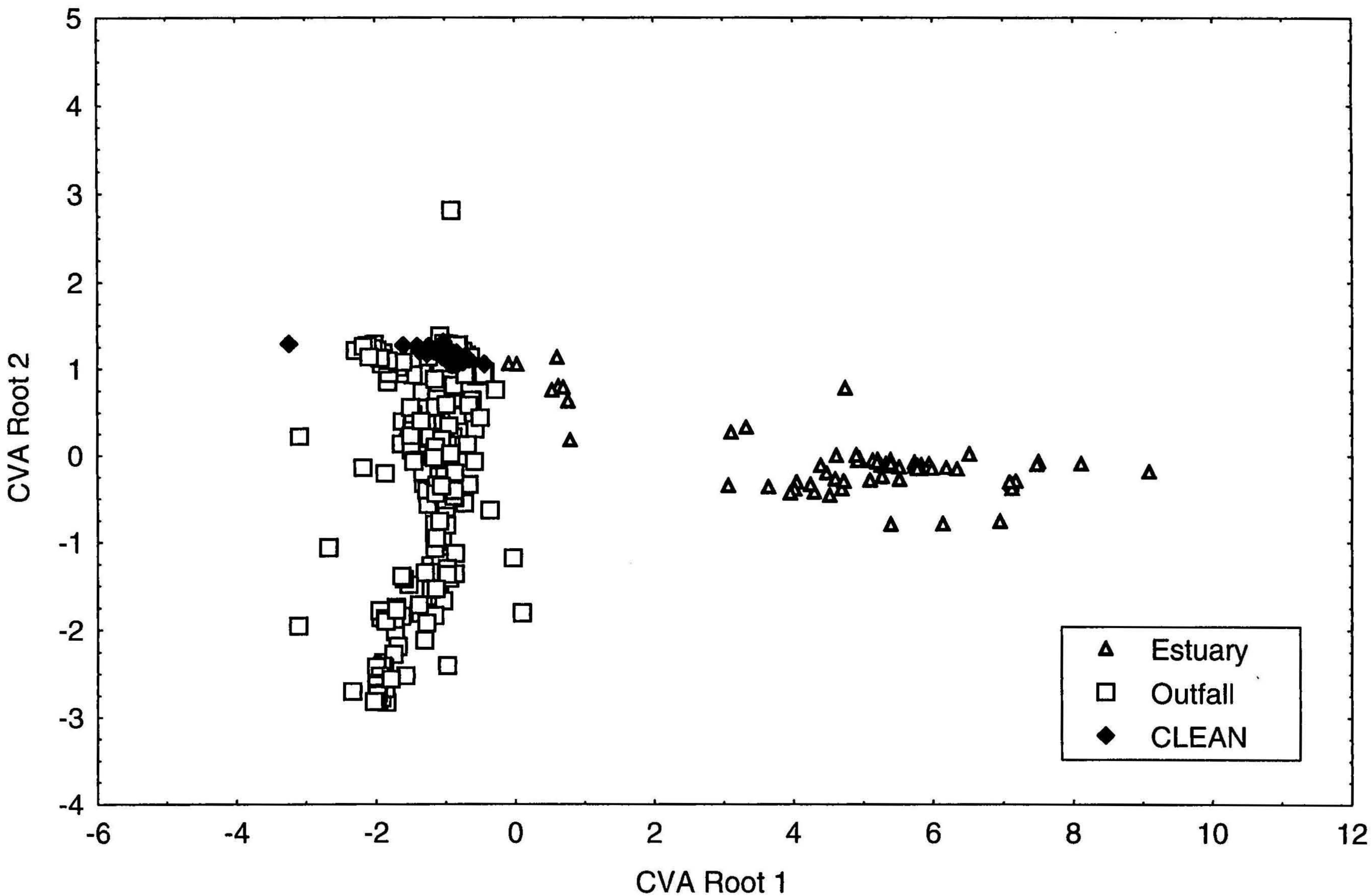


Figure 50. Cross plot of first and second canonical variates calculated using vertical profile in three groups: Ocean Outfalls, Estuaries and Background Ocean Water.

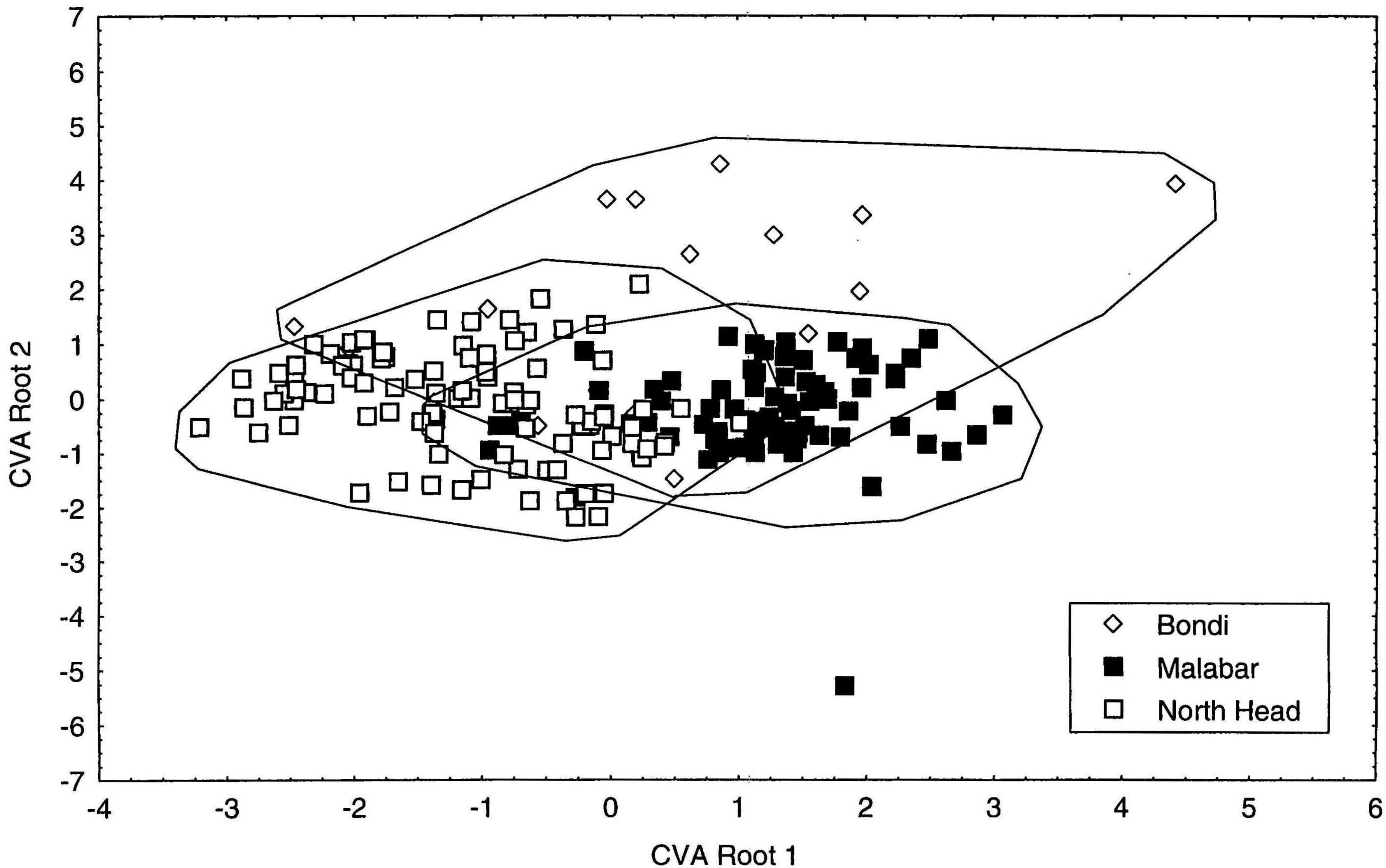


Figure 51. Cross plot of first and second canonical variates calculated using vertical profiles from North Head, Malabar and Bondi Outfalls.

9. Spatial distribution of light hydrocarbons in the coastal zone: Results

The spatial distribution of light hydrocarbons in the coastal waters off Sydney was examined by conducting a series of longshore transects with the tow-fish set at four different depths: 5 m, 25 m, 45 m and one transect 15 m above the sea floor. The latter transect was prematurely terminated when the tow-fish was lost off Bondi. The ship tracks during these DHD surveys are shown in Figure 5 to 9.

Hydrocarbons anomalies were detected at each depth with methane and THC values exceeding background values by an order of magnitude and more. Contour maps of hydrocarbon concentration were produced by fitting a 1 km grid to the data using a polynomial surface fitting routine. Smoothed contours were then fitted to the extrapolated grid.

The following provides a brief description of the spatial distribution of hydrocarbons detected in these transects.

9.1 Survey at 5 m depth

This survey was undertaken with the fish deployed at a depth of 5 m and passed directly over the North Head, Bondi and Malabar Outfalls. It also included a survey line extending into Bate Bay, located immediately to the south of Botany Bay.

Methane concentrations are near background (<3.5 ppm) in most of this plot (Figure 52) but there is a distinct plume of moderately increased methane concentration (maximum concentration 15 ppm) to the south of the Bondi and Malabar Outfalls, off Botany Bay and within Bate Bay. There is little evidence of enhanced methane concentrations in the vicinity of the North Head Outfalls at this depth.

Elevated levels of C_{2+} saturated hydrocarbons (ethane, propane and butane) and high values of percent wetness were found offshore of Botany Bay and within Bate Bay, (ethane, propane and percent wetness are shown in Figure 53 to Figure 55). Unsaturated hydrocarbons (ethylene and propylene) were generally close to background but were also elevated in the vicinity of both the ocean outfalls and the entrance to Botany Bay (ethylene concentrations are shown in Figure 56). Ethylene concentrations were also elevated in the western portion of the survey, closer to the shore line.

9.2 Survey at 25 m depth

This survey, undertaken with the fish deployed at a depth of 25 m, passed directly over the North Head, Bondi and Malabar Outfalls, but did not extend into Bate Bay.

Methane levels at this depth ranged from background to 50 ppm with elevated levels of methane found in the immediate vicinity and downstream of the ocean outfalls and off Botany Bay (Figure 57). Elevated levels of C_{2+} saturated hydrocarbons (ethane, propane and butane) and wetness values were generally restricted to the vicinity of Botany Bay and further south (ethane, propane and wetness shown in Figure 58 to Figure 60). Unsaturated hydrocarbons were generally close to background but were slightly elevated inshore and close to the entrance to Botany Bay (ethylene distribution is shown in Figure 61).

9.3 Survey at 45 m depth

Methane concentrations found at this depth range from background to 110 ppm, and were the highest recorded in the horizontal transects. Highest levels of methane were found in the northern part of the survey in the immediate vicinity and to the north of the Bondi outfall. Elevated concentration were also found to the north of North Head Outfall, near the Malabar Outfall and off Botany Bay to the south (Figure 62).

Elevated levels of C_{2+} saturated hydrocarbons and wetness values were generally restricted to the vicinity of Botany Bay and further south (ethane, propane wetness values are shown in Figure 63 toFigure 65. Concentrations of saturated hydrocarbons were generally close to background but had elevated concentrations similar to the entrance to Botany Bay and offshore to the south (ethylene concentrations are shown in Figure 66).

9.4 Survey at 15 m (approx.) above the seafloor

This survey (lines 112016 and 112017 see Figure 8) was run with the tow-fish deployed approximately 15 m above the sea-floor. Unfortunately, the tow-fish was lost on survey line 112017, immediately to the north of the Bondi Outfall, when it became snagged on an unknown obstruction protruding from the seafloor. However, despite the restricted nature of the survey elevated levels of methane (> 30 ppm), ethane (> 0.1 ppm), propane (> 0.4 ppm) and minor amounts of C_{2+} hydrocarbons were found (Figure 67 and 68).

9.5 Supplementary Transects

At the completion of the main CGT survey along the coast, two small DHD lines were surveyed in the vicinity of the North Head Outfall (112/018; 112/019). Hydrocarbon anomalies, albeit weak, were detected on the transects (112/018; 112/019) over North Head Outfall, although some elevated C_{5+} hydrocarbons were found.

Plots of methane; ethane, propane and butane; and percent wetness for surface waters (5 m) in Port Jackson are shown in Figure 69.

The data indicate typical background levels of hydrocarbons offshore, which systematically increase toward the inner Harbour. Methane increases to about 50 ppm (> ten-fold background) near Pyrmont and all other hydrocarbons increase in concentrations between the coastal zone, Sydney Harbour and Pyrmont.

