

1997/34
copy 3

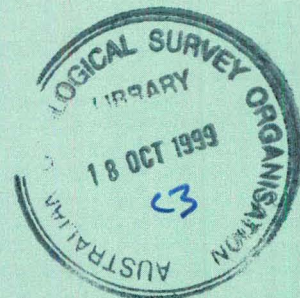
AGSO

PRODUCED FORMATION WATER DISCHARGE FROM A PRODUCTION PLATFORM TO THE NORTH WEST SHELF, 1995

AGSO Marine Survey 152

by

D. Holdway, D.T. Heggie & C. Tindall



AGSO RECORD 1997/34

COMMERCIAL IN CONFIDENCE
until 27th February, 2001
except where approval to publish
material herein is sought from &
granted by APPEA

AGSO



AUSTRALIAN
GEOLOGICAL SURVEY
ORGANISATION

BMRComp
1997/34
copy 3

AGSO RECORD 1997/34

COMMERCIAL IN CONFIDENCE
until 27th February, 2001
except where approval to publish
material herein is sought from &
granted by APPEA

PRODUCED FORMATION WATER DISCHARGE
FROM A PRODUCTION PLATFORM
TO THE NORTH WEST SHELF, 1995

AGSO Marine Survey 152

by

D. Holdway, D.T. Heggie & C. Tindall

Petroleum & Marine Division
Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT 2601
Australia

DEPARTMENT OF PRIMARY INDUSTRIES AND ENERGY

Minister for Primary Industries and Energy: Hon. J. Anderson, M.P.

Minister for Resources and Energy: Senator the Hon. W.R. Parer

Secretary: Paul Barratt

AUSTRALIAN GEOLOGICAL SURVEY ORGANISATION

Executive Director: Neil Williams

© Commonwealth of Australia 1997

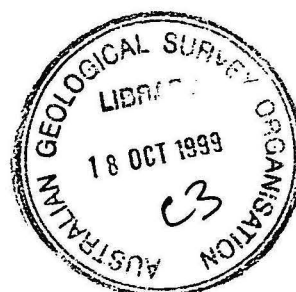
ISSN: 1039-0073

ISBN: 0 642 25044 8

This work is copyright. Apart from any fair dealings for the purposes of study, research, criticism or review, as permitted under the *Copyright Act 1968*, no part may be reproduced by any process without written permission. Copyright is the responsibility of the Executive Director, Australian Geological Survey Organisation. Requests and inquiries concerning reproduction and rights should be directed to the **Principal Information Officer, Australian Geological Survey Organisation, GPO Box 378, Canberra City, ACT, 2601.**

AGSO has endeavoured to use techniques and equipment to achieve results and information as accurately as possible. However such equipment and techniques are not necessarily perfect. AGSO has not and does not make any warranty, statement or representation about the accuracy or completeness of any information contained in this document. **USERS SHOULD NOT RELY SOLELY ON THIS INFORMATION WHEN CONSIDERING ISSUES WHICH MAY HAVE COMMERCIAL IMPLICATIONS.**

| | |
|---|-------------|
| EXECUTIVE SUMMARY | III |
| LIST OF FIGURES | V |
| LIST OF TABLES | VII |
| ACKNOWLEDGMENTS | VIII |
| INTRODUCTION | 1 |
| 1.1 Background | 1 |
| 1.2 Location and Industry Setting | 2 |
| 1.3 Produced Formation Water | 2 |
| 1.4 Objectives and Program | 3 |
| 1.5 Survey Description | 4 |
| Statistics | 5 |
| METHODS | 6 |
| 2.1 Continuous Geochemical Tracers (CGT) | 6 |
| Equipment | 6 |
| Strategy | 7 |
| 2.2 Hydrographic data acquisition | 8 |
| 2.3 Vertical Profiles of hydrocarbons and hydrography | 8 |
| 2.4 PFW Headspace Analysis | 8 |
| 2.6 Isotope tracers of PFW | 10 |
| 2.7 Navigation | 10 |
| RESULTS AND DISCUSSION | 14 |
| 3.1 Hydrocarbon Concentrations and Dispersion Mapping | 14 |
| Hydrocarbon dispersion, neap tides 1-1.5 m (survey Lines 4, 5 &7) | 15 |
| Hydrocarbon dispersion, spring tides, 3 m, (survey Lines 9, 11 &12) | 17 |
| 3.3 Modelling of plume dispersion | 37 |
| 3.4 Vertical Profiles | 42 |
| 3.5 PFW Analyses | 44 |
| 3.5 Isotopic Analysis | 46 |
| DIC Isotopes | 46 |
| Methane Isotopes | 51 |



| | |
|--------------------|-----------|
| CONCLUSIONS | 54 |
| REFERENCES | 61 |

Executive Summary

During September 1995, the Australian Geological Survey Organisation and the Australian Institute of Marine Science took part in a joint survey aboard the 'Lady Basten' to monitor the dispersion, fates and effects of Produced Formation Water (PFW) discharged from the Harriet 'A' production platform on the North West Shelf. The AGSO component of the work involved using Continuous Geochemical Tracer (CGT) analysis of specific light hydrocarbons (C_1 - C_6 , benzene and toluene) to map the shape and extent of the discharged PFW plume in surface waters at 2 m. depth. Hydrographic parameters including water temperature, dissolved oxygen, pH, salinity and turbidity were also continuously profiled. Four hydrocarbon vertical profiles were completed at various distances from the platform and several surface water samples collected for isotopic analysis. The profiling was conducted at speeds of 2 to 8 knots resulting in a typical data-point spacing of 180 metres. A total of 993 line kilometres of geochemical and hydrographic data were collected during the survey period in a tidal range which varied from 1.5 to 3.0 metres.

Benzene and toluene proved to be sensitive tracers of PFW, with concentrations in seawater being 100 fold higher than typical 'detectable background' levels. Benzene concentrations varied from >140 ng/L, within the PFW plume to < 1 ng/L at background and toluene ranged from >250 ng/L in the plume to about 2 ng/L. Concentrations of C_1 through C_6 hydrocarbons were a maximum 1500 ng/L in the plume to <180 ng/L at background seawater levels. PFW collected at the Harriet A platform contained 3.75 mg/L of C_1 - C_6 hydrocarbons; 1.59 mg/L benzene and 1.72 mg/L toluene, and these results suggest apparent dilutions of about 10,000 of PFW hydrocarbons in seawater.

Dissolved inorganic carbon (DIC) and methane and their isotopic compositions also showed distinct contrasts between background seawater and PFW, and therefore are potential tracers and indicators of PFW reactivity in seawater. Despite the high temperature of the PFW discharge (70°C), the PFW plume is not evident in seawater temperature distributions.

The PFW plume was mapped in a NNW and SSE direction on each tide to a maximum distance of approximately 10 kilometres from the production platform. A net westerly drift of the plume was evident on both the ebb and flood tides toward the Montebello Islands and Varanus Is., rather than toward the east and the mainland. A one dimensional dispersion model found hydrocarbons are dispersed from Harriet A, with characteristic half-dispersion distances of about 3.5 km on a spring tide. Vertical profiles of PFW hydrocarbons suggest that within 1 km of the platform the PFW plume is primarily a surface feature but beyond 1 km all hydrocarbons are well mixed throughout the water column. Benzene and toluene are sensitive tracers of the plume and appear to be more reactive in seawater than C₁-C₆ hydrocarbons.

LIST OF FIGURES

| | Page |
|---|------|
| Figure 1: Survey location and the extent of the PFW plume dispersion using the BTEX hydrocarbon, toluene as the tracer | 12 |
| Figure 2: System schematic of AGSO's hydrocarbon CGT system as configured for the survey | 13 |
| Figure 3: A chromatogram of PFW headspace gases from Harriet 'A' | 14 |
| Figure 4: A typical GC trace from clean seawater | 14 |
| Figure 5: C ₁ -C ₆ dispersion contour map; Line 7 | 21 |
| Figure 6: Toluene dispersion contour map; Line 7 | 22 |
| Figure 7: Benzene dispersion contour map; Line 7 | 23 |
| Figure 8: Temperature contour map; Line 7 | 24 |
| Figure 9: Dissolved oxygen contour map; Line 7 | 24 |
| Figure 10: Salinity contour map; Line 7 | 25 |
| Figure 11: Density contour map; Line 7 | 25 |
| Figure 12: C ₁ -C ₆ dispersion contour map; Line 9 | 26 |
| Figure 13: Toluene dispersion contour map; Line 9 | 27 |
| Figure 14: Benzene dispersion contour map; Line 9 | 28 |
| Figure 15: Temperature contour map; Line 9 | 29 |
| Figure 16: Salinity contour map; Line 9 | 29 |
| Figure 17: Dissolved oxygen contour map; Line 9 | 30 |
| Figure 18: Density contour map; Line 9 | 30 |
| Figure 19: An example of a chromatogram of 'plume' hydrocarbons from both PFW and drilling rig derived sources | 31 |
| Figure 20: C ₁ -C ₆ combined dispersion contour map; Lines 11 and 12 | 32 |

| | |
|---|----|
| Figure 21: Toluene combined dispersion contour map; Lines 11 and 12 | 33 |
| Figure 22: Benzene combined dispersion contour map; Lines 11 and 12 | 34 |
| Figure 23: Temperature contour map; Line 12 | 35 |
| Figure 24: Salinity contour map; Line 12 | 35 |
| Figure 25: Dissolved oxygen contour map; Line 12 | 36 |
| Figure 26: Density contour map; Line 12 | 36 |
| Figure 27: Hydrographic tracers of the plume; anomalous density and temperature profiles across the plume centreline on Line 9 | 37 |
| Figure 28: Plume centreline hydrocarbon concentrations as a function of distance from the platform | 56 |
| Figure 29: Benzene and toluene/C ₁ -C ₆ X-plots for Lines 7, 9, 11 and 12 and BTEX/C ₁ -C ₆ ratios | 57 |
| Figure 30: C ₁ -C ₆ , benzene and toluene vertical profiles for VP's 1 to 4 | 58 |
| Figure 31: Benzene / C ₁ -C ₆ and toluene / C ₁ -C ₆ concentration X-plots for vertical profiles 1 to 4 | 59 |
| Figure 32: Carbon-14, carbon-13 and oxygen-18 isotopic composition of dissolved inorganic carbonate for PFW and seawater | 60 |
| Figure 33: Carbon-14 and carbon-13 isotopic composition of methane as potential tracers of the PFW plume | 61 |

LIST OF TABLES

| | Page |
|---|------|
| Table 1: Summary of survey operations | 4 |
| Table 2: Survey statistics | 5 |
| Table 3: Gas chromatograph specifications and operating parameters | 6 |
| Table 4: PFW daily discharge volumes and oil concentrations | 16 |
| Table 5: Exponential curve parameters α and Co and dilution coefficients (PFW/ Co) for survey lines 7, 9, 11 and 12 | 42 |
| Table 6: Harriet Alpha treated produced formation water discharge parameters derived from survey data and Apache Energy records | 46 |
| Table 7: Water samples collected on the 1994 pilot study for isotopic analysis | 48 |
| Table 8: NIWA DIC isotopic (^{14}C , $\delta^{13}C$ & $\delta^{18}O$) analysis; 1994 survey | 49 |
| Table 9: Water samples collected on the 1995 survey for isotopic and salinity determinations | 50 |
| Table 10: NIWA DIC isotopic (^{14}C , $\delta^{13}C$ & $\delta^{18}O$) analysis; 1995 survey | 52 |
| Table 11: INGS gas (CH_4) isotopic (^{14}C & $\delta^{13}C$) analysis | 53 |

ACKNOWLEDGMENTS

We wish to thank the staff of the Australian Institute of Marine Science for their cooperation in this project. In particular we acknowledge the support and assistance of Dr Miles Furnas and Dr Kathryn Burns and their helpful suggestions throughout and thank the crew of the AIMS vessel RV 'Lady Basten' for their consistent efforts during the course of the survey.

Funding for this project was provided primarily by the Australian Petroleum Production and Exploration Association (APPEA), which is the national representative of the oil and gas exploration and production industry in Australia and the Energy Research Development Corporation (ERDC). The remainder of the financial and in-kind support was contributed by AIMS and AGSO.

We also appreciate the work by the staff at the National Institute of Water and Atmospheric Research in New Zealand and in particular Gordon Brailsford, who have ably provided the isotopic analysis for this work.

The following are also acknowledged for their contribution to and/or review of this paper: Dr. Andrzej Radlinski and Dr. Dave Fredericks.