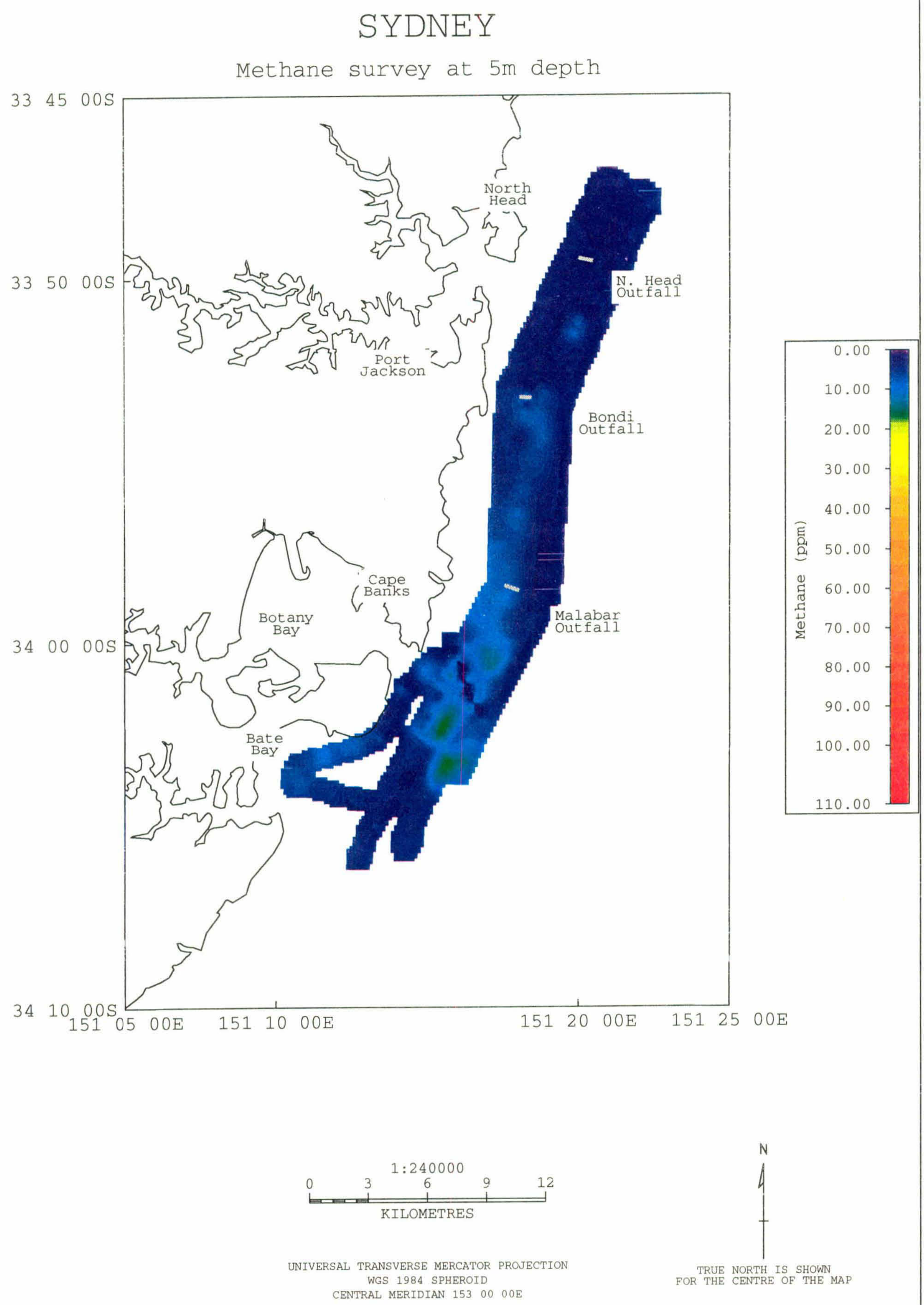

SYDNEY
Methane survey at 5m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
N. Head Outfall
Port Jackson
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Methane (ppm)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 52

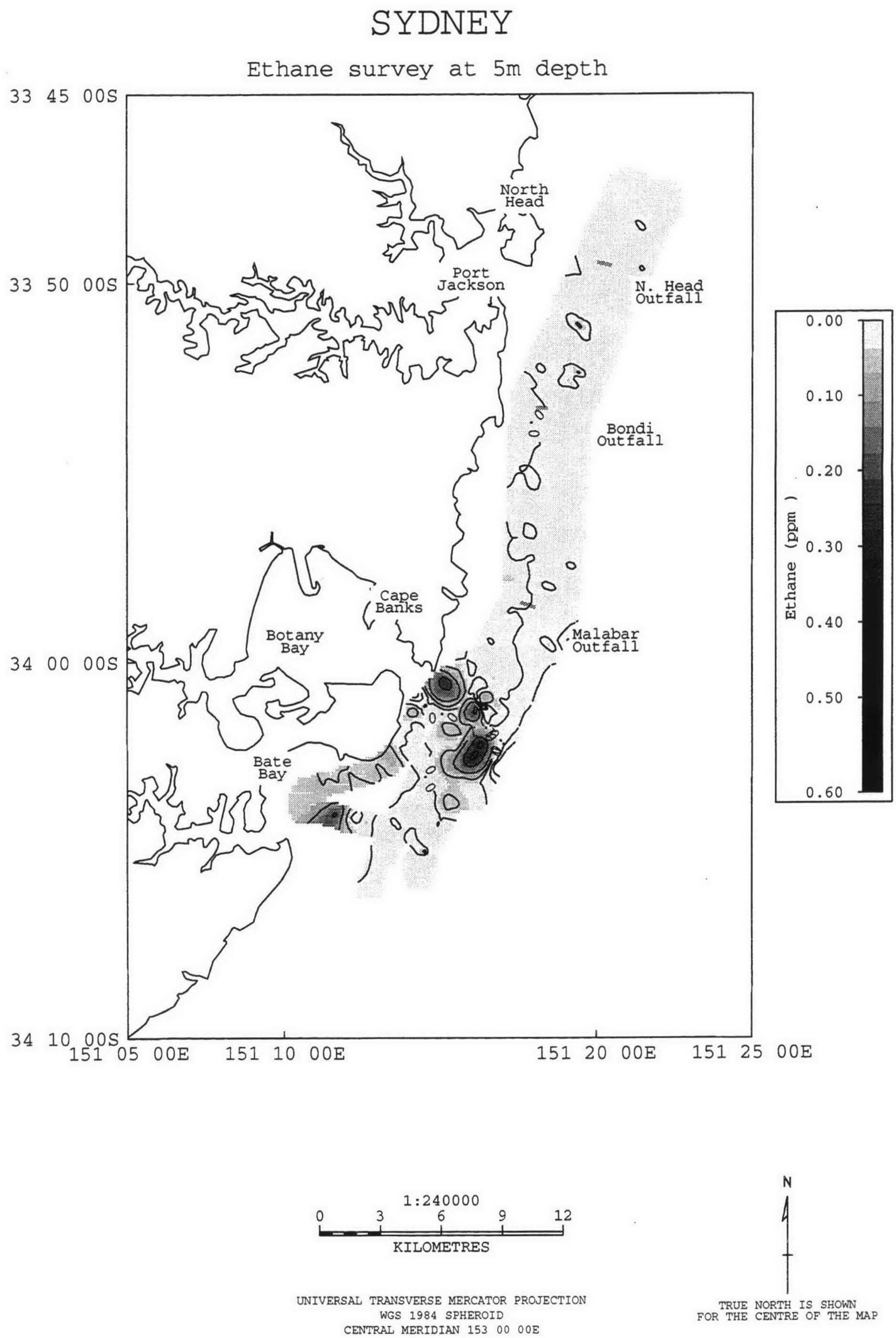
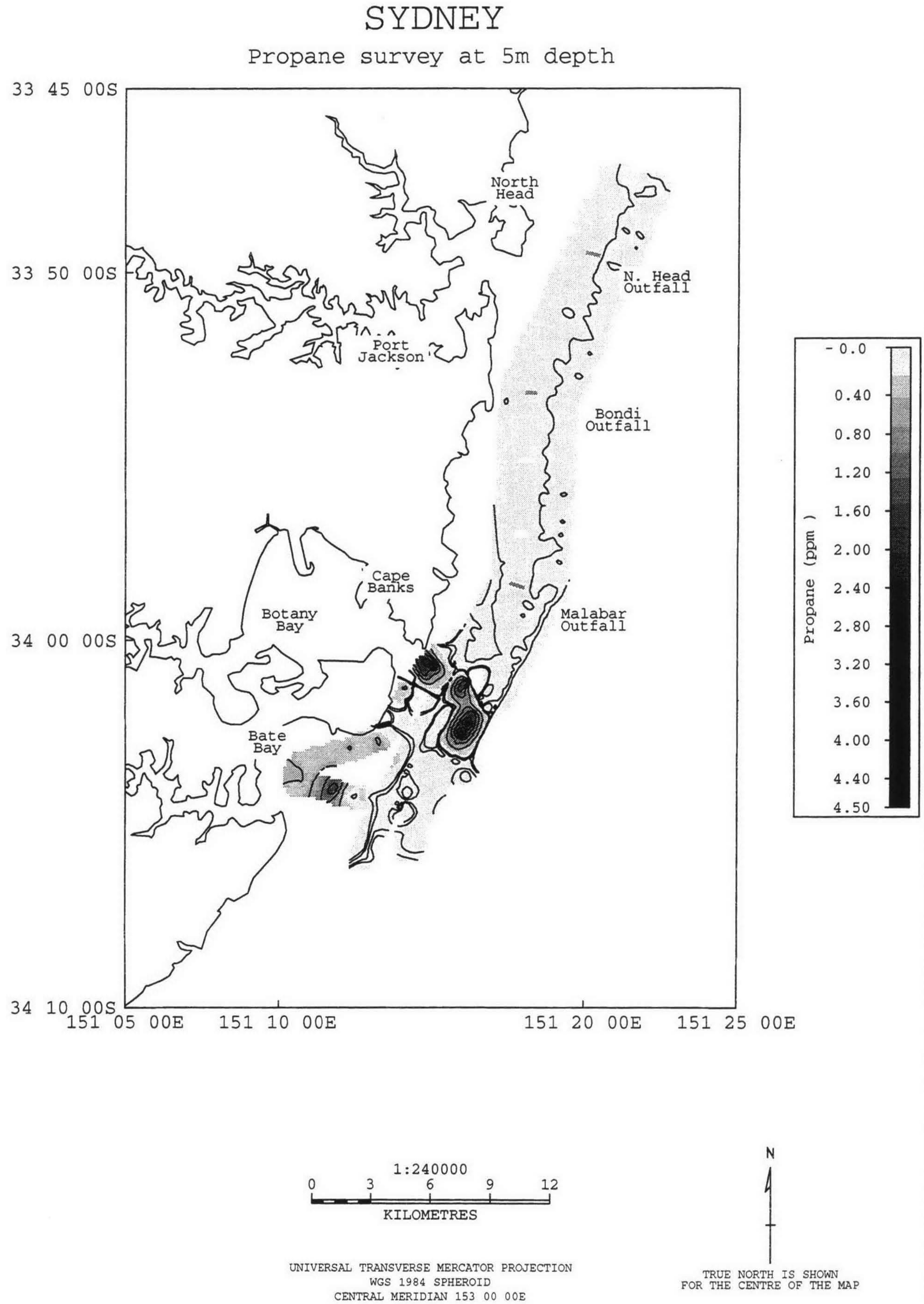

SYDNEY
Ethane survey at 5m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Ethane (ppm)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1:240000
0 3 6 9 12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 53



SYDNEY
Propane survey at 5m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
N. Head Outfall
Port Jackson
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
- 0.0
0.40
0.80
1.20
1.60
2.00
2.40
2.80
3.20
3.60
4.00
4.40
4.50
Propane (ppm)
1:240000
0
3
6
9
12
KILOMETRES
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
N
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 54

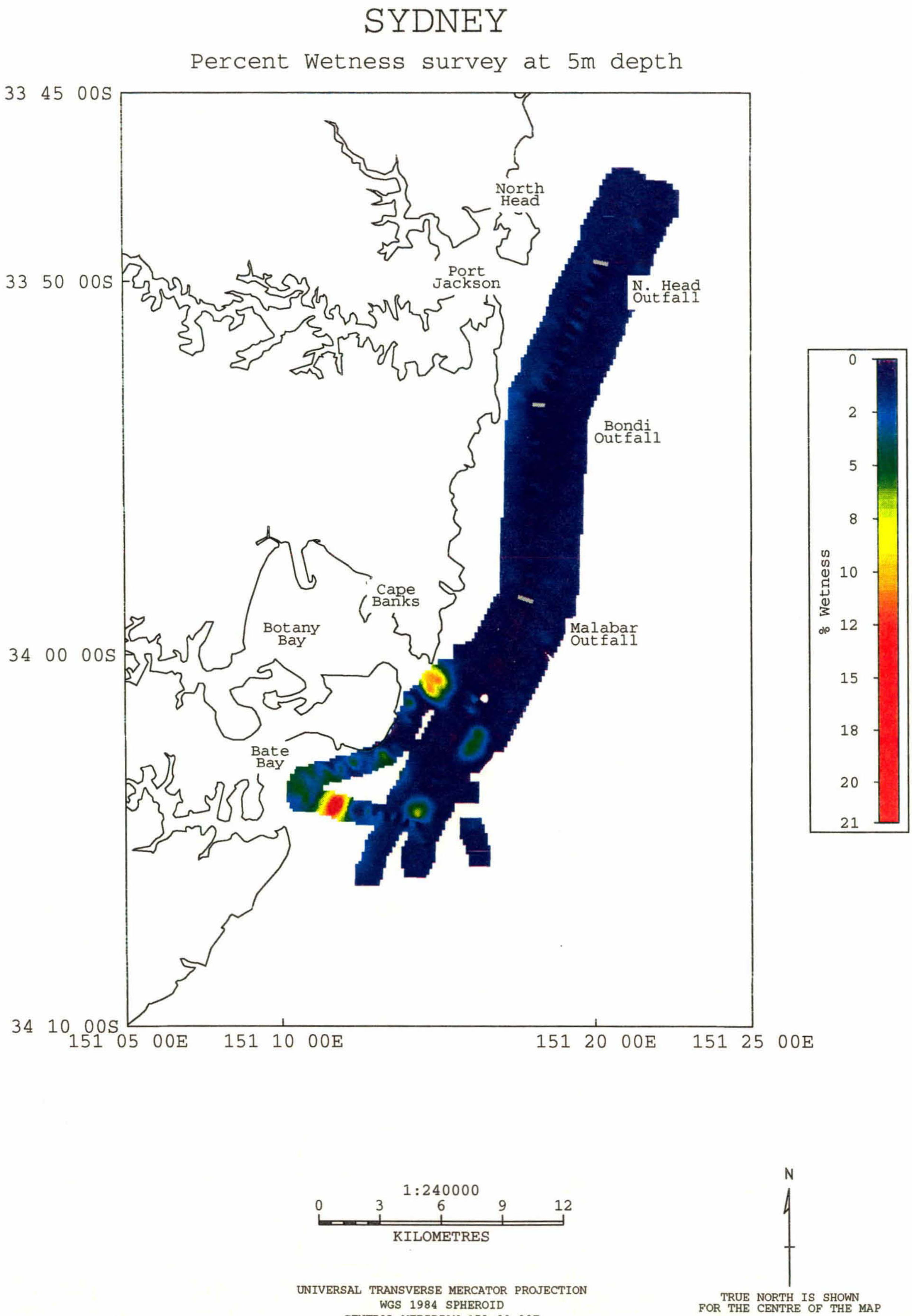

SYDNEY
Percent Wetness survey at 5m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
% Wetness
0
2
5
8
10
12
15
18
20
21
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 55

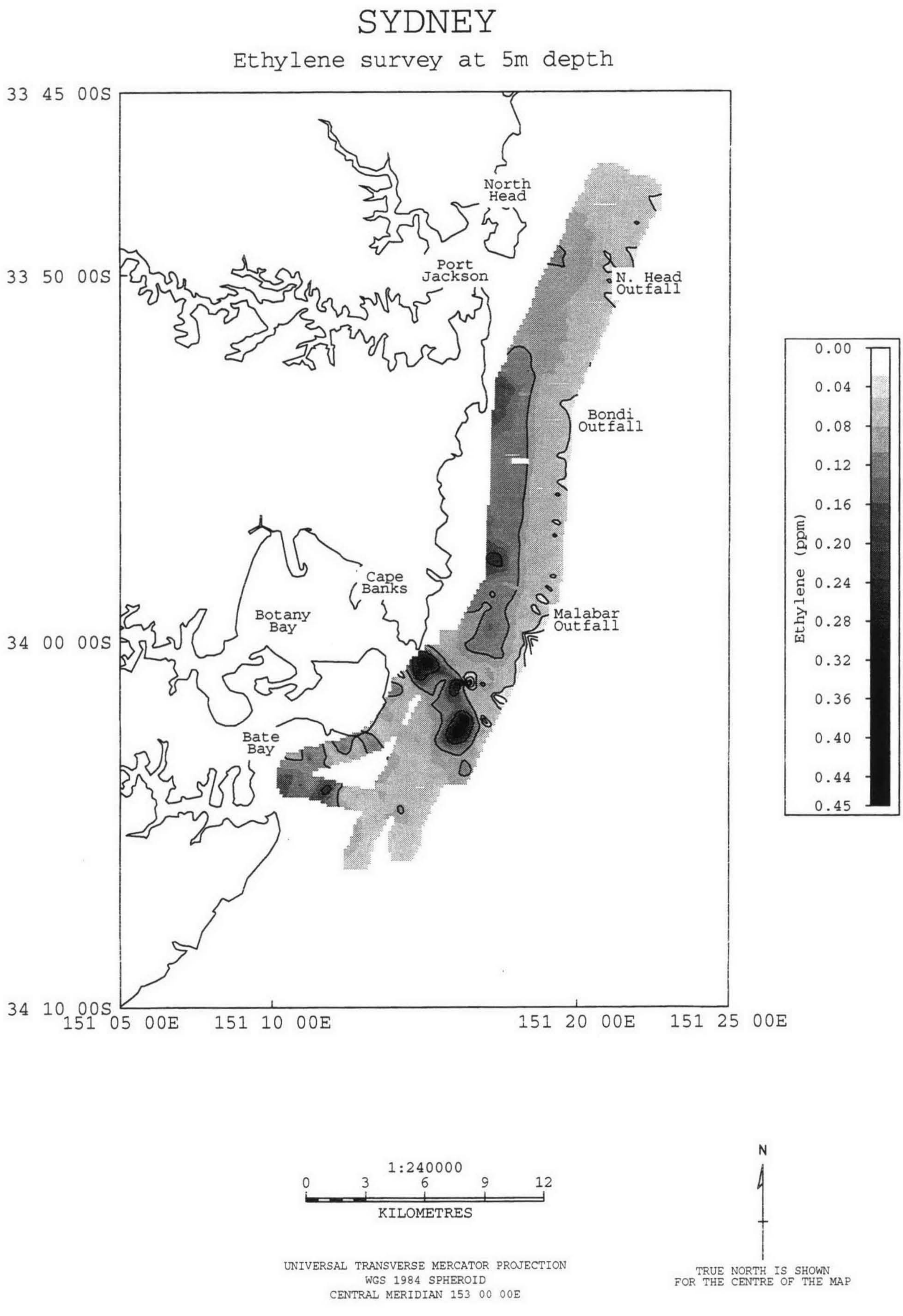

SYDNEY
Ethylene survey at 5m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Ethylene (ppm)
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.45
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 56

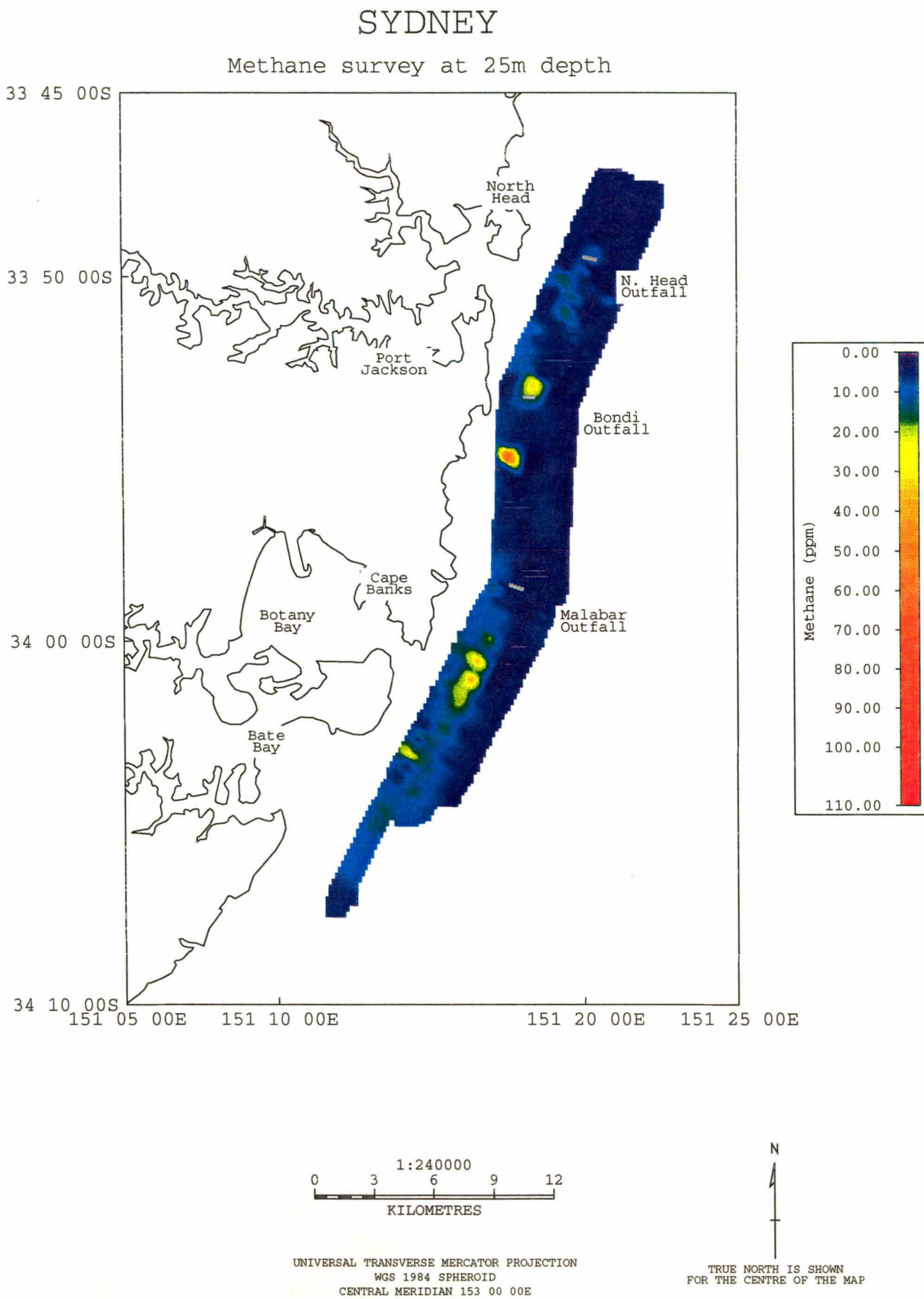

SYDNEY
Methane survey at 25m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
N. Head Outfall
Port Jackson
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
Methane (ppm)
1:240000
0 3 6 9 12
KILOMETRES
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
N
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 57

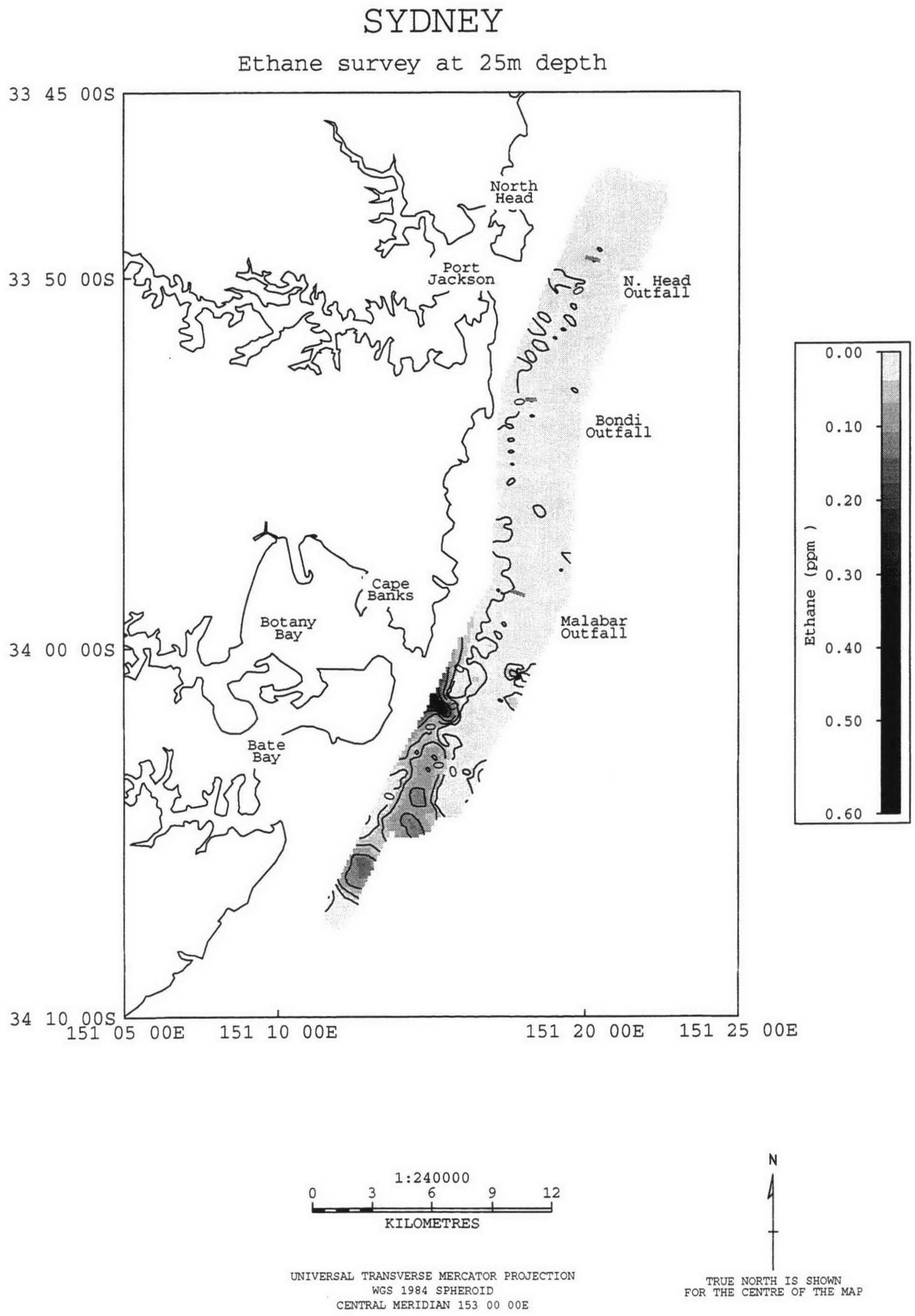

SYDNEY
Ethane survey at 25m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Ethane (ppm)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
1:240000
0 3 6 9 12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 58