INTRODUCTION

1.1 Background

During September 1994 AGSO and AIMS conducted a collaborative survey to the North West Shelf to test a variety of techniques to trace the dispersion of Produced Formation Water discharged into the sea from the petroleum production platform, Harriet A. The Australian Institute of Marine Science (AIMS), together with the Australian Geological Survey Organisation (AGSO) and the Australian Nuclear Science and Technology Organisation (ANSTO) as joint collaborators, subsequently successfully tendered a proposal to the Energy Research and Development Corporation (ERDC) and the Australian Petroleum Production and Exploration Association (APPEA) for a more detailed environmental investigation of PFW discharge from the Harriet A production platform.

A combination of oceanographic, biological and geochemical methods - including in-situ hydrocarbon profiling, were selected to monitor the dispersion, fates and effects of treated Produced Formation Water (PFW) discharge to a tropical, shallow water marine environment.

With the cooperation of Apache Energy Pty Ltd (the oil field operator) the survey was conducted from September 16th to September 30th 1995, with joint participation with AIMS onboard their vessel the RV 'Lady Basten'. This record details the AGSO component of the work which primarily involved measuring a variety of light hydrocarbons in seawater using a gas chromatograph based Continuous Geochemical Tracer (CGT) system in the field, and the subsequent mapping of the PFW plumes in this area.

NOTE: *The data collected as part of this work is 'commercial in confidence' for a period of 5 years after the completion of the project, as outlined in the terms of the ERDC contract documents. Within this period dissemination of the data and*

publications relating to the work require the specific approval and acknowledgment of ERDC and APPEA.

1.2 Location and Industry Setting

The survey was conducted in the immediate vicinity of the Harriet 'A' (Alpha) petroleum production platform on the North West Shelf, approximately 120 km west of Dampier / Karratha and 20 km north-east of Barrow Island. A location map is presented in Figure 1. This figure also shows the geographical extent of the survey-lines conducted and concentration contours of toluene (a tracer of PFW), in the survey area. The data from these lines are discussed in the text below.

Varanus Island which is located 7 km to the south-west of Harriet is a major production terminal where oil from oil producing wells is stored for shipment and gas from gas producing platforms is pumped to the mainland by pipeline. There are three Harriet production platforms - Alpha, Bravo and Charlie. Oil is produced from at least 12 wells serviced by these platforms. However only at Harriet 'A' is treated produced formation water pumped into the sea for disposal.

Produced water from 'B' platform is discharged into the lost circulation zone of a disused well while produced water from 'C' platform is directed to Harriet 'A' for treatment and discharge. PFW from the gas fields to the north (Campbell and Sinbad) and the Tanami oil field (adjacent to Varanus Is.) are discharged into a shallow disposal well on Varanus Island (Swan et al, 1992).

1.3 Produced Formation Water

Produced formation water is derived from at least two sources. Firstly, fossil artesian or sub-artesian water that has been trapped for millennia within the oil bearing sedimentary strata and is pumped to the surface with oil and gas during production. This component of the formation water varies greatly in composition and quantity with the volume increasing during the life of the oil field, as drawdown increases and the oil is depleted. The second source is injection water which is used to increase the

reservoir pressure and thereby improve production of oil and gas, extending the life of the field. Small amounts of both dispersed (droplet) and dissolved oil remain in the treated PFW when it is discharged into the ocean. Two groups of petroleum hydrocarbons of environmental concern are the (i) aromatic hydrocarbons, including benzene, toluene, ethyl benzene and xylenes (BTEX) and (ii) polynucleic aromatic hydrocarbons (PAH). BTEX are soluble in seawater and are toxic to marine organisms. PAH are less soluble in seawater than BTEX and generally concentrations are lower in PFW. Toxicity to marine organisms has been shown in previous studies to be due largely to benzene and naphthalene's (Brand et al, 1989).

The PFW on Harriet 'A' is divided into two paths for oil reduction treatment. A hydrocyclone processes over 7 megalitres of PFW per day and a gas flotation unit handles the remainder of about 1 megalitre per day. During this survey the two flows were discharged at separate points. The hydrocyclone discharges at 4 m above mean sea level and the gas flotation unit at 9.1 metres below sea level. (Apache Energy Report, 1996). The properties of the PFW are tabulated in section 4.5.

1.4 Objectives and Program

The objectives of the AGSO component of the survey were:

1. To measure the concentrations of C₁-C₆ hydrocarbons and BTEX (specifically benzene and toluene) in a systematic manner around Harriet 'A' production platform that would allow the dispersion envelope of the PFW plume to be mapped under a variety of tidal conditions.
2. To determine the vertical distributions of hydrocarbons in the water column.
3. To examine the processes of PFW dispersion (dilution and chemical reaction) by utilising BTEX concentrations and the isotopic contents i.e. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and ^{14}C of dissolved inorganic carbon and other PFW tracers, such as methane, which may prove to be auxiliary tracers of PFW.

4. To document the oceanographic conditions in the survey area by continuously acquiring hydrographic data including temperature, salinity, (ie., seawater density), dissolved oxygen, pH and turbidity.

To achieve these objectives a variety of operations were conducted from the Lady Basten between 15 and 30 September 1995, and these are summarised in Table 1.

1.5 Survey Description

A brief summary of the survey operations is shown below in Table 1.

Table 1. Summary of survey operations

| Day | Time | Operation | Observation |
|--------------------------|----------------|---|--|
| 15.9.95 to 16.9.95 | 08.45 (WST) | Equipment installation and testing in Dampier | Calibration of dual columns to reduce offset to a minimum |
| | 21.00 | Installation complete | |
| 17.9.95 | 0200 | Depart for Varanus Is. arrive at 0900 | Calibration of columns continuing |
| | 1309 | Depart Varanus to deploy current meter | Line 2 CGT data collected |
| 18.9.95 | 0815 | Commenced Line 3 - box grid around platform | SDL not working; CGT data OK |
| 19.9.95 | 14.28 | Deployed bottom sampling gear; CGT commenced | Small grid to south of platform in PFW on flood tide - Line 4 |
| 20.9.95 | 11.00 | Two loops around platform - Line 5 | Surface slick controlled largely by wind and heading east north east |
| | 1500 | Zigzag pattern to east and south | |
| | | First PFW analysis | |
| 21.9.95 | 0800 | Line 6 to 'clean' seawater to north | CGT and isotopic samples collected |
| 22.9.95 | 0800 | AIMS sampling, SDL repaired and working | Good CGT profile with highs in plume. Pumping time offset noticeable however on reciprocal lines |
| | 1420 | Line 7 CGT grid to north on ebb tide | VP's completed from 2 m to 20 m; |
| 23.9.95 | 0730 | CGT 'box' around platform | boat drift a potential problem |
| | 1100 | Three VP's to north west of platform | Chromatogram shows HC's associated with drilling operations |
| 24.9.95 | 0830 | Jack-up drill platform moved; Line 8 | Excellent definition of plume out to 4.5 nautical miles |
| | | traverse to south to 'clean' water | |
| 25.9.95 | 0800 | Transit back to Harriet - Line 9; | Zigzag CGT lines on flood tide to south following drogue |
| | 1215 | CGT grid to north on 3 metre tide | CGT again on flood tide; more comprehensive coverage than Line 10 |
| 26.9.95 | 0900 | AIMS VP and box core; drogue released; CGT Line 10 started | CGT results consistent with previous days results on a flood tide |
| | 1010 | AIMS VP and sediment trap; CGT | Discontinued CGT sampling when hydrocarbon levels decreased to background concentrations |
| 27.9.95 | 0630 | Line 11 commenced | |
| | 0745 | Similar to previous day; again Line 12 | |
| 28.9.95 | 0730 | followed a zigzag path to south | |
| 29.9.95 | 0800 | Recovered tide gauges; continued CGT Line 13 from Harriet due east toward Dampier | |

Statistics

Each survey line represents one day's activities. Detailed profiling of the PFW 'plume' occurred on lines 4, 5, 7, 9, 10, 11 and 12. Other lines were primarily associated with biological experiments or provide information on clean seawater conditions. Table 2 lists the major statistics for the survey.

Table 2. **Survey statistics**

| Parameter | Totals |
|---|--------|
| Number of survey lines | 12 |
| Total line kilometres | 993 |
| Number of hydrocarbon data points | 2680 |
| Hydrocarbon data point spacing @ 3 knots (in metres) | 186 |
| Number of hydrographic data points | 6720 |
| Number of vertical hydrocarbon profiles | 4 |

METHODS

2.1 Continuous Geochemical Tracers (CGT)

Equipment

As a result of experience gained during the pilot study a Direct Hydrocarbon Detection (DHD) system was specifically configured for the project. A schematic of the system is shown in Figure 2. The hardware consisted of an AGSO gas extractor, a single Shimadzu gas chromatograph fitted with dual 15 metre J&W AT-Alumina PLOT columns and two PC's for data acquisition and control. Seawater from 2 metres below the sea surface was delivered to the system via the 'aquarium' seawater pump on the 'Lady Basten'. The gas extractor was installed on the after deck with the remainder of the equipment located in the ship's laboratory. Column specifications and operating conditions are tabulated in Table 3.

Table 3. Gas chromatograph specifications and operating parameters

| Equipment/Parameter | Specification |
|----------------------|-------------------------------------|
| pre-column | 15 metre of 0.5 mm ID DB-1 megabore |
| main column | 15 metre of 0.53 mm ID Alumina PLOT |
| temperature | |
| oven | 160°C |
| detector | 250°C |
| column head pressure | |
| carrier 1 | 0.90 kg/cm ⁻² |
| carrier 2 | 0.75 kg/cm ⁻² |

The gas extractor columns were adjusted to give identical chromatograms logging C₁ to C₆ (methane through hexane), benzene and toluene. The columns were operated alternately with each column producing a chromatogram every 4 minutes and thus overall, a hydrocarbon determination every 2 minutes.

Higher column flow rates were used on this survey than on previous AGSO projects, and this allowed an increase in sample frequency. By employing helium as the carrier gas rather than nitrogen, resolution was not compromised.

Typical chromatograms of a PFW sample and 'clean' seawater are illustrated in Figures 3 and 4.

A number of calibrations and corrections were applied to the CGT data during the data gathering process or subsequently in post processing:

- (1) A calibration gas was used daily to check the performance of the gas chromatograph.

- (2) The elapsed time taken for seawater to pass from the seawater inlet to the gas extractor was calculated so that the exact navigational coordinates could be assigned to each sample.

Two methods were used to calculate the offset:

- (a) by the use of a calibration line (Line 152009) where traverses were run on reciprocal headings at right angles to the direction of plume movement and

- (b) by calculating pumping time from an estimate of inlet pipe volume and pumping capacity.

From these calculations a pumping offset time of 2 minutes was estimated and applied in post processing.

Strategy

The continuous profiling was conducted at 3 to 8 knots and line spacings from approximately 0.2 to 0.5 nautical miles with the lower speeds and smaller spacings used nearer the platform. Thus a typical 3 knot transect speed provides a data point every 185 metres over the sea floor.

The procedure adopted for the survey was tide dependent. At the turn of the tide (slack tide), one or two 'box' grids were profiled by circumnavigating the platform at 500 to 1000 metres distance. As the plume direction on the ebb (or flood) tide was

established, the plume was then tracked with a series of near parallel transects normal to the current flow at increasing distances from the discharge in the direction of the tidal flow.

On three occasions sediment trap drogues were deployed by AIMS, on a flood tide, while the CGT survey was in progress. These provided confirmation of tidal direction and plume movement.

2.2 Hydrographic data acquisition

Hydrographic data were acquired using a YEOKAL/CSIRO Submersible Data Logger. This was mounted over the side of the 'Lady Basten' on a pipe stem at a depth of 1.5 metres. The parameters recorded were:-conductivity (salinity), temperature, pressure (water depth), pH, dissolved oxygen, and turbidity.

The data logger transceiver was located in the laboratory as part of the CGT system.

2.3 Vertical Profiles of hydrocarbons and hydrography

The CGT system was also used to acquire vertical profiles of hydrocarbon concentrations. A Jabsco pump delivered seawater to the gas extractor via 15 mm I.D. medical grade nylon tubing attached to the shipboard hydrographic wire. This technique enabled continuous sampling at discrete vertical intervals throughout the water column.

2.4 PFW Headspace Analysis

Samples of produced formation water were supplied to the 'Lady Basten', on two occasions, from the production platform. Headspace analysis of dissolved hydrocarbons in PFW was then carried out to determine concentrations at the discharge point and allow conversion of the CGT results to seawater concentrations.

The procedure involved adding 5 ml of PFW to a 50 ml syringe which was then sealed and shaken for about 10 minutes. A sample of the headspace gases was then injected into the GC to measure the hydrocarbon concentrations. Residual gas was then expelled from the syringe and a second extraction conducted. A comparison of results from the two extracts was then used to determine the partition coefficient (P) for each hydrocarbon which in turn allowed the conversion of the CGT results to seawater concentrations.