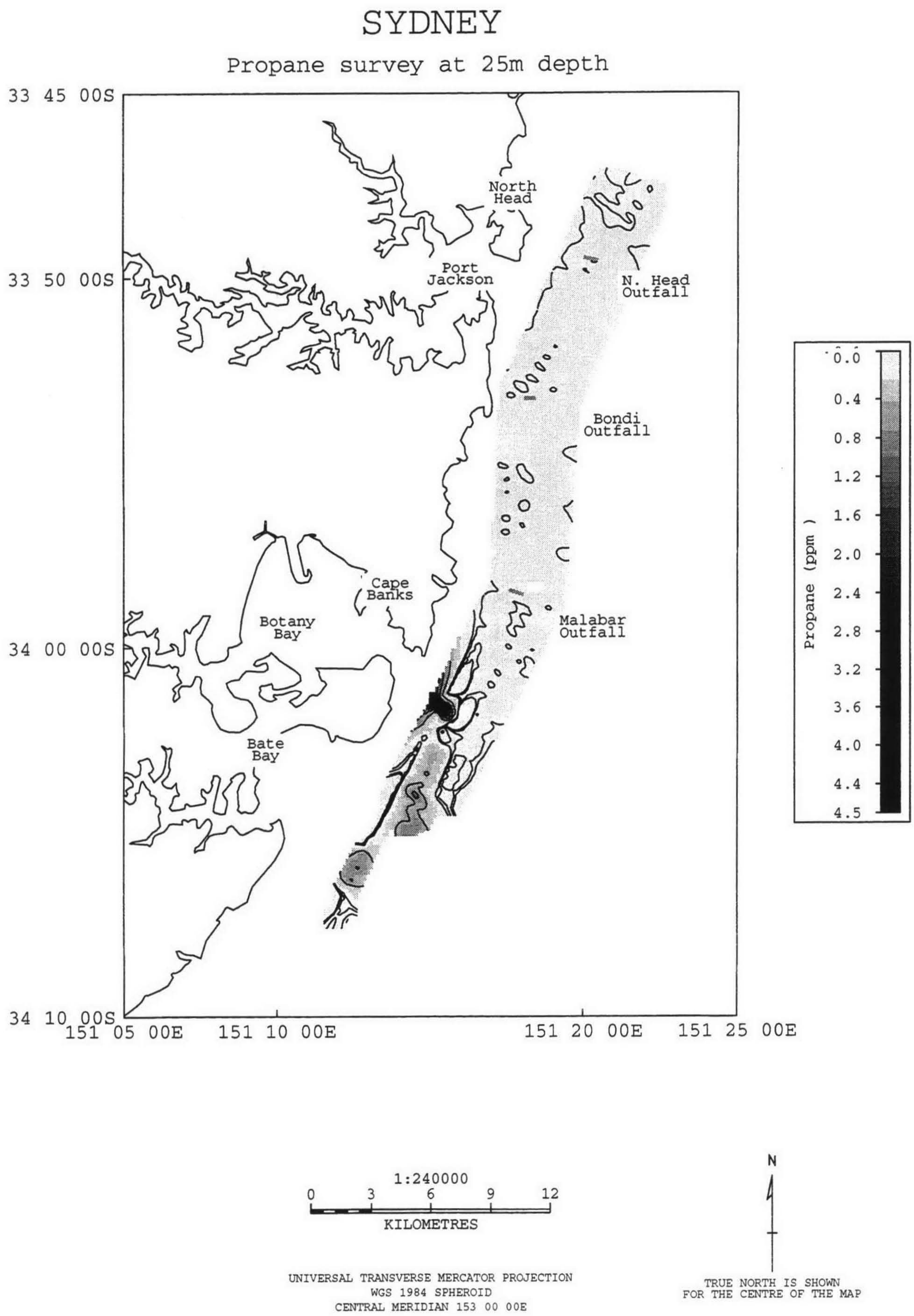
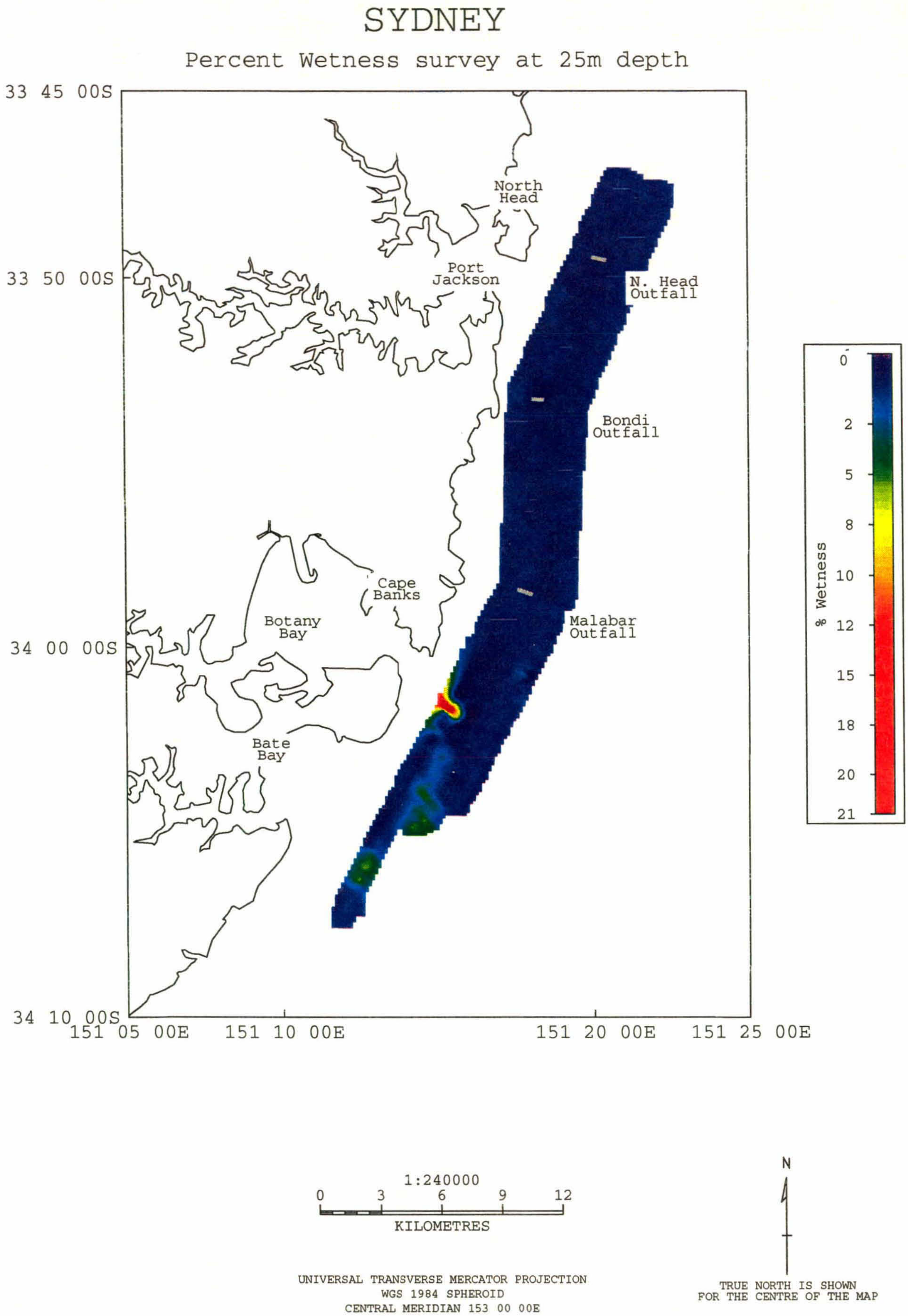

SYDNEY
Propane survey at 25m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Propane (ppm)
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.5
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN FOR THE CENTRE OF THE MAP

Figure 59



SYDNEY
Percent Wetness survey at 25m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
% Wetness
0
2
5
8
10
12
15
18
20
21
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 60

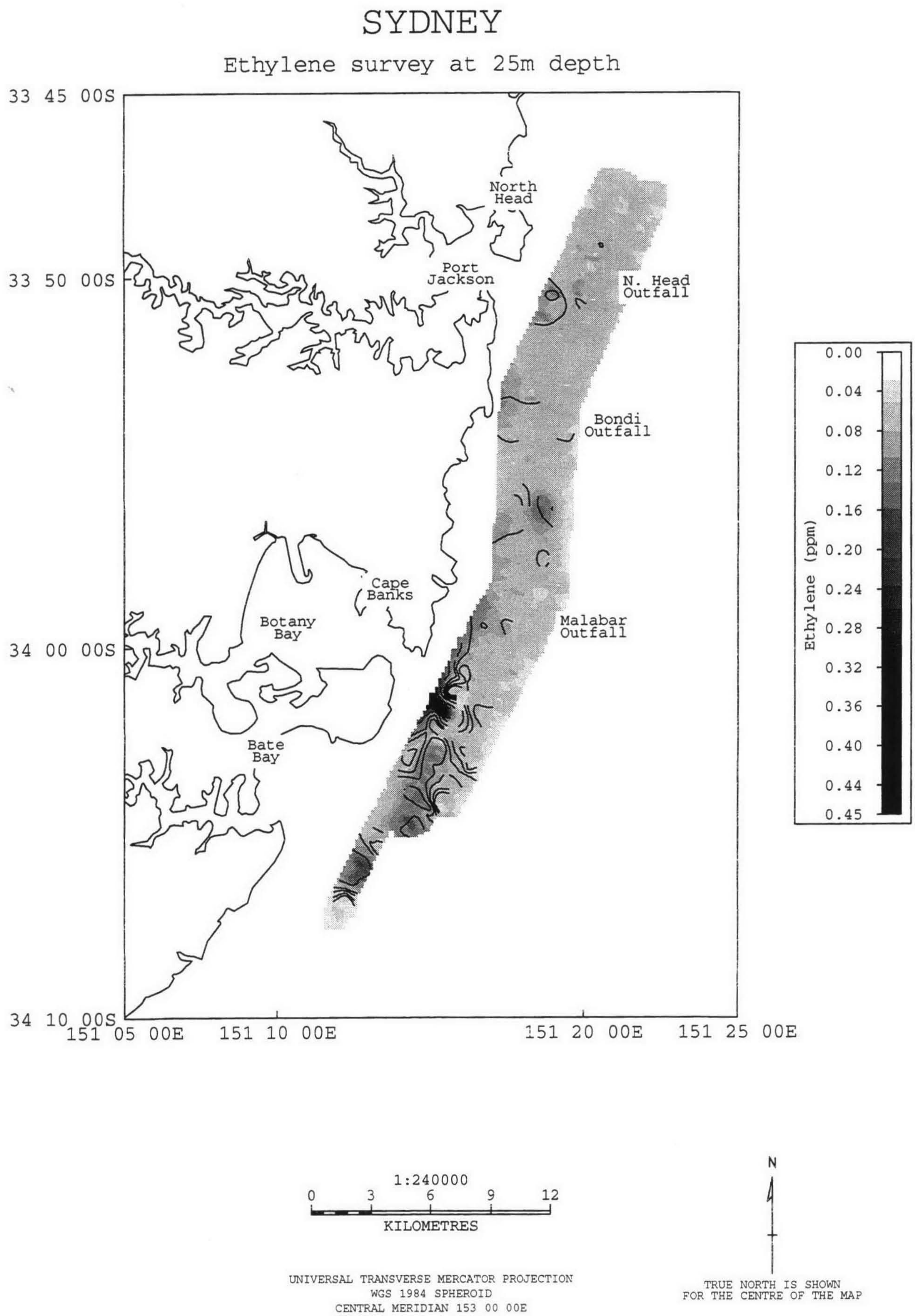

SYDNEY
Ethylene survey at 25m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Ethylene (ppm)
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.45
1:240000
0 3 6 9 12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 61