2.5 Partitioning Coefficients and Concentration Conversions

PFW Concentrations.

The following steps were used to convert ppm headspace concentrations of PFW and seawater samples to seawater concentrations in either nl/L or ng/L. PFW hydrocarbon headspace concentrations were calculated from extract 1 and extract 2 results for each hydrocarbon:

$$C_{\text{PFW}} (\text{nl/L}) = C_{\text{HS}} [\text{ppm}] \times 10^4 / P$$

where C_{HS} is the hydrocarbon headspace concentration and P is the partitioning coefficient for each hydrocarbon (methane through xylene) and is estimated by:

$$P = (1 - [\text{hydrocarbon in extract 2} / \text{hydrocarbon in extract 1}])$$

CGT Seawater Concentrations.

The total gas load S (oxygen + nitrogen + argon) in seawater at 24 degrees C. and 36 ppt (per mil) seawater salinity was estimated using gas solubility tables (Weiss, 1970). From the tables the headspace gases N_2 , O_2 and Ar, consist of 8.87 ml/L, 4.66 ml/L and 0.23 ml/L respectively, giving a total of 13.76 ml/L dissolved gases.

The conversion of CGT concentrations in ppm hydrocarbon headspace units to seawater concentrations follows:

(Concentrations in units of nL/L were converted to units of nM by division by 22.4, or to ng/L by further multiplication by the molecular weight of the hydrocarbon.)

Note: All concentrations given in units of nM and ng/L throughout this record, are calculated for NTP and have not been converted to concentrations at ambient temperature and pressure.

2.6 Isotope tracers of PFW

Samples of seawater were collected in 1 litre Schott bottles and approximately 15 mg of HgCl_2 added as a bactericide. Of these a total of 22 samples were subsequently selected and sent to the National Institute of Water and Atmospheric Research (NIWA), for analysis of $\delta^{13}\text{C}$, ^{14}C and $\delta^{18}\text{O}$ content in dissolved inorganic carbonate (DIC). These samples were collected where anomalous hydrocarbon concentrations were detected and also at those locations representing 'background' hydrocarbon levels. The ship's position and CGT hydrocarbon concentrations for each sample were noted.

Similarly, where anomalous hydrocarbon levels were detected, samples of extracted gas were collected and sent to the National Institute for Geological Sciences (NIGS) for isotopic analysis of the methane component. These samples were provided from the 1994 pilot survey.

2.7 Navigation

A Trimble NavTrac GPS installed in the ship's laboratory and connected to both the CGT data acquisition PC and a laptop PC supplied by AIMS was used for navigation. MicroMariner navigation and plotting software allowed real time plotting of the ship's track in the field using a digitised Admiralty chart (AUS742) as the base map for the area. Navigation coordinates for each data point were recorded with the CGT data and also on floppy disk as a MicroMariner file.

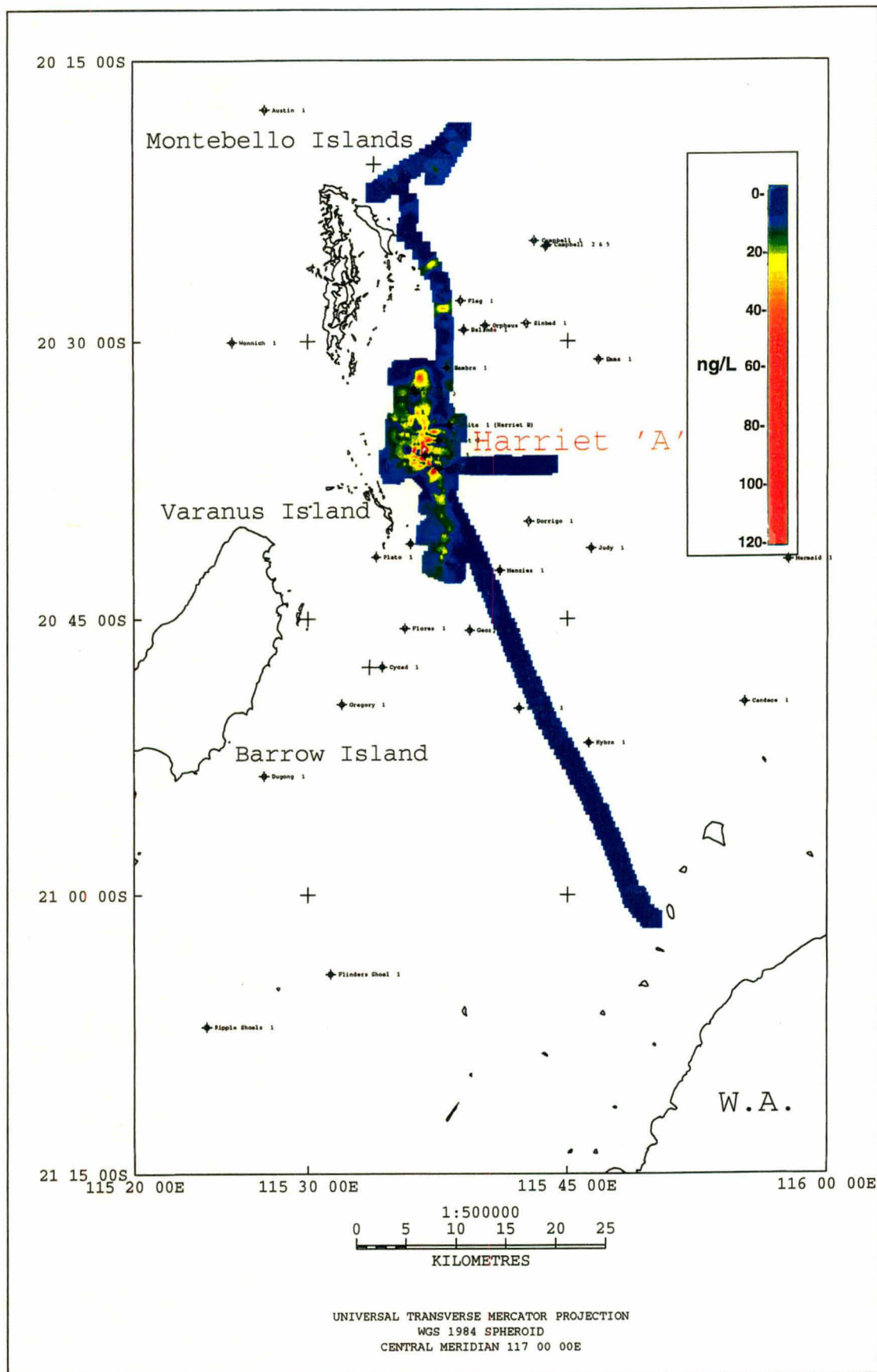


Figure 1. Survey location and the extent of the PFW plume dispersion using the BTEX hydrocarbon, toluene as the tracer

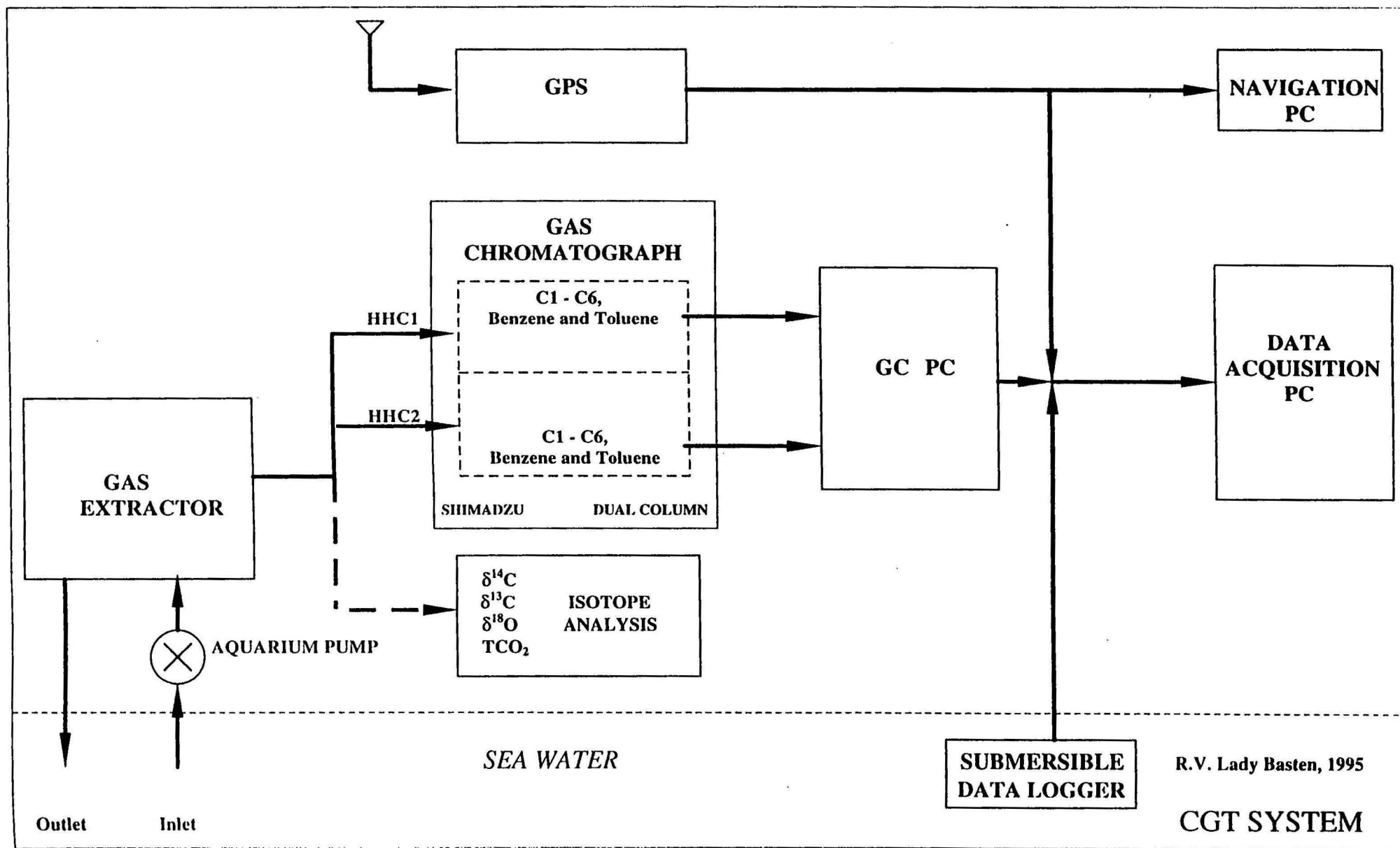


Figure 2. Hydrocarbon CGT system configuration

Sample Name : Heavy Hydrocarbons
 Filename : A:\DATA\UNC100JA.PAM
 Method : HPLC.M
 Start Time : 8.00 min
 Scale Factor: 0.0

Sample #: 1
 Date : 11/15/95 02:59 PM
 Time of Injection: 12/29/95 12:27 PM
 Low Point : 0.00 mV
 High Point : 20.00 mV
 Plot Scale: 20.0 mV

Page 1 of 1

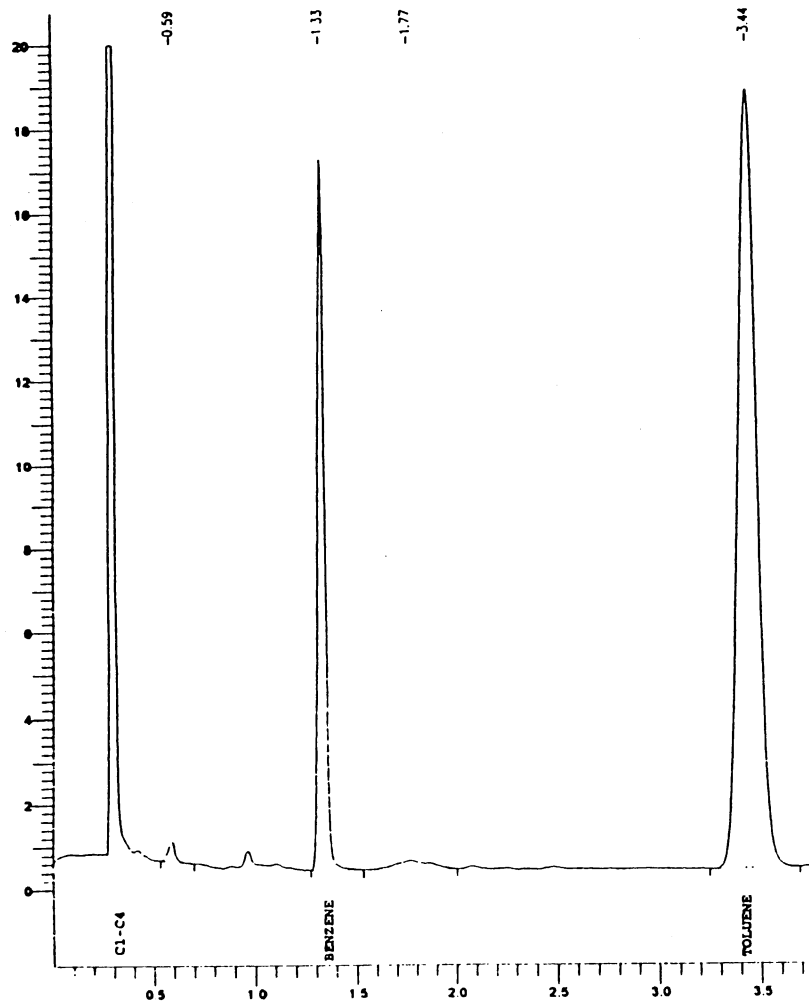


Figure 3. A chromatogram of PFW headspace gases from Harriet 'A'

Sample Name : Heavy Hydrocarbons
 Filename : A:\DATA\UNC100JC.PAM
 Method : HPLC.M
 Start Time : 0.00 min
 Scale Factor: 0.0

Sample #: 1
 Date : 11/15/95 02:54 PM
 Time of Injection: 12/29/95 11:25 AM
 Low Point : 0.00 mV
 High Point : 20.00 mV
 Plot Scale: 20.0 mV

Page 1 of 1

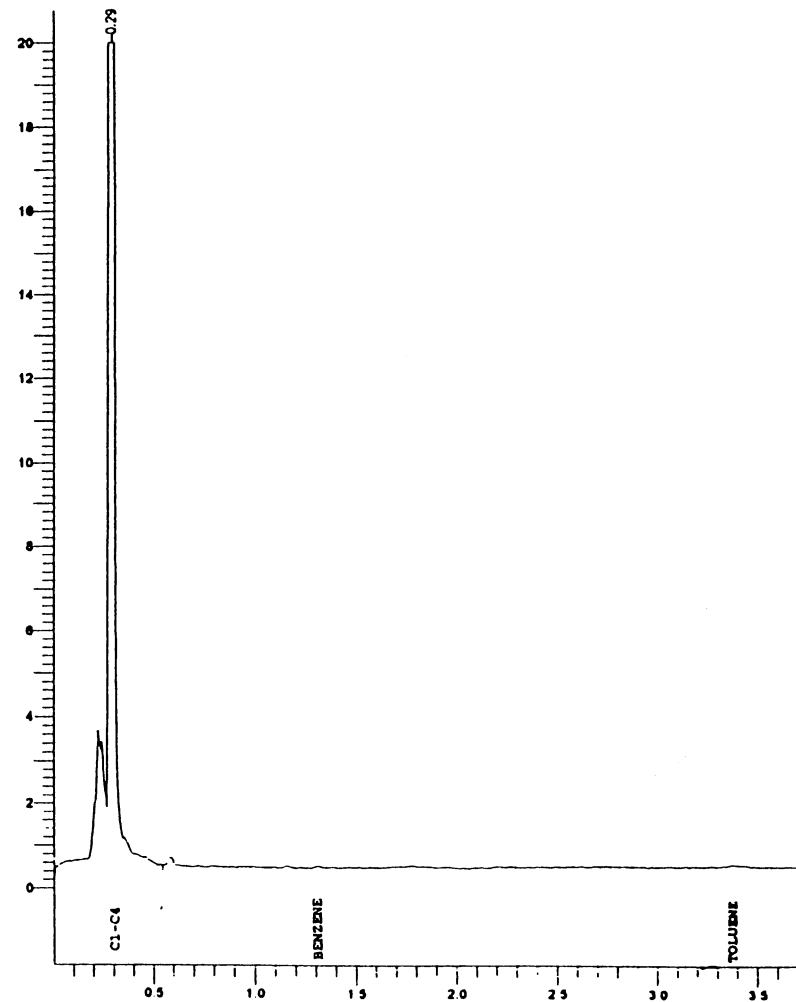


Figure 4. A typical chromatogram for 'background' clean seawater

RESULTS AND DISCUSSION

3.1 Hydrocarbon Concentrations and Dispersion Mapping

The concentrations of C₁-C₆ hydrocarbons varied from 180 ng/L (8.40 nM) seawater at 'background' levels to 1500 ng/L (70 nM) in the PFW plume. The reported concentrations of C₁-C₆ hydrocarbons are approximate only as they represent a combination of methane and higher saturated hydrocarbons as well as the unsaturated hydrocarbons. Previous experience suggests that the predominant component of this C₁-C₆ mixture is methane, which probably comprises close to 50% of the concentrations reported. Typical methane levels in seawater at the temperatures and salinities reported in the survey are about 3 nM (approximately 50 ng/L).

Benzene varied from <0.75 ng/L (0.01 nM) to >140 ng/L (1.79 nM) seawater and toluene from <1.5 ng/L (0.02 nM) at background to >250 ng/L (2.72 nM) seawater in the plume. The benzene and toluene 'background levels' were at the limit of detection of the equipment. The higher anomalous concentrations of benzene and toluene were more than 100 fold higher than their typical background levels. These data compare with levels recorded in seawater off Kingfish 'B' production platform in Bass Strait by ESSO of <1 ng/L using a solvent extraction GCMS method (Terrens and Tait, 1996).

Some variation in PFW discharge volumes and fluctuations in oil content occurred on a daily basis during the survey period. Apache Energy Ltd provided details concerning the discharge (Table 4), as background information for the study.

Table 4. PFW daily discharge volumes and oil concentrations (Apache Energy)

| Date | Line | Discharge at C8[at 3 m above the sea-surface] | | Discharge at Z2 [at 9 m below the sea-surface] | |
|---------|-----------|---|-------------------|--|-------------------|
| | | Volume (m ³) | Oil content (ppm) | Volume (m ³) | Oil content (ppm) |
| 16.9.95 | | 7155 | 28.0 | 1255 | 30.0 |
| 17.9.95 | 2 | 7155 | 24.5 | 1262 | 34.5 |
| 18.9.95 | 3 | 7155 | 17.0 | 1279 | 28.5 |
| 19.9.95 | 4 | 7155 | 17.0 | 1259 | 29.0 |
| 20.9.95 | 5 | 7155 | 24.0 | 1253 | 26.0 |
| 21.9.95 | 6 | 7155 | 11.5 | 1147 | 30.0 |
| 22.9.95 | 7 | 7155 | 21.5 | 1251 | 23.0 |
| 23.9.95 | VP 1, 2&3 | 3883 | 11.0 | 0 | 0 |
| 24.9.95 | 8 | 7155 | 14.0 | 420 | 28.0 |
| 25.9.95 | 9 | 7155 | 18.0 | 1277 | 38.0 |
| 26.9.95 | 10 | 7155 | 21.0 | 1235 | 52.5 |
| 27/9/95 | 11 & VP 4 | 7155 | 18.5 | 1235 | 22.5 |
| 28.9.95 | 12 | 7155 | 41.0 | 991 | 59.5 |
| 29.9.95 | 13 | 7155 | 24.0 | 857 | 45.5 |
| 30.9.95 | | 7155 | 14.0 | 1020 | 19.0 |

Hydrocarbon dispersion, neap tides 1-1.5 m (survey Lines 4, 5 &7)

During the survey the tidal range was in the vicinity of 1 to 3 metres; a three metre range is the maximum for this region (Australian National Tide Table, 1995). Hydrographic properties generally varied over small ranges; sea surface temperatures ranged between 23.1°C and 23.9°C; salinity 35 to 36.3 ppt; dissolved oxygen measurements varied from 5.5 to 7 mg/L (172 µmole to 218 µmole); and seawater density (sigma T) values ranged from 23.8 to 24.9. Turbidity values were also recorded and were generally in the range 2.5 to 2.8 tdu's.

The hydrocarbon dispersion mapping, during the neap tides, was conducted between September 19-20, and is represented by survey Lines 4, 5 and 7. Lines 4 and 5 were 'box' patterns around the platform with limited spatial coverage's on the flood tides to the south. Because of the limited coverage, hydrocarbon contours are not shown for these lines, but the concentrations of C₁-C₆ hydrocarbons, benzene and toluene varied between typical background levels and 600 ng/L for C₁-C₆; and 20 to 35 ng/L for benzene and toluene respectively, at distances of less than 2 km from Harriet A. Line 7 provided particularly good coverage of the extent of the plume on the ebb tide to the

north. Figures 5 through 7 show the dispersion of the measured hydrocarbons around Harriet A on Line 7, with C₁-C₆ varying between background seawater levels of 180 ng/L to a maximum of about 1000 ng/L; and benzene and toluene between 1 and 15 ng/L and 2 and 25 ng/L respectively.

The PFW plumes mapped on Line 7 over one ebb tidal cycle, extend to approximately 5 kilometres miles from Harriet 'A' in a north-north-easterly direction. Contemporaneously AIMS acquired tidal current data near Harriet 'A' using two InterOcean S4 current metres; one at 1.5 metres from the seabed and one at mid-depth (10 metres from the sea bed). The mid-depth currents were flowing to the north during this survey Line. The wind data from the Bureau of Meteorology at Barrow Island indicate that the prevailing winds were westerly to south-westerly during this survey Line 7. Collectively these data indicate that the north-north-east 'drift' of the hydrocarbon plume is influenced by the combination of both ebb tide and local wind direction.

The contours of hydrographic properties from Line 7 are shown in Figures 8-11. Local temperatures vary between about 23.3 - 23.9 deg. C, and salinity varies between about 35.1-35.5 ppt, with highest values to the west (in shallower water). Dissolved oxygen in the survey area varied between about 195-210 µM (Figure 9). The PFW is discharged into the sea at a temperature of about 70°C, a salinity of 27 ppt (measured by refractometer on the PFW samples provided to the survey vessel), and is probably devoid of oxygen, because of the microbial activity while buried in the sediments. Despite these contrasts between PFW characteristics and the local hydrographic data, the PFW discharge is not evident in any of the measured hydrographic parameters (T, S ppt and dissolved oxygen), and seawater density contours, i.e. the hydrocarbon plumes identified in Figs 5-7 are not apparent in Figs. 8-11.

Hydrocarbon dispersion, spring tides, 3 m, (survey Lines 9, 11 & 12)

The extent of hydrocarbon dispersion during spring tides was surveyed on Lines 9 (September 25; Table 1), and 11 & 12 (September 26 & 27; Table 1). Hydrocarbon data from Line 9 are shown in Figures 12-14, and hydrographic data in Figures 15-18.

The distributions of hydrocarbons from Line 9, conducted on the ebb tide, show that the movement of the PFW plume is north north-westerly, with an accumulation of hydrocarbons concentrated more to the west than the east (Figures 12-14). Hydrocarbon concentrations clearly decrease rapidly to the east and hydrocarbons preferentially accumulate to the west of Harriet A. We suggest that the higher concentrations to the west are remnants of the previous flood tidal drifts and the local bathymetry. Anomalous PFW hydrocarbons were detected to distances of about 10 km north of Harriet A on this tide. Comparison between the plume direction and current meter data show that the PFW discharge is largely controlled by the high current flow conditions of the spring tide and the effect of the prevailing westerly winds are apparently not as significant as during the neap tides.

A jack-up drilling rig was operating at the platform up to and including September 25th when data from Line 9 were collected (Table 1). Non-PFW hydrocarbon components, specifically hexanes and heptanes were noticeable on the chromatograms and these hydrocarbons characterised this 'rig' discharge as distinct from the PFW discharge from Harriet A (Fig. 19). The hexanes and heptanes were recorded at distances up to about 10 km from Harriet A.

The temperature data from Line 9 (Fig. 15) show a range of about 0.5 deg. C over the survey area, and indicate a 'cooler' body of water to the north. A 'tongue' of this cool water appears to penetrate into the vicinity of the Harriet A platform. While there is no pattern evident of a plume in the salinity distributions (Fig. 16), the 'cool' water is also evident in the sigma-t distributions (Figure 18). Higher oxygen levels were observed to the north in the 'cooler' seawater (Figure 17); an observation predicted from the oxygen seawater solubility tables. Although there appears to be no direct

evidence of a PFW discharge in the hydrographic parameters temperature, salinity and dissolved oxygen, probable indirect evidence is discussed below.

Survey Lines 10, 11 and 12 were completed on consecutive days on September 26, 27 and 28th (Table 1), and recorded hydrocarbon dispersion during the flood tide to the south. A sediment trap 'drogue' was deployed by AIMS, on these occasions, to collect a variety of samples and trace the tidal movement. The hydrocarbon data from these survey lines 11 and 12 were combined and these are mapped in Figures 20-22.