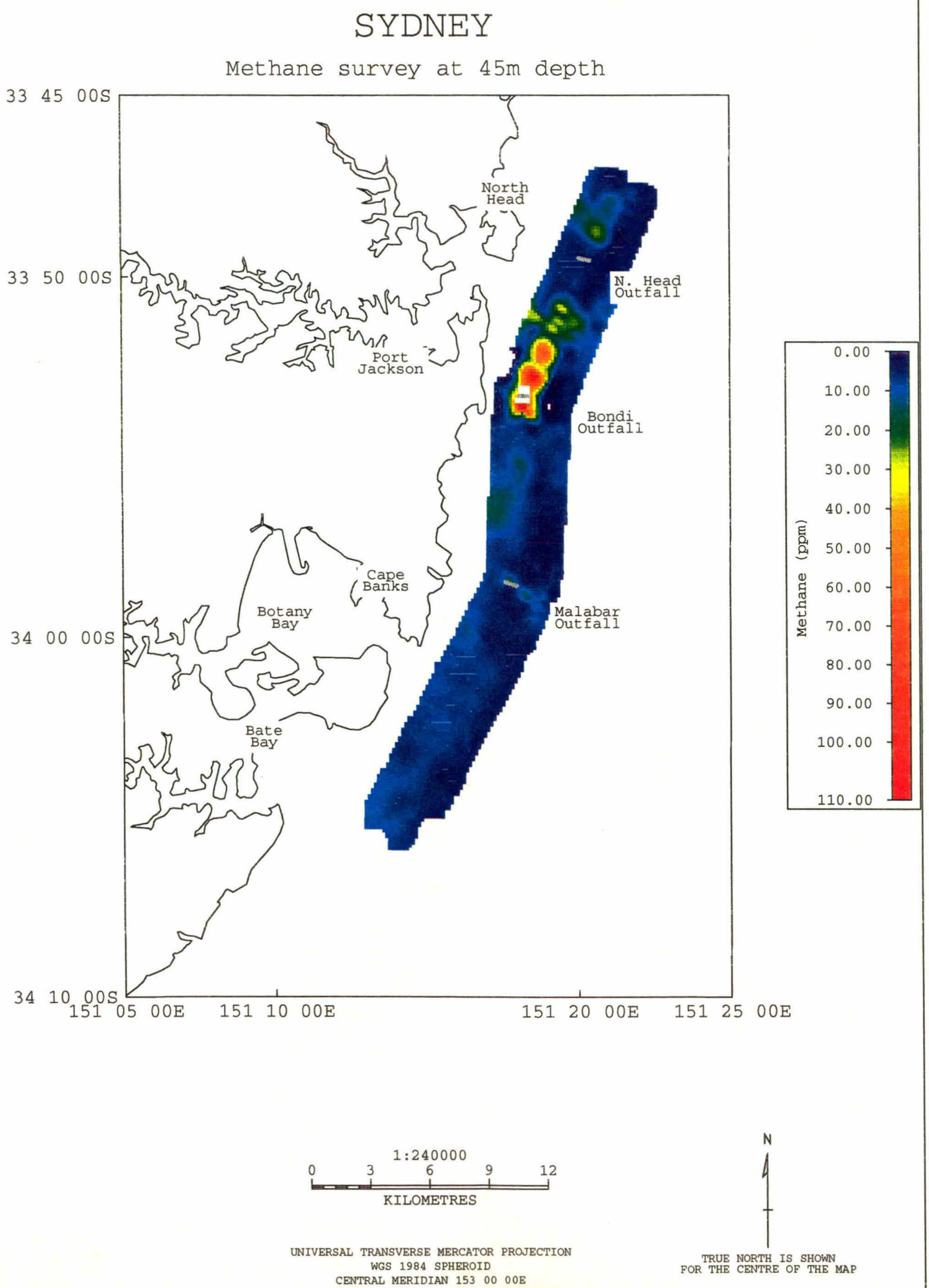

SYDNEY
Methane survey at 45m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
N. Head Outfall
Port Jackson
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Methane (ppm)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
1:240000
0 3 6 9 12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN FOR THE CENTRE OF THE MAP

Figure 62

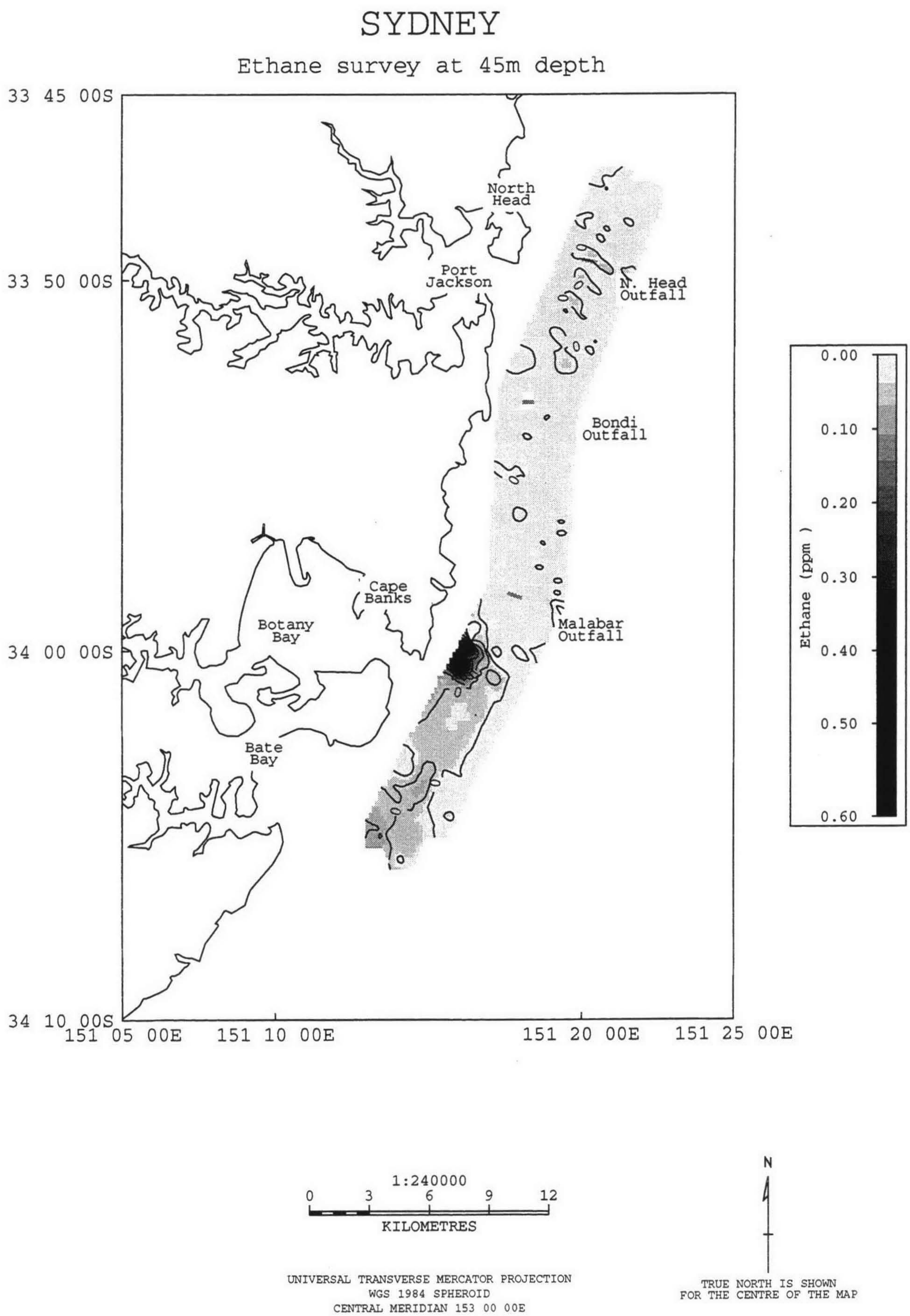
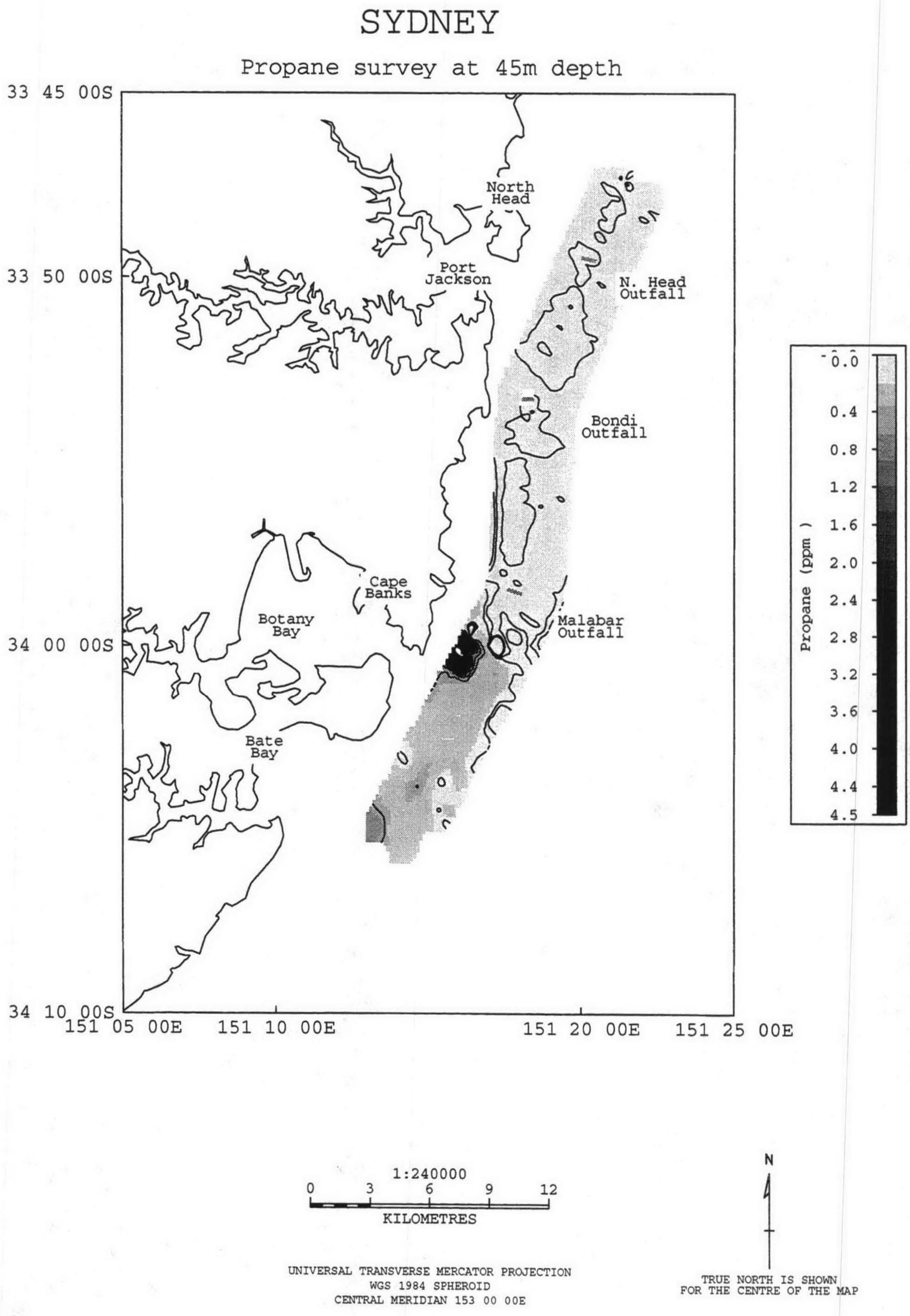

SYDNEY
Ethane survey at 45m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
0.00
0.10
0.20
0.30
0.40
0.50
0.60
Ethane (ppm)
1:240000
0 3 6 9 12
KILOMETRES
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
N
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 63



SYDNEY
Propane survey at 45m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.5
Propane (ppm)
1:240000
0 3 6 9 12
KILOMETRES
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
N
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 64

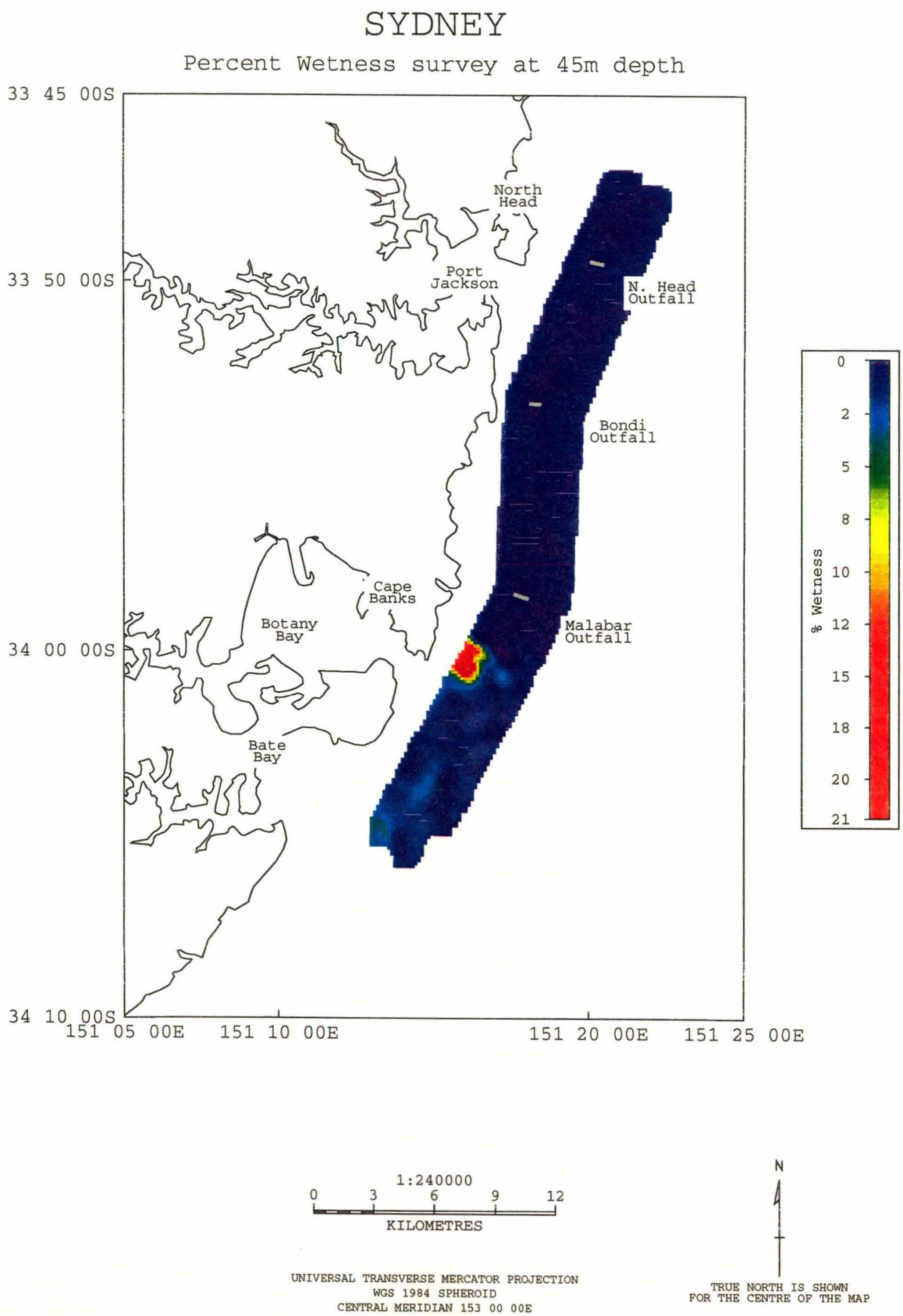

SYDNEY
Percent Wetness survey at 45m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
% Wetness
0
2
5
8
10
12
15
18
20
21
1:240000
0
3
6
9
12
KILOMETRES
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
N
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 65