The drift of the drogue and the mapping of the hydrocarbon data both indicate a tidal movement in a SSE direction. There is a distinct plume of hydrocarbons evident, although it is not apparently simply dispersed; as suggested by the 'broken' contours of Figures 20-22. PFW hydrocarbons on this Line were evident at distances of more than 10 km to the south. The hydrocarbon contours suggest that the plume trends to the west and is recycled northward (on subsequent ebb tides), along the eastern coast of Varanus Island. Hydrocarbon concentrations were generally observed to decrease rapidly with increasing distance to the east, indicating comparatively little transport toward the mainland. There does not appear to be any evidence of a PFW plume in contours of the hydrographic data including dissolved oxygen (Figures 23-26)

Thus on any tidal (ebb and flood) cycle there is a north-to-south movement of the PFW plume about the platform together with, what appears to be a net westerly dispersion on both the ebb and flood tides toward the Lowendall and Montebello Island Groups, rather than toward the east and the mainland.

The hydrographic parameter of most interest as a tracer of the PFW discharge is temperature (and computed density). The PFW is discharged at 70°C and therefore the a PFW plume might have been expected to show positive temperature anomalies in seawater. These are not evident in any of the contour maps of temperature nor density. However, select data from Line 9, show some interesting observations.

An inspection of hydrocarbon, temperature and sigma-t sections on several transects across the PFW plume on Line 9 show some correlation. In the figure the solid lines

represent the density profiles and the broken lines the temperature profiles. Sections through the plume north of the platform (at latitudes 20° 35.6', 20° 35.2' and 20° 34.0') are shown in Figure 27. The transect at 20° 35.6' was surveyed in both directions ie. west to east and then east to west. Low temperatures correspond with higher sigma-t values (a result expected from the equation of state of seawater at these temperatures), and this temperature 'front' appears to delimit the hydrocarbon anomalies. This is a surprising observation because the PFW is discharged from Harriet at about 70 deg. C - about fifty degrees warmer than surrounding seawater. Each traverse at different latitudes exhibits consistent anomalies in both temperature and sigma-t which coincide closely with the hydrocarbon anomaly. Temperature anomalies of 0.3 to 0.4°C, lower than ambient, and sigma-t anomalies of 0.1 to 0.2 appear to characterise this 'front'; higher hydrocarbon levels consistently appear to the west of the hydrographic 'front' than to the east.

Despite these observations there appears to be no consistent evidence of a well defined plume in both the temperature and sigma-t contours (Figs. 18) as compared to the hydrocarbon plume evident in Figures 12-14. The features noted above are therefore perhaps only local and indirect, and we can only speculate that they may result from (i) evaporative cooling at the edge of the plume or (ii) local 'upwelling' of cooler and somewhat deeper water associated with tidal movement. These features became less distinct with increasing distance to the north from Harriet and were apparently dissipated entirely at distances of about 4 km from the platform. The observations between temperature, sigma-t and hydrocarbons noted above on the ebb tide were not evident on data collected on the flood tide, further suggesting these are local features only.