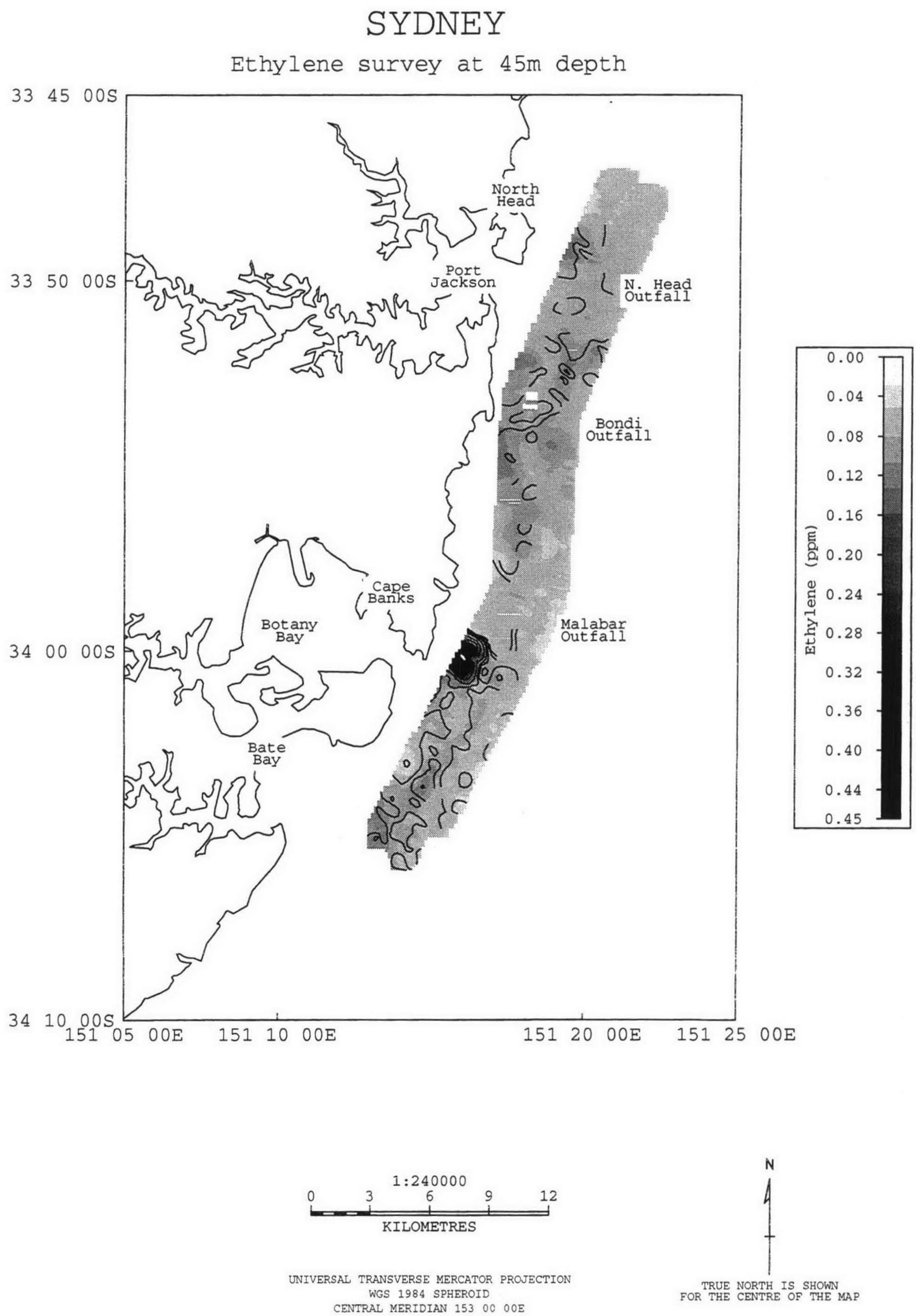
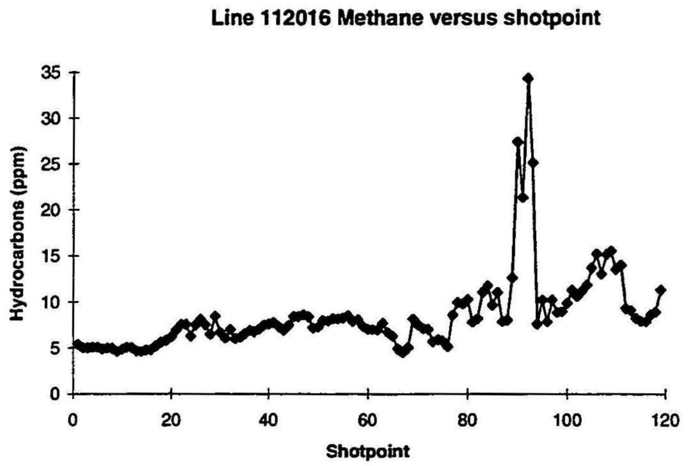
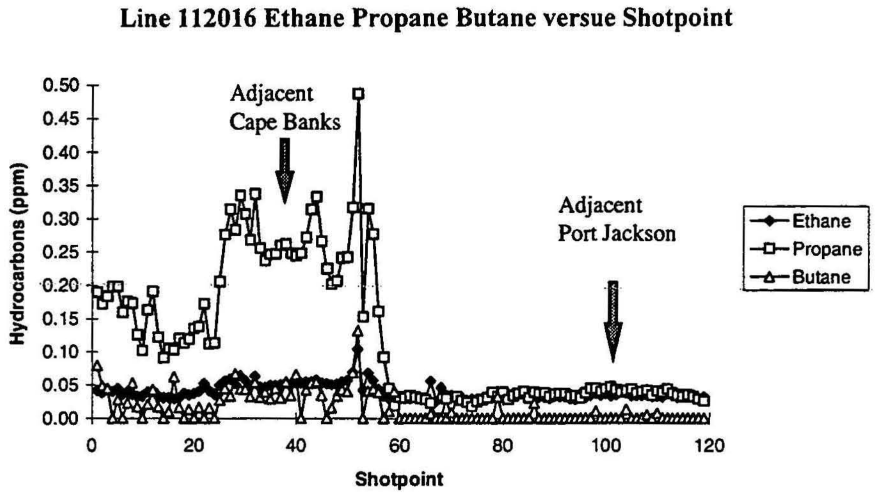

SYDNEY
Ethylene survey at 45m depth
33 45 00S
33 50 00S
34 00 00S
34 10 00S
151 05 00E
151 10 00E
151 20 00E
151 25 00E
North Head
Port Jackson
N. Head Outfall
Bondi Outfall
Cape Banks
Botany Bay
Malabar Outfall
Bate Bay
Ethylene (ppm)
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.45
1:240000
0
3
6
9
12
KILOMETRES
N
UNIVERSAL TRANSVERSE MERCATOR PROJECTION
WGS 1984 SPHEROID
CENTRAL MERIDIAN 153 00 00E
TRUE NORTH IS SHOWN
FOR THE CENTRE OF THE MAP

Figure 66





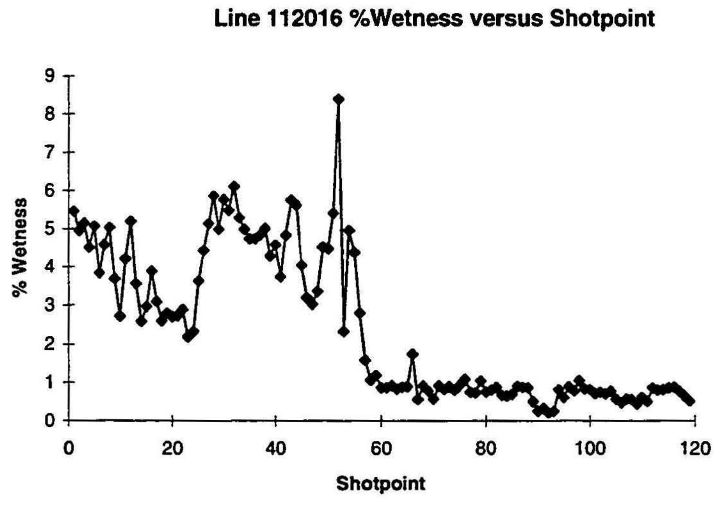
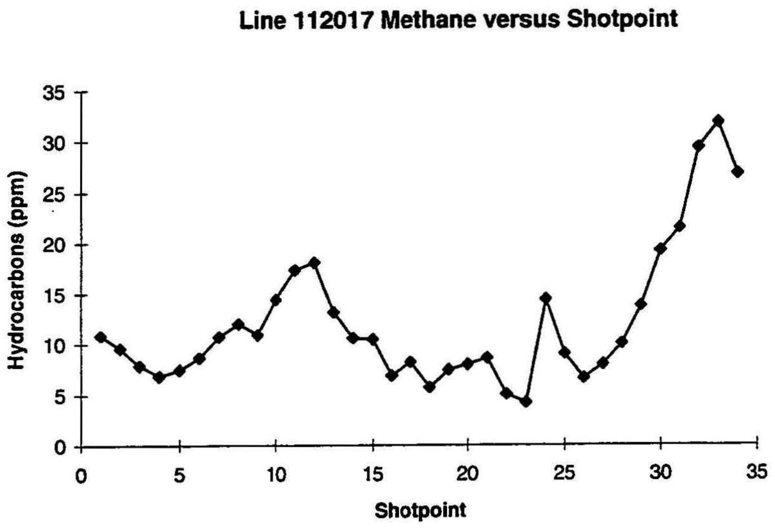
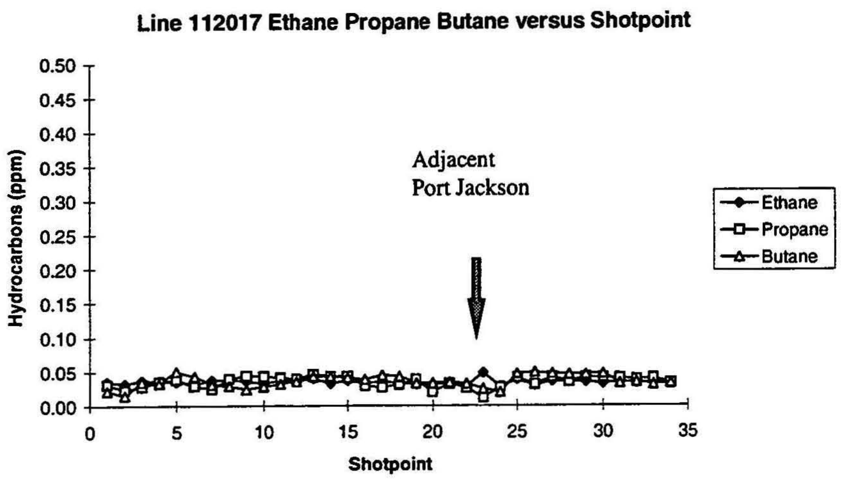


Figure 67. Longitudinal distribution of % wetness and light hydrocarbons methane, ethane, propaneand butane along survey line 112016.





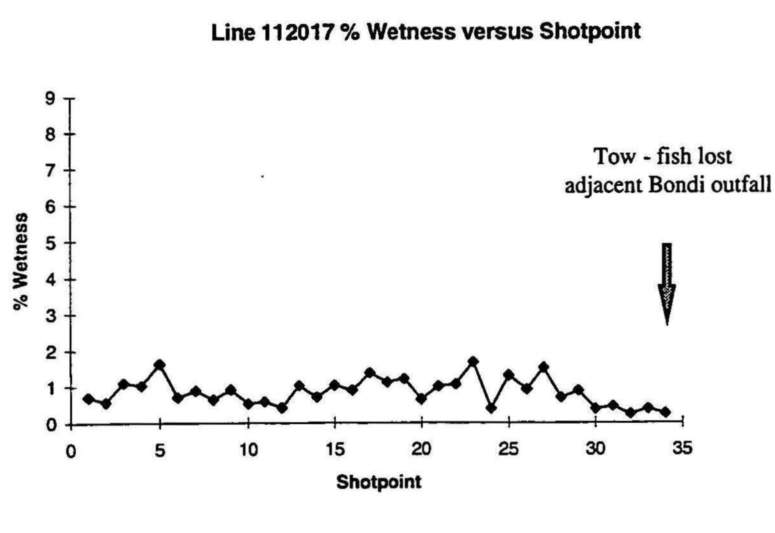
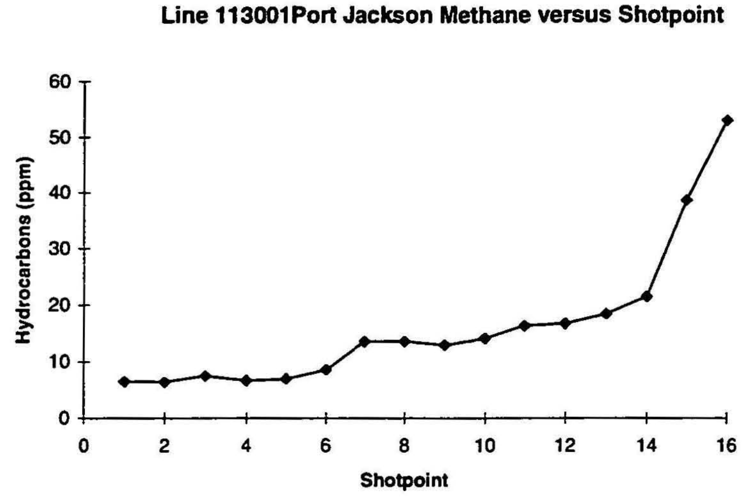
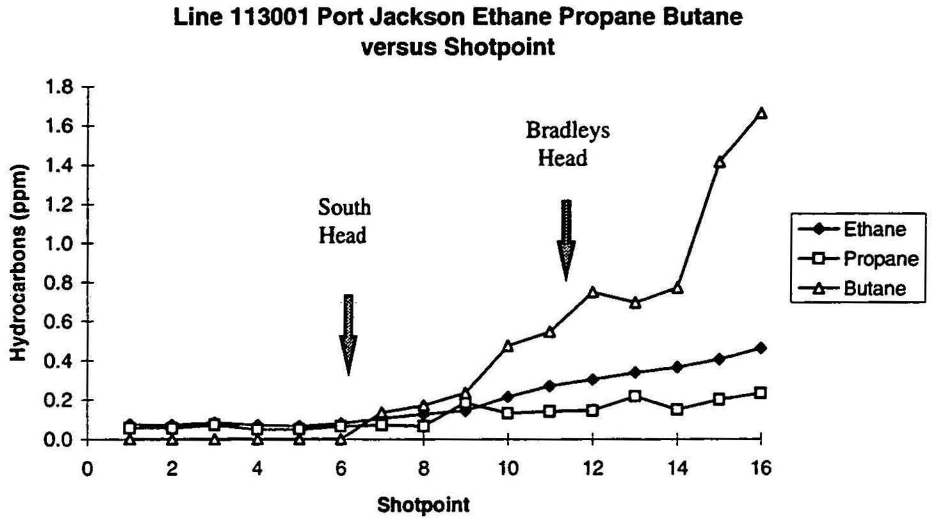


Figure 68. Longitudinal distribution of % wetness and light hydrocarbons methane, ethane, propaneand butane along survey line 112017.





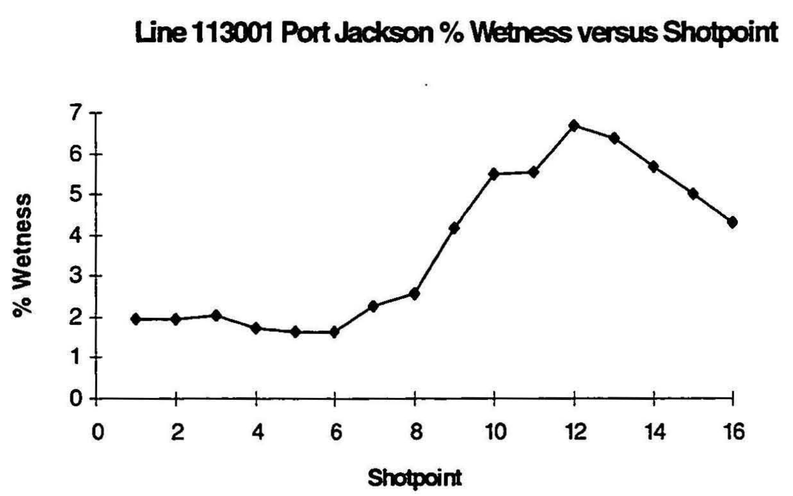


Figure 69. Longitudinal distribution of % wetness and light hydrocarbons methane ethane, propane and butane along survey line 113001 entering Sydney Harbour.

10. Distributions of light hydrocarbons in the coastal zone: Discussion.

Consideration of the vertical distribution of hydrocarbons established that the relative abundance of various light hydrocarbons could be used to distinguish between hydrocarbon source and that methane and wetness were useful indicators of input from each source. This section first considers whether the relationships identified in the vertical profiles, collected in the immediate vicinity of the hydrocarbon sources are also found in wider transects offshore. If these signatures appear stable then they can be used to map the distribution of hydrocarbons sources such as sewage effluent and river/estuarine outflow.

10.1 Hydrocarbon Signature

A cross-plot of methane versus percent hydrocarbon wetness for all survey lines (112004 through 112017) at the four transect depths is shown in Figure 70. Two trends are again evident. One trend with the highest methane values measured on the survey (> 100 ppm) is accompanied by very low wetness values (< 2 %) and this trend includes data from around the ocean outfalls. The other trend shows very high wetness values (nearly 40 %) at methane values <10 ppm. High wetness values were found only near the entrance to Botany Bay and in Bate Bay, to the south. The trends observed in these data coincide closely with those observed in the analysis of the vertical profiles and suggest hydrocarbon signatures are conservative at least in the study area. The results indicate that the dispersion of ocean outfall and estuarine derived waters can be mapped using methane concentration, wetness index and other hydrocarbon signatures.

Estuarine waters are probably best mapped using the wetness index but may also be mapped using the concentration of C_{2+} hydrocarbons (ethane, propane or butane) or discriminant functions (which uses all hydrocarbon concentrations) shown in Table 9.

If required, the dispersion of waters discharged from individual estuaries can be mapped using discriminant functions shown in Table 7.

The dispersion of sewage effluent may be mapped using either methane concentrations or the discriminant functions given in Table 9. Methane is not a unique indicator of outfall effluent as small amounts of methane may be derived from estuarine sources. However, methane concentrations in estuarine waters are in all cases less than 10 ppm whereas methane concentrations in the vicinity of the outfalls reach values of 60 ppm. The potential for interference is greatest in the vicinity of Botany Bay and Bate Bay where several hydrocarbon sources occur.

The indicators described above are now applied to the interpretation of the spatial data sets to establish the distribution of discharges from Botany Bay, Port Jackson and the deep ocean outfalls.

10.2 Estuaries

There are two major estuaries or bays which may discharge waters into the coastal zone within the study area: Port Jackson and Botany Bay. Broken Bay, into which the Hawkesbury River discharges was located to the north of the survey area and did not appear to have a hydrocarbon signature significantly different to background. Port Hacking occurs on the southern margin of the survey and may have an impact on Bate Bay.

10.2.1 Port Jackson

There is no evidence of waters with hydrocarbons derived from Port Jackson offshore of the harbour entrance at any depth and there is no evidence of any significant increase in propylene, propane, ethane or butane (refer to Figure 52 through Figure

65). The high methane concentrations found offshore from Port Jackson must therefore be derived from ocean outfalls.

10.2.2 Botany Bay

High values of wetness and C_{2+} hydrocarbons were found off the entrance to Botany Bay at all levels in the water column with concentrations generally increasing with depth (refer to Figure 52 through 65). At 5 m and 25 m depths high percent wetness values and high concentrations of C_{2+} hydrocarbons occur in the central to southern parts of the mouth of Botany Bay but at 45 m the hydrocarbons are found to the north off Cape Banks. This suggests a variation in the direction of tidal or other currents issuing from the bay with depth or a general change in direction between survey times. In the 5 m survey (Figure 55) there are also high wetness values indicative of a "Botany Bay source" in Bate Bay (these lines could not be repeated at greater depth because of the relative shallow water in this region).

The percent hydrocarbon wetness and the ethane, propane and butane abundances are tracers of that water outflowing from Botany Bay at all depths. The general increase in wetness values and C_{2+} concentration with depth in both the vertical profiles and in the horizontal transects suggests a greater discharge of bay waters with depth. These observations and other unpublished data suggest that waters from Botany Bay appear to flow into the coastal zone with an inverse estuary circulation, where more dense Botany Bay waters sink and flow under the less dense coastal waters south of the Malabar Ocean Outfall.

10.3 Deep Ocean Outfalls

The distributions of effluent derived hydrocarbons in Sydney Coastal waters are best shown by methane concentrations. At 5 m depth the methane concentrations are close to background in the northern part of the study area indicating little input of effluent to surface waters in this part of the study area. Higher concentration of methane (up to 15 ppm) are found in the central and southern part of the study area in the immediate vicinity of the Bondi Outfalls and as a plume to the south. Further to the south the highest concentrations of methane are found as a large and complex plume in the vicinity of, and to the south of the Malabar Outfall. These data indicate that effluent discharged from the deep ocean outfalls is penetrating into the surface waters in the southern part of the survey area.

Higher concentrations of methane are found at 25 m. High concentrations are found in relatively small patches in the immediate vicinity of Bondi Outfall and North Head Outfall. A relatively complex plume with a number of "hotspots" of methane concentration is found to the south of Malabar .

The highest recorded concentrations of methane (100 ppm) are found at a depth of 45 m. Bondi is the most prominent outfall with high concentrations of methane occurring in the immediate vicinity of the outfall and as a plume to the north. A small plume is also detectable to the north of North Head and in the vicinity of Malabar. Methane concentrations above background are also found to the south of Malabar. At both 25 m and 45 m the plumes appear to be broken up into patches of higher concentration material separated by approximately 1 km.

The data presented here indicates that effluent near the Malabar Ocean Outfall is found as a large well dispersed southward trending plume that penetrated to relatively shallow depths (5 m). In contrast, effluent hydrocarbons near the Bondi Outfalls are present as small "hot spots" of high concentration at 25 m and 45 m to the north and south of the outfall but with low concentrations observed at 5 m. In the vicinity of the North Head Outfall effluent derived hydrocarbons are detectable but are found at relatively low concentrations (<15 ppm) at all depths.

The general distribution of effluent derived methane observed in this survey fits a general pattern of rapid dilution of effluent in rising jets (near field) in the immediate vicinity of the outfalls and dispersal of effluent as a plume to the south under the influence of a south flowing current.

The survey did not detect "hotspots" or rising jets associated with the outfalls at each depth but this was probably a function of the relatively small size of these features, and the depths of the DHD tow-fish. The data also suggest a northward dispersion of effluent at 45 m, particularly for the North Head and Bondi Outfalls. The dispersion of effluent from individual outfalls could not be determined since it was not possible to differentiate between outfalls based on their hydrocarbon signature. Thus it is not possible to determine whether the high methane concentrations found in the southern part of the survey area were derived from an individual outfall, such as Malabar, or result from the mixing of effluent discharged from all of the outfalls.

10.4 Summary

The above discussion illustrates five important points.

1. The hydrocarbon signatures measured at each potential location identified by the vertical profiles, coincide closely with signatures measured in the transects undertaken in the survey area, between Broken Bay and Port Hacking, offshore Sydney. The hydrocarbons signatures of these sources appear to be conservative and can therefore be used to map the dispersion of estuarine waters and effluent discharged into the coastal zone.
2. The effluent discharged from the outfalls is characterised by relatively high levels of methane and low abundances of C_{2+} compounds and can be identified and mapped using methane concentrations or discriminant functions determined from Canonical Variates Analysis.

3. Port Jackson is characterised by high concentrations of methane, ethane, ethylene, propylene, propane and butane; however, it does not appear to contribute light hydrocarbons to the coastal zone.
4. Estuarine waters derived from Botany Bay are characterised by high concentrations of C_{2+} hydrocarbons particularly ethane, ethylene, propane, propylene and butane. Hydrocarbons from Botany Bay are found offshore where they are mixed with ocean outfall hydrocarbons. However, both sources have unique hydrocarbon signatures and can readily be distinguished from each other in ocean waters.
5. Plume dispersion is complex but there is strong evidence for significant penetration of effluent to surface waters particularly in the southern part of the survey area during the time of this survey.

11. Carbon isotope composition of light hydrocarbons.

The isotopic compositions of various light hydrocarbons (notably methane) are other tools that may be useful to discriminate between different sources of hydrocarbons added to the coastal zone. Methane produced biogenically tends to be enriched in the light isotope of carbon, while methane (and other light hydrocarbons) derived from thermogenic (petroleum) sources is enriched in the heavier isotope of carbon (Fuex, 1977; Bernard *et al.*, 1977). To investigate differences in isotopic compositions of methane from the different geographic areas of the survey, several 1 litre samples of mixed light hydrocarbons were collected when significant water-column anomalies were found.

These samples were collected by diverting some of the gas stream from the gas extractor and displacing water from an inverted 1 litre glass bottle. These samples were logged and stored for subsequent analyses. Select samples were sent to the NIWA (National Institute for Water and Atmospheric Research Ltd.) in NZ for analysis of the carbon isotopic and percent modern carbon (pMC) of methane. These results are summarised in Table 11. The locations of samples are shown in Figure 71.

11.1 $\delta^{13}CH_4$ in marine waters

Biogenic methane ($\delta^{13}CH_4 \approx$ -65 to -75 ‰) is in general 20 ‰ to 40 ‰ depleted in ^{13}C relative to thermogenic (petrogenic) methane (Hoefs, 1980). Bacterial action generating methane results in the preferential uptake of ^{12}C whereas in deeply buried sediments increasing temperatures and chemical processes producing methane from the breakdown of longer chain hydrocarbons results in an isotopically heavier methane (less negative $\delta^{13}CH_4$).