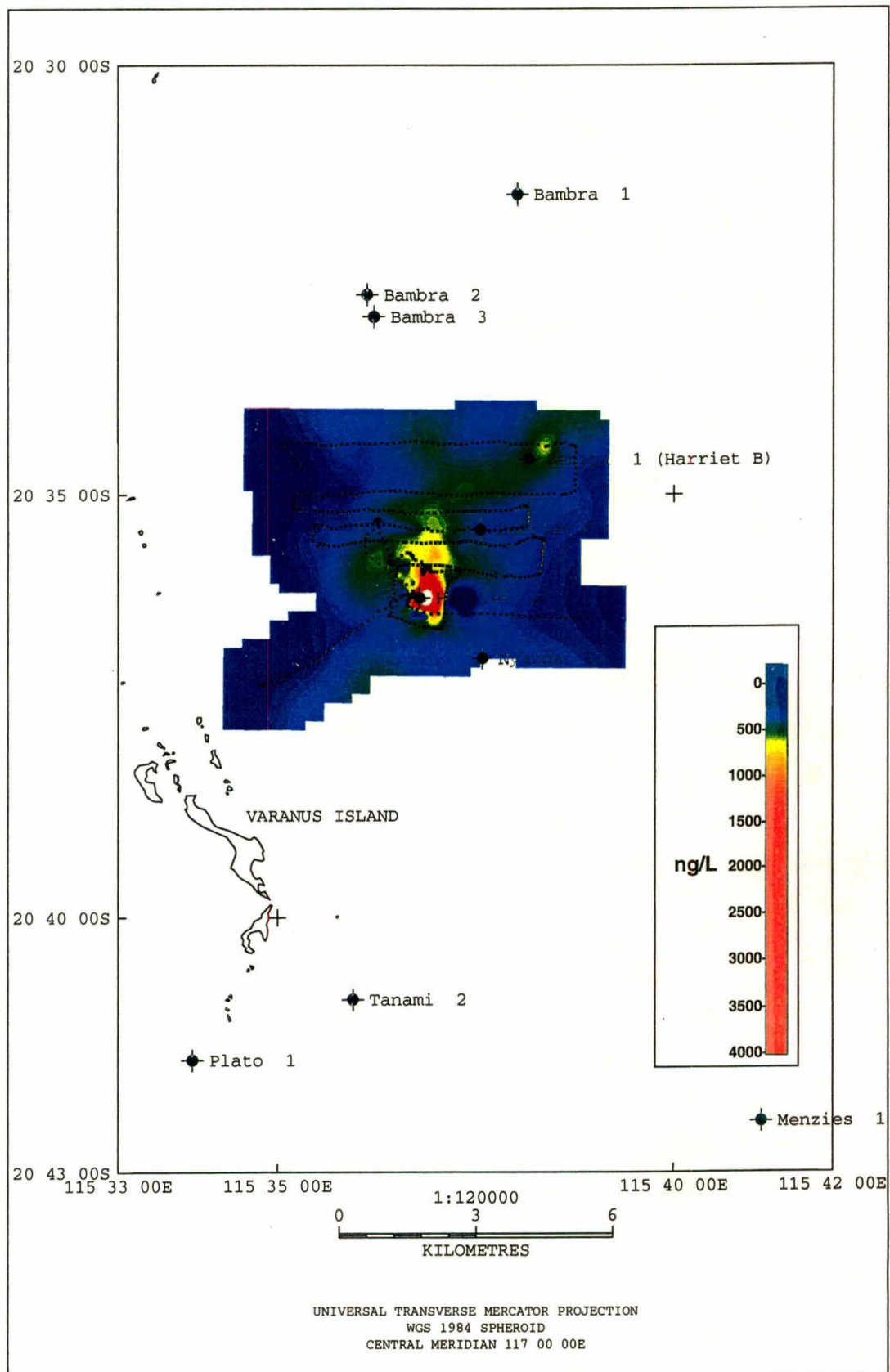


Figure 5. C1 to C6 dispersion contour map; Line 7

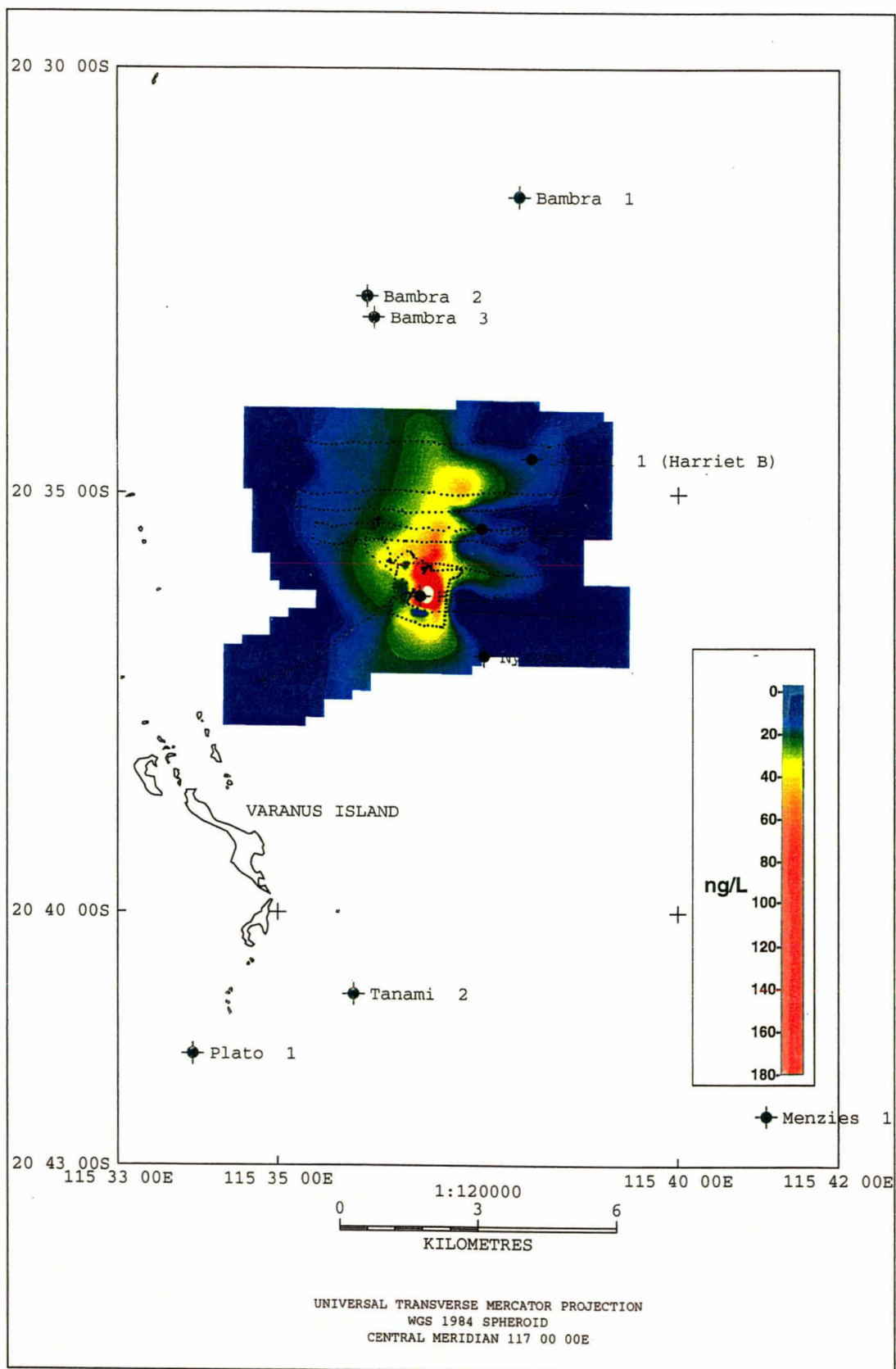


Figure 6. Toluene dispersion contour map; Line 7

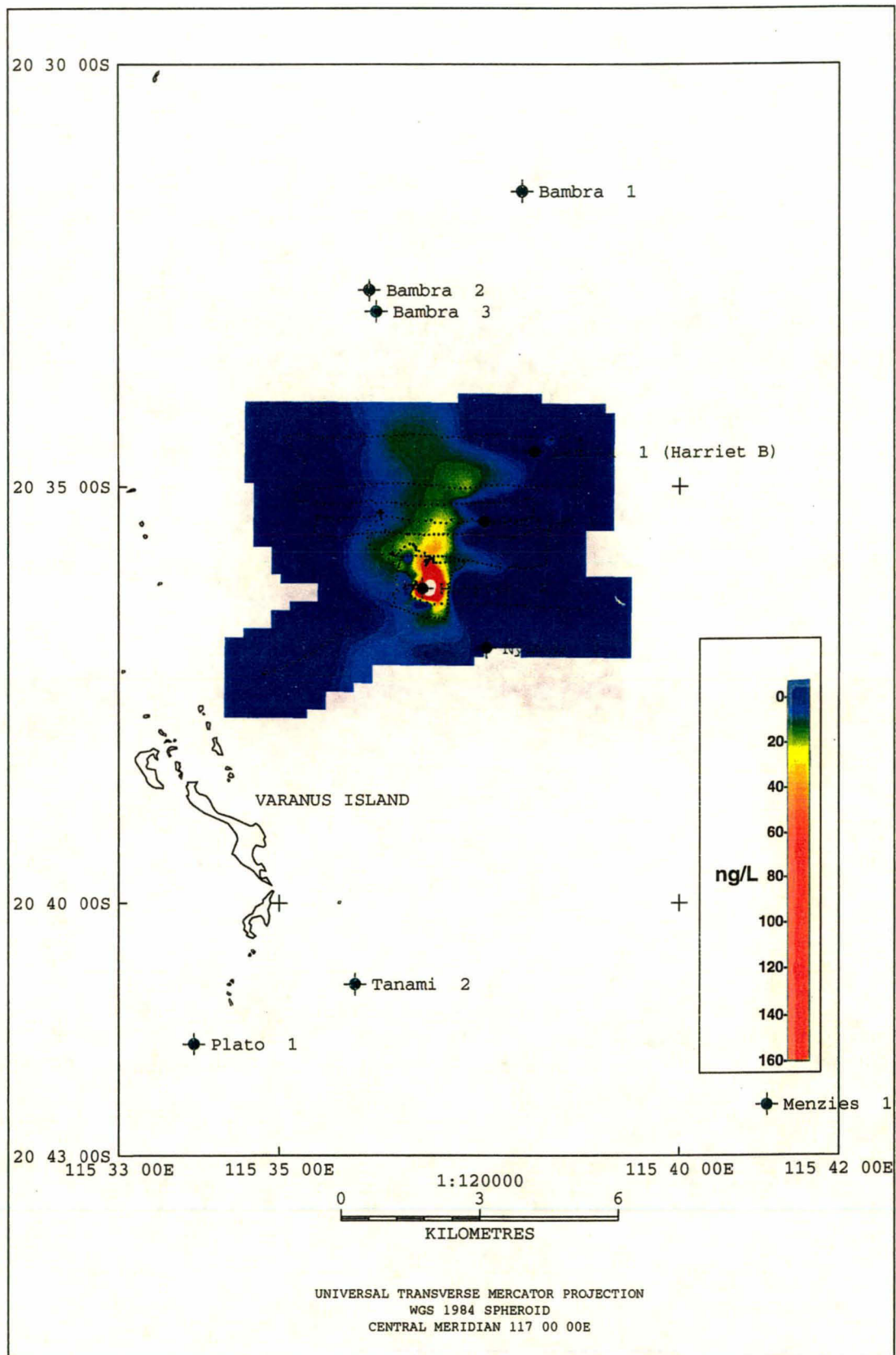


Figure 7. Benzene dispersion contour map; Line 7

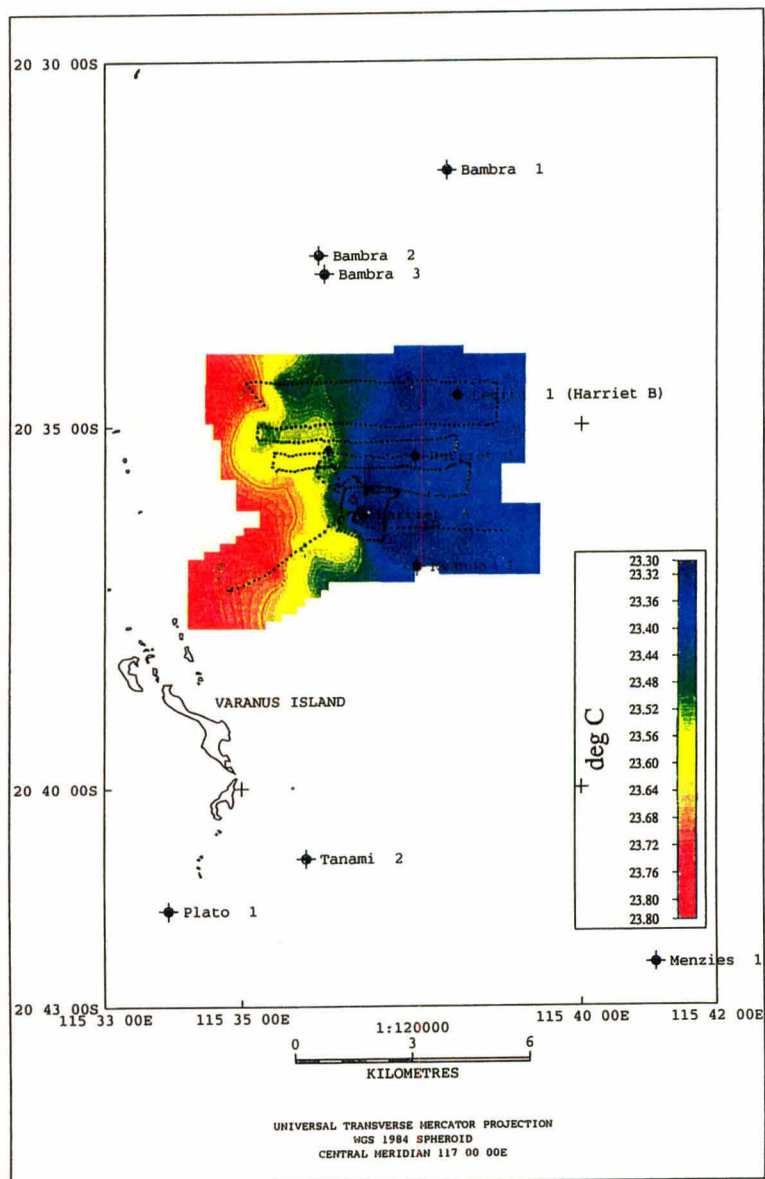


Figure 8. Temperature contour map; Line 7

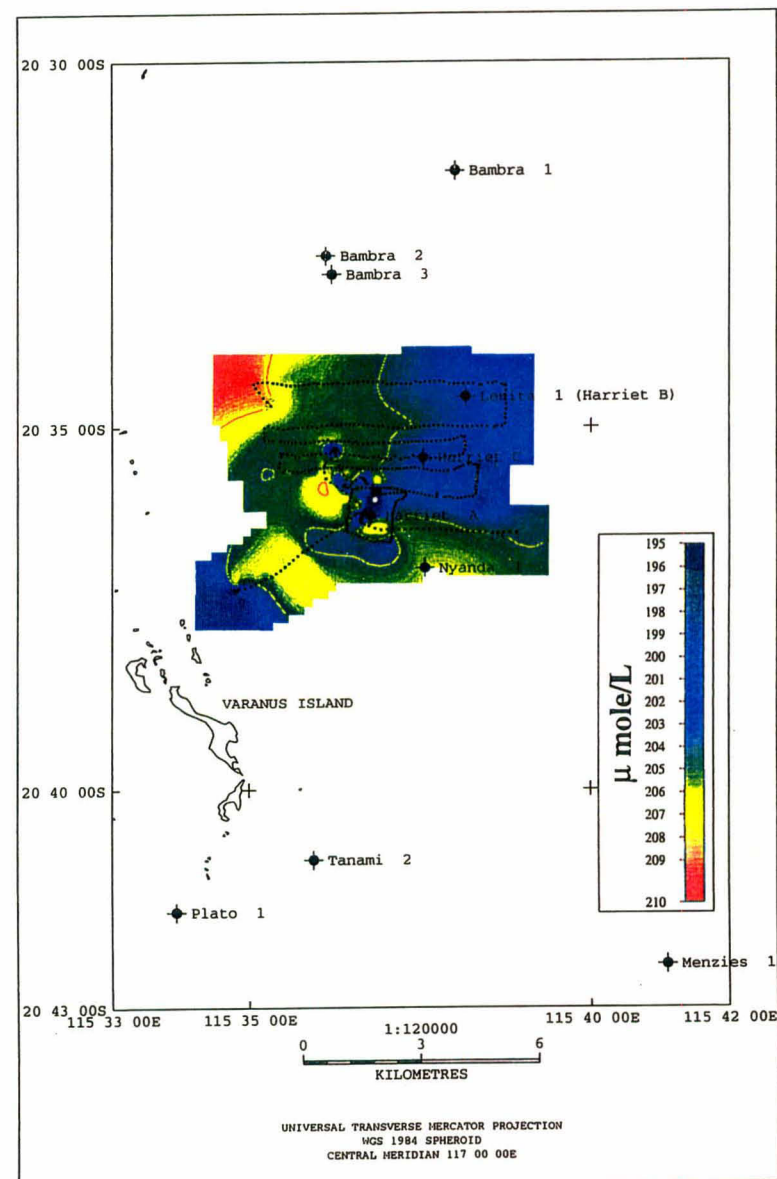


Figure 9. Dissolved Oxygen contour map; Line 7

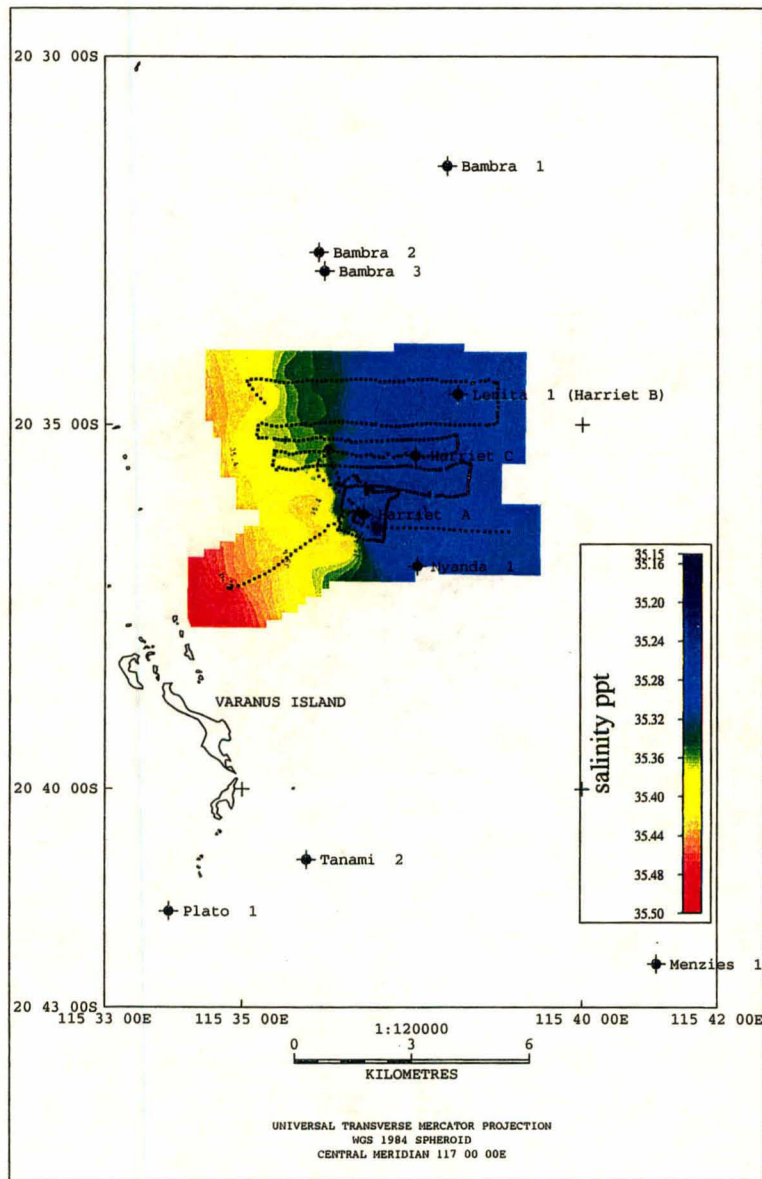


Figure 10. Salinity contour map; Line 7

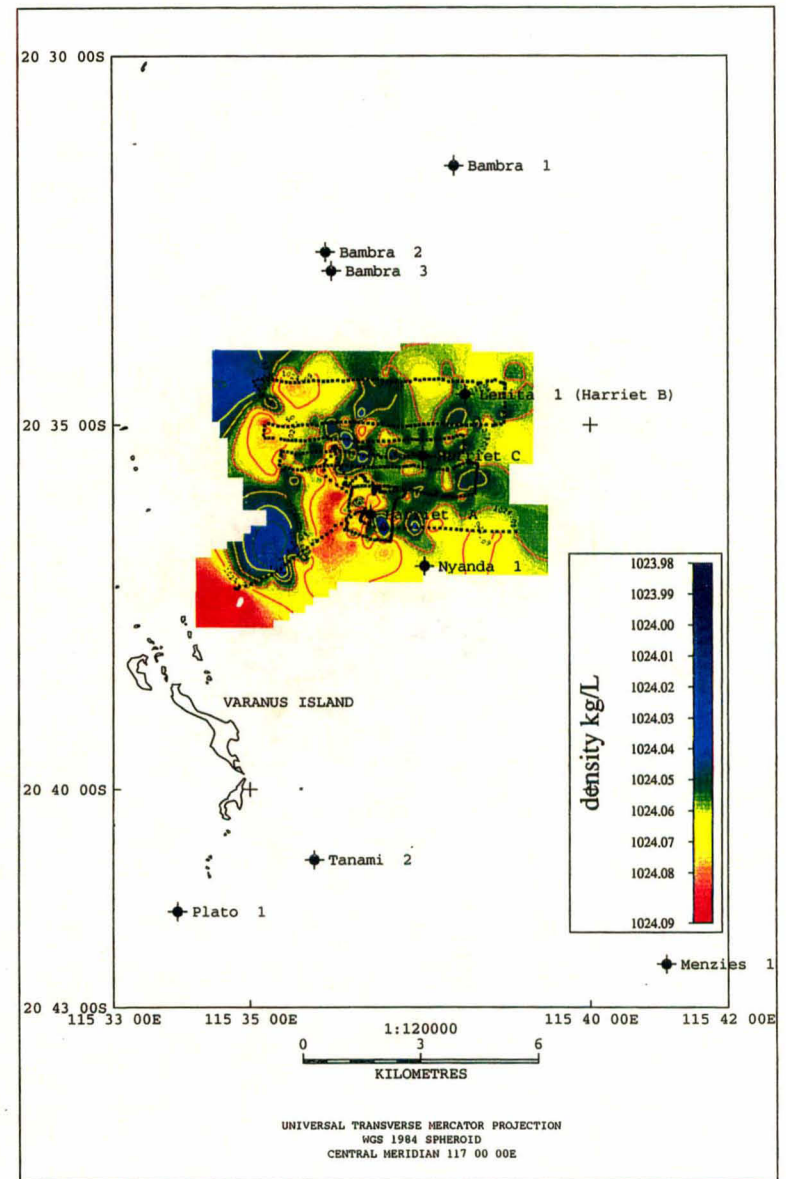


Figure 11. Density contour map; Line 7

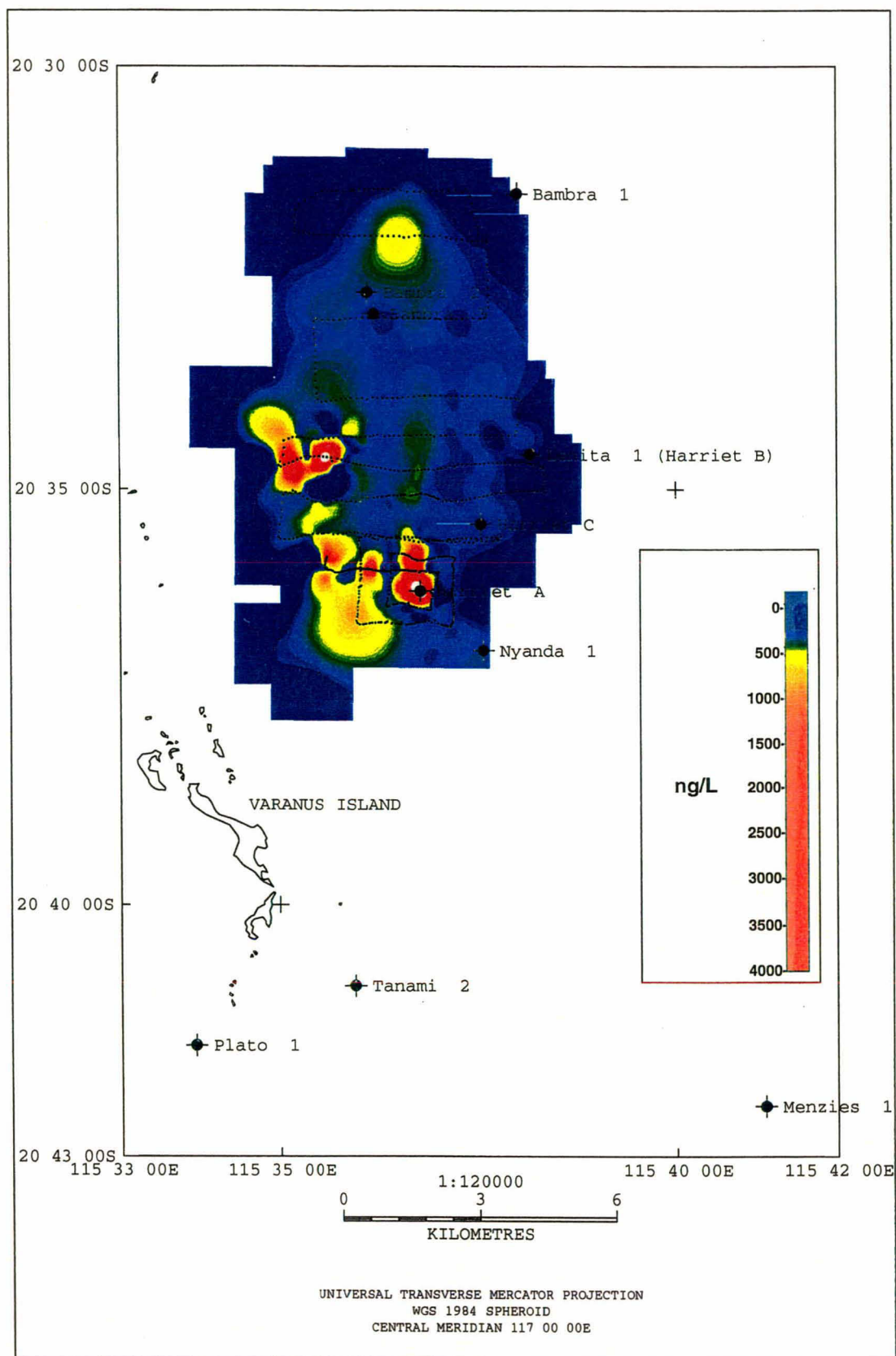


Figure 12. C1 to C6 dispersion contour map; Line 9

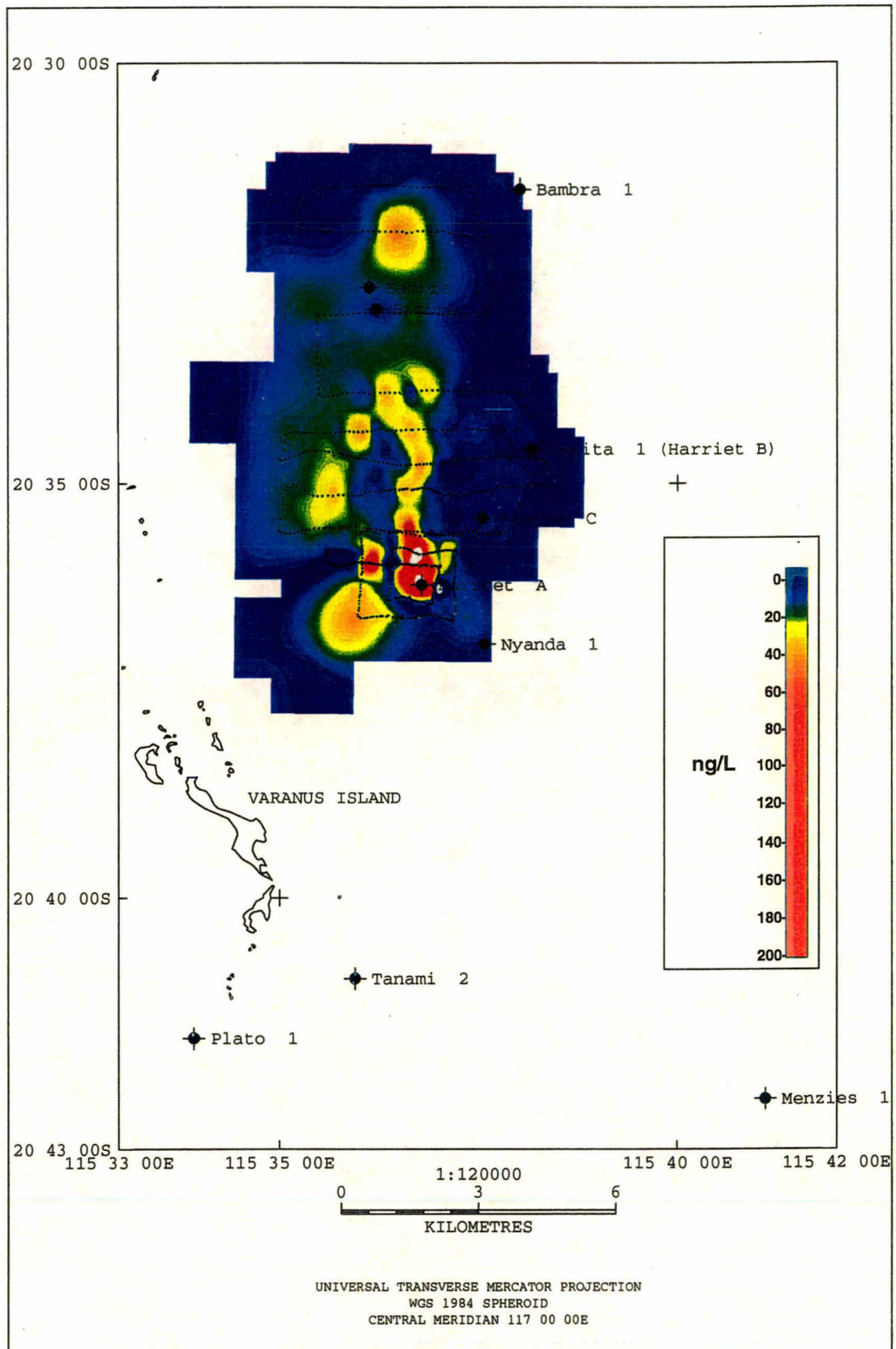


Figure 13. Toluene dispersion contour map; Line 9

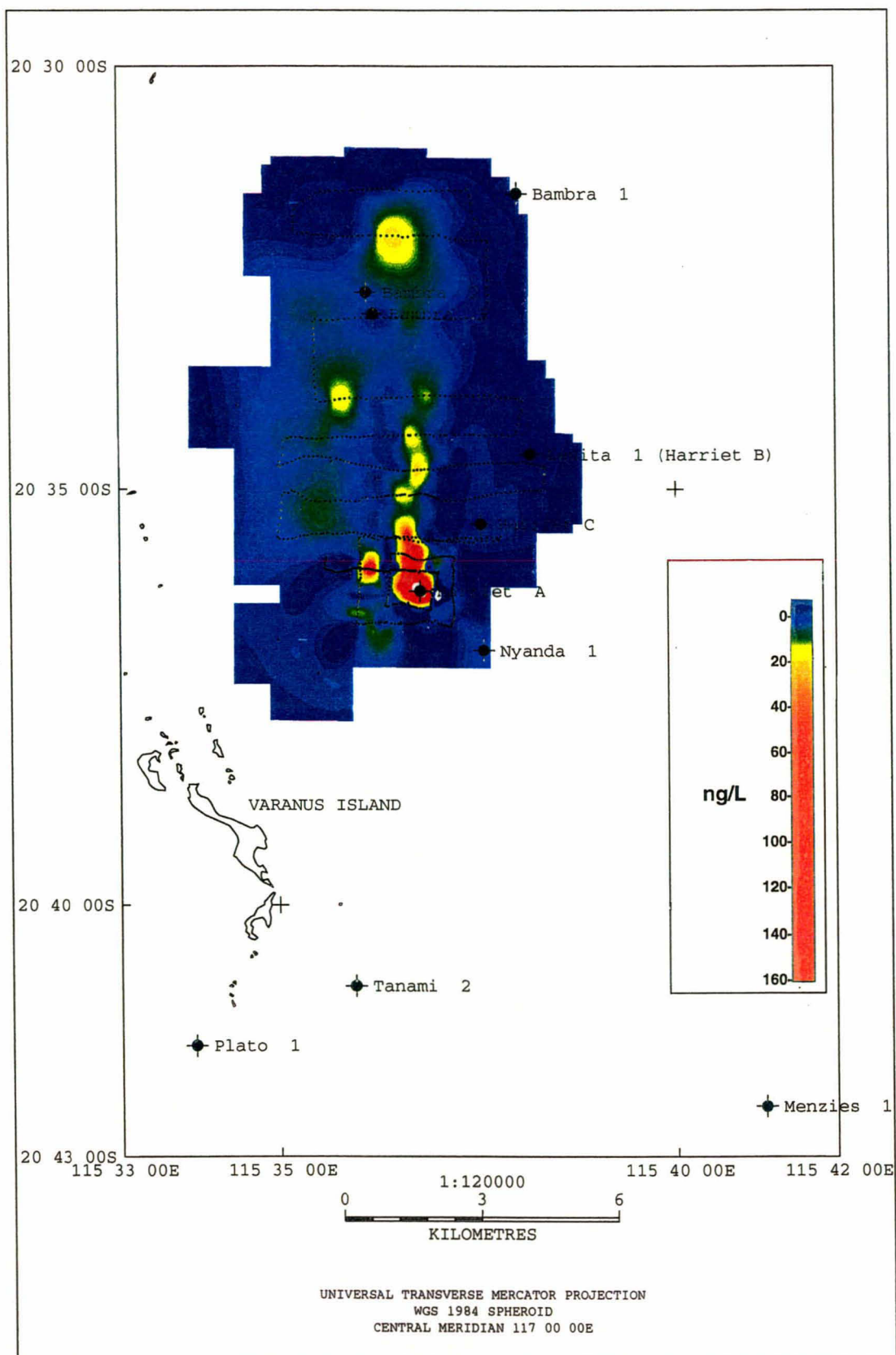


Figure 14. Benzene dispersion contour map; Line 9

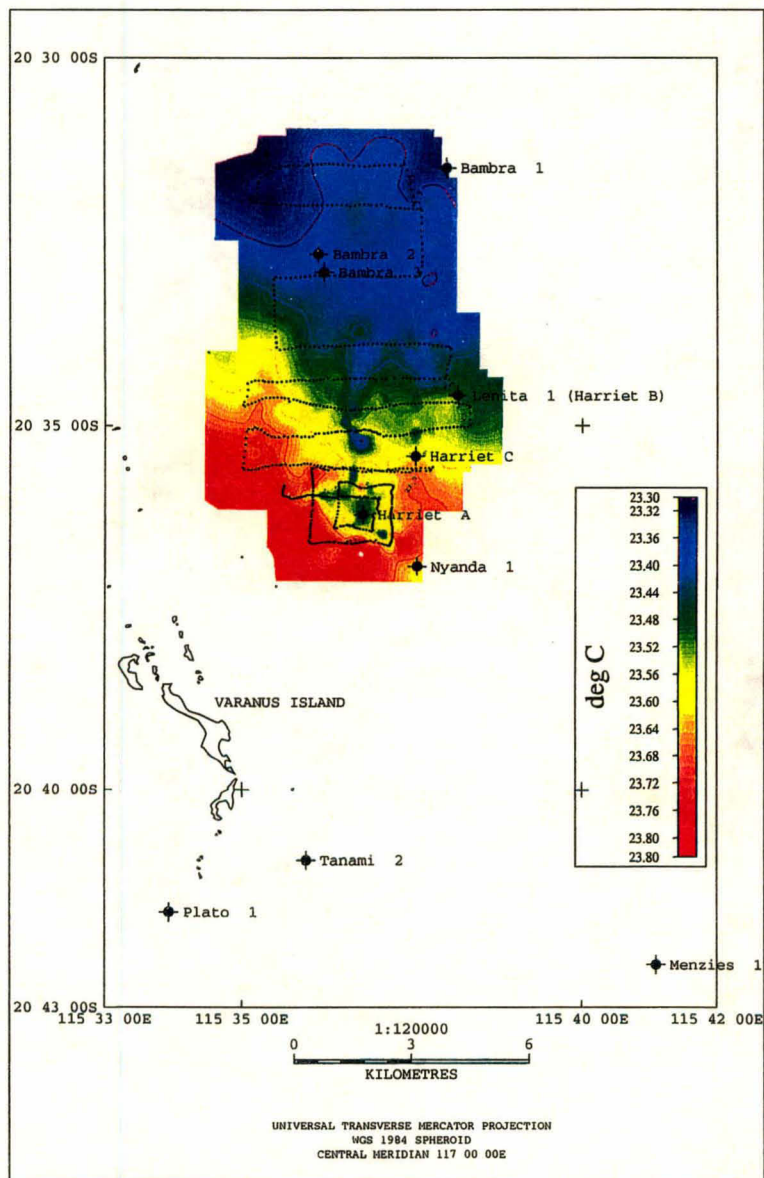


Figure 15. Temperature contour map; Line 9

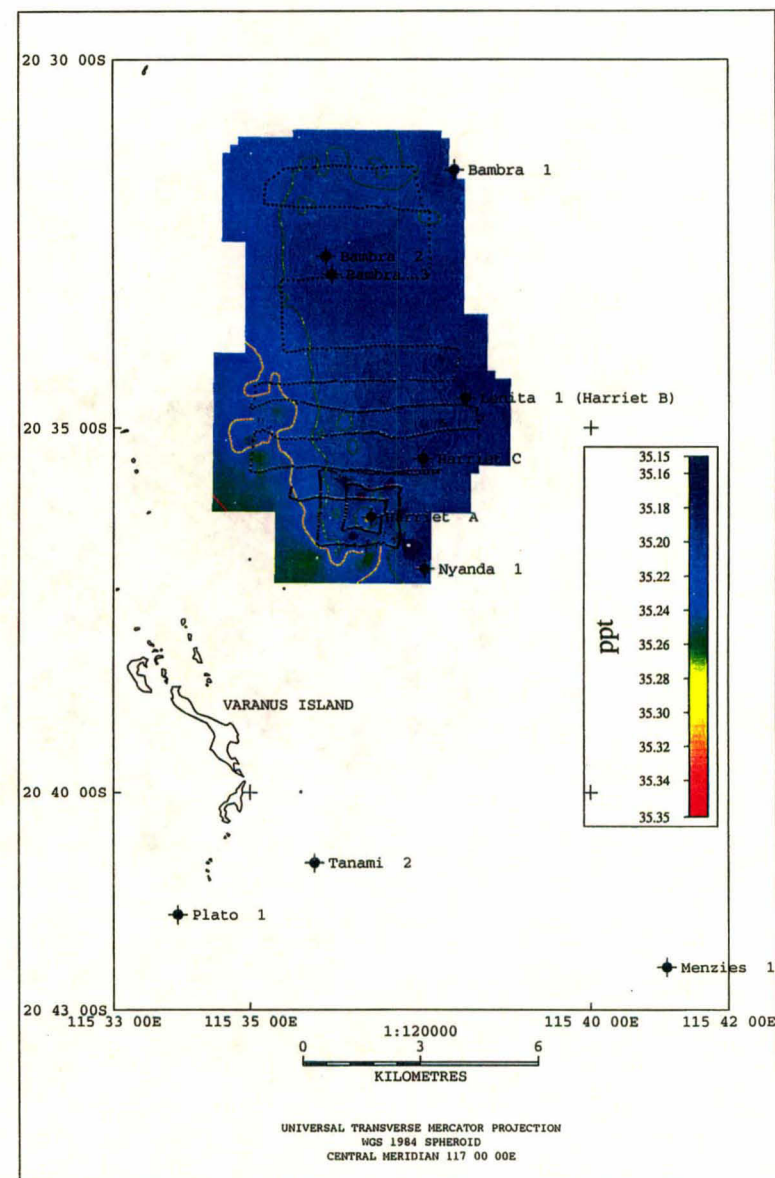