Measurements of the isotopic composition of methane relevant to this work include: (i) The composition of methane in a sample of sewage collected from the Malabar Outfall during 1994 was $\delta^{13}C$= -43.7 ‰ with a pMC content of 87.6 %. This result suggests a contribution of 'old' carbon to the sewage methane. (ii) The isotopic composition of 'background' seawater collected offshore Sydney and as far south as Eden varied between -42.9 and -45.3 ‰; with pMC contents between 97.2 % and 104 %. (iii) The isotopic compositions of methane in the survey area offshore Sydney varied between -42.3 ‰ and -24.1 ‰ with pMC contents between 90.3 % and 107.7 %. (iv) A sample collected in Sydney Harbour (alongside No.13 wharf at Pyrmont) had an isotopic composition of -41.5 %.

A comparison of these data indicate: (i) The isotopic composition of methane in sewage and background seawater are comparable and as such these measurements are not useful tracers of sewage derived methane in the sea. (ii) The wide variations in isotopic compositions of methane measured in coastal waters suggests a variable input from petrogenic hydrocarbon sources, but this observation is contradicted by the apparently 'modern' content of carbon in the methane (90.3 % - 107.7 %. The only apparent explanation for these data is for oxidation of sewage methane in the 'far field' around the outfalls. Oxidation of modern methane results in a residual methane enriched in the heavy isotope (less negative values) but with a modern pMC value.

12. Summary

The DHD component of *Rig Seismic* Survey 112 was conducted to evaluate the potential application of continuous real-time measurements of light hydrocarbons in seawater as geochemical tracers of anthropogenic inputs into the coastal zone.

Approximately 500 line-km of DHD data were collected from the coastal zone between Broken Bay and Port Hacking. Most data were collected from twelve survey lines between North Head and Port Hacking. Four survey lines were run at each water depth, 5 m, 25 m, 45 m, and two survey lines at 10 to 15 m above the seafloor. These lines traversed the ocean outfalls at North Head, Bondi and Malabar. Additional, shorter lines were run near the entrance to Botany Bay and extended into Bate Bay; in the vicinity of Broken Bay and, at the conclusion of the survey, into Port Jackson (Survey 113).

The vertical distributions of light hydrocarbons in the water column were measured at eighteen stations in the survey area. These vertical profiles were located near the ocean outfalls and also the entrances to Port Jackson, Broken Bay, Botany Bay and Port Hacking.

Analysis of hydrocarbon compositions from the vertical profiles indicate that hydrocarbon mixtures from Port Jackson, Botany Bay and the ocean outfalls are distinct but that individual ocean outfalls have similar characteristics. The light hydrocarbons from the outfalls are characterised by high methane with minor amounts of C_{2+} hydrocarbons (ethane only), and hence, have characteristically low wetness values (<0.5 %). Effluent discharged from the deep ocean outfalls can be mapped effectively using methane concentration or using Discriminant Functions which utilise a range of hydrocarbon concentrations.

In contrast, hydrocarbons in the vertical profiles collected from near the entrances to the estuaries comprised lower methane concentrations with an increasing abundance of C_{2+} hydrocarbons, and hence, have high wetness values. Methane concentrations from estuarine sources typically do not exceeded 10 ppm or about three times background. The distribution of estuarine derived hydrocarbons can be mapped effectively using C_{2+} hydrocarbons (ethane, ethylene, propane, propylene and butane) or Discriminant Functions which use a combination of hydrocarbons.

Detailed maps of hydrocarbon concentration and other indicators such as wetness values and discriminant functions were prepared to show the dispersion of hydrocarbon sources to the coastal zone. Elevated concentrations of light hydrocarbons were detected throughout the survey area. Methane was the most abundant hydrocarbon and is primarily an indicator of discharge from the deep ocean outfalls. The highest concentrations (fifty-fold background concentrations) were measured in relatively small hot-spots at 25 m and 45 m water depths between the Bondi and Malabar Ocean Outfalls. At 5 m water depth high methane concentration (up to five-fold background concentrations) were found mostly in the southern sector of the survey area, south of the Bondi Outfall but with highest concentrations south of Malabar, and indicate that the discharged effluent is penetrating into surface waters at the time of the survey.

The C_{2+} hydrocarbons were also found at concentrations in excess of their background seawater concentrations. High concentrations of these saturated hydrocarbons may be linked to anthropogenic sources, but unsaturated hydrocarbons are naturally occurring and imply a natural biogenic source. The highest concentrations of C_{2+} hydrocarbons, both saturated and unsaturated (> 1 ppm) were found offshore and south of Botany Bay indicating that Botany Bay is a significant source of hydrocarbons to coastal waters. There was no evidence of significant discharge from Port Jackson to coastal waters.

These observation indicate that light hydrocarbons are a useful tool to distinguish between a wide range of inputs to the coastal zone. These light hydrocarbons and the concentrations measured here from various sources are generally low and may not, in themselves, present an environmental hazard. We have shown that hydrocarbons associated with discharges to the coastal zone have unique and clearly distinguishable signatures that can be used to identify and map the dispersion of both anthropogenic and naturally occurring inputs to coastal waters and, as such, are a useful environmental monitoring tool.

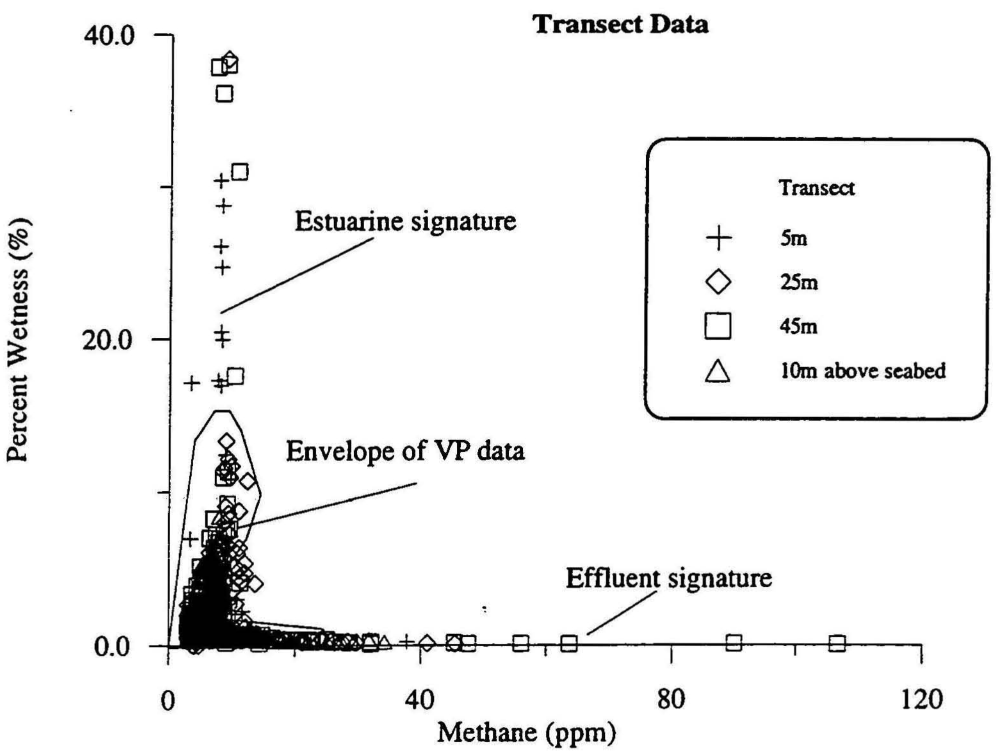
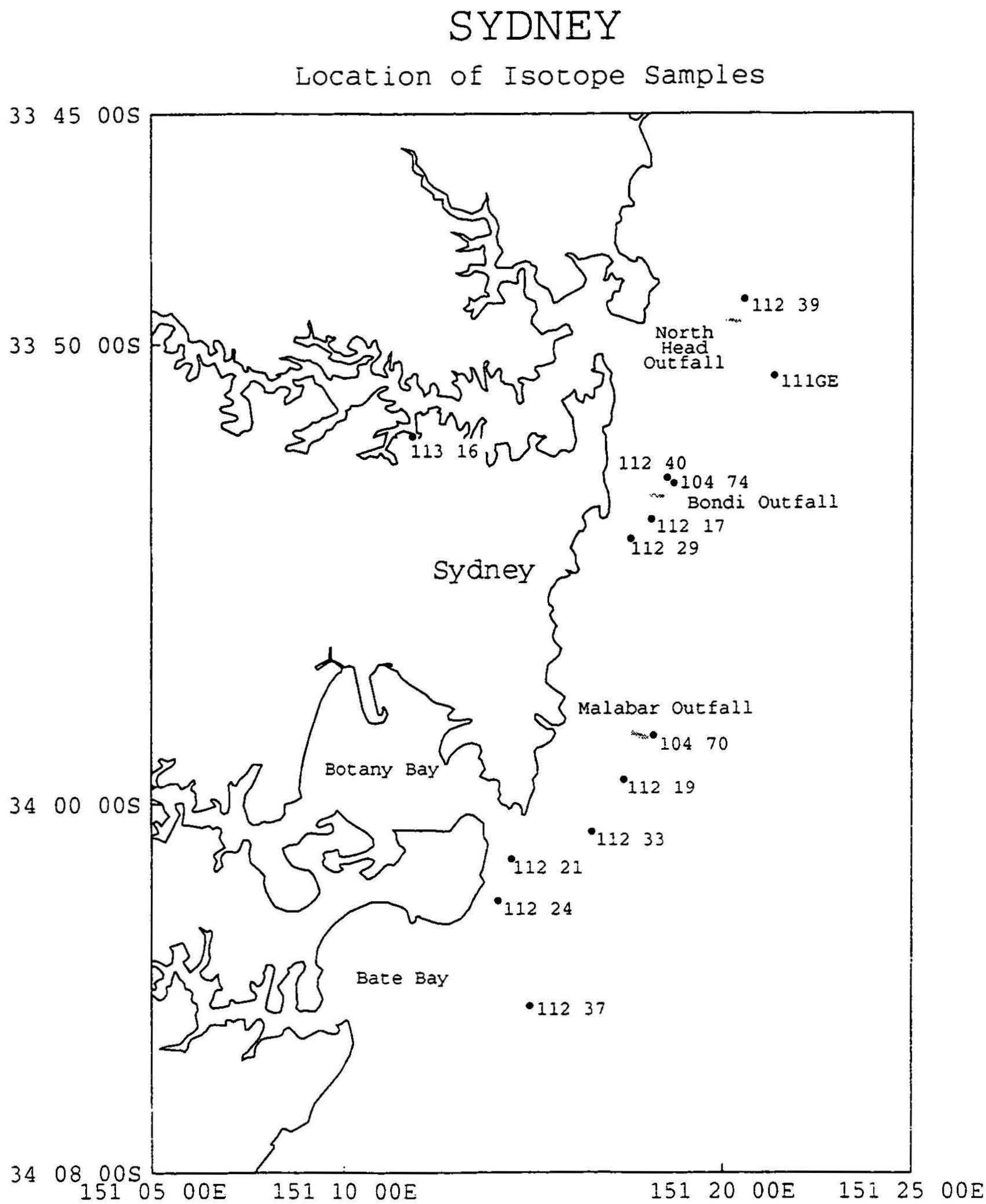


Figure 70. Cross Plot of Methane versus percent wetness for each depth



Sample 112NZ1 (background) is located about 50 km east in "clean" water.

Sample 34GE is located about 40 km to the south east.

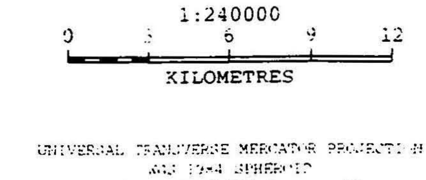


Figure 71

Table 11 Carbon isotopic compositions, percent modern carbon and average methane of samples analysed for isotopic data.

Survey	Survey Line	Sample No.	Sample Depth (m)	Methane (ppm) headspace	Delta 13C (% PDB)	(pMC)	Comments
"Rig Seismic"	Transit	112 NZ1	10	nm	-23.8	102.7	Background values 50 km to the east
"Rig Seismic"	VP112006	112 17	25	19 - 23	-42.3	nm	Near Bondi Outall
"Rig Seismic"	VP112017	112 21	1 - 9.	3.2 - 11.1	-24.1	90.3	Entrance to Botany Bay
"Rig Seismic"	112 003	112 24	2 - 11.	3.3 - 6.0	-28.2	103.2	Between Botany Bay and Bate Bay
"Rig Seismic"	112 008	112 29	25	4.7 - 45.5	-30.9	nm	2 km SSW of Bondi Outfall
"Rig Seismic"	VP112008	112 19	68	3.1 - 4.5	-28.8	99.4	2 km SSW of Malabar Outfall
"Rig Seismic"	112 013	112 40	18	24 - 107	-41.9	nm	1 km north Bondi Outall
"Rig Seismic"	112 009	112 33	26	8.3 - 30.0	-29.5	98.1	5 km SSW of Malabar Outfall
"Rig Seismic"	112 013	112 39	38 - 40	4.0 - 25.0	-32.0	107.7	1 km north of North Head Outfall
"Rig Seismic"	112 010	112 37	25	8.1 - 10.0	-25.2	nm	7 km east of Bate Bay
"Rig Seismic"				~ 280	-43.7	87.6	Malabar sewage
"Rig Seismic"		113 16	8	~ 50	-41.5	95.4	Alongside No. 13 Pymont
"Rig Seismic"	10470	104 70.1	29	12.3	-45.5	185.6	Near Malabar Outfall
"Rig Seismic"	10474	104 74.1	43	22	-48.7	98.6	Near Bondi Outfall
"RV Franklin"		IIIGE	5	nm	-43	nm	Franklin Sample
"RV Franklin"		34GE	5	nm	-41	nm	Franklin Sample

footnotes
nm = not measured

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