Figure 16. Salinity contour map; Line 9

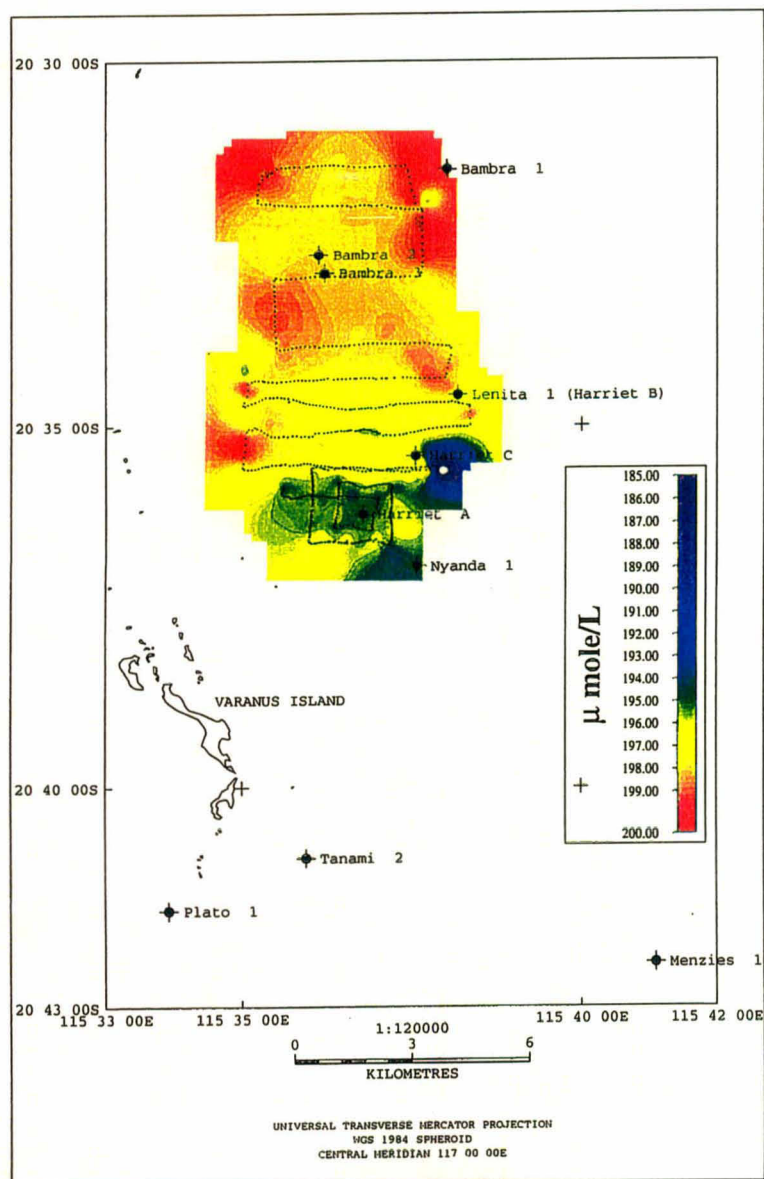


Figure 17. Dissolved oxygen contour map; Line 9

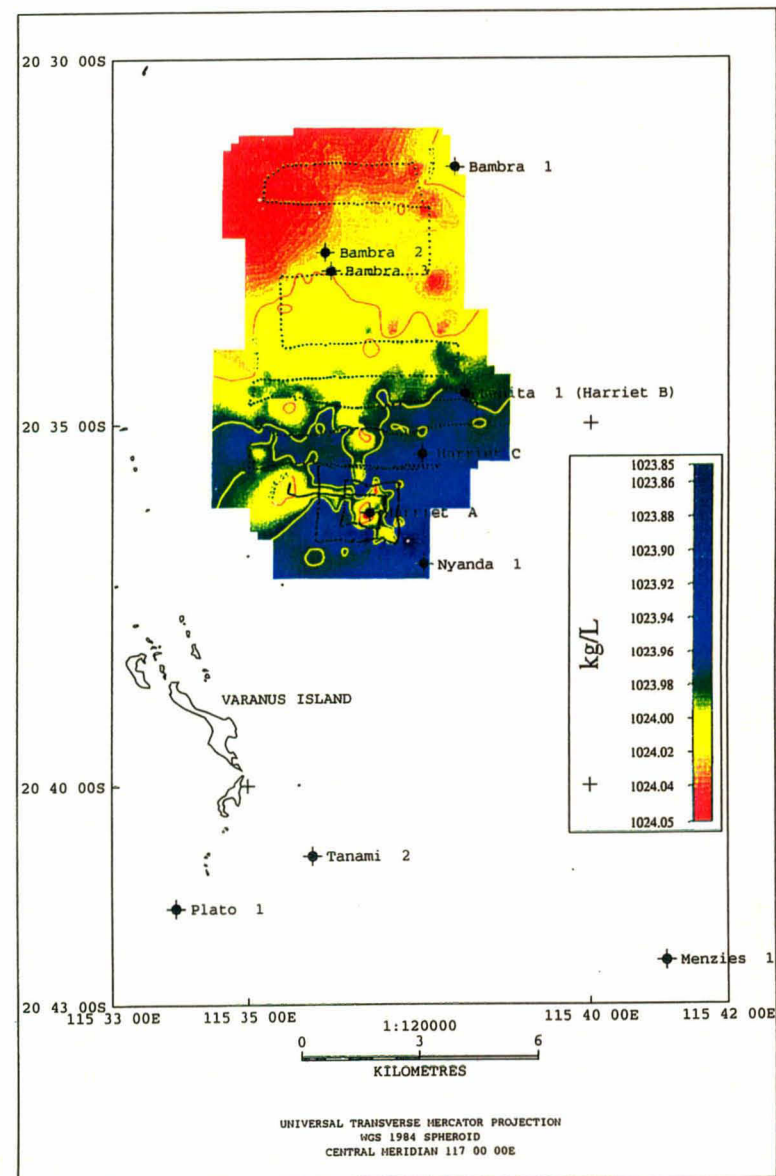


Figure 18. Density contour map; Line 9

Sample Name : Heavy Hydrocarbons1
File Name : A:\DATA\HHC10052.RAW
Method : HHCL.MTH
Start Time : 0.00 min
Scale Factor: 0.0

End Time : 3.80 min
Plot Offset: 0 mV

Sample #: Page 1 of 1
Date : 11/15/95 03:08 PM
Time of Injection: 9/26/95 02:40 PM
Low Point : 0.00 mV High Point : 20.00 mV
Plot Scale: 20.0 mV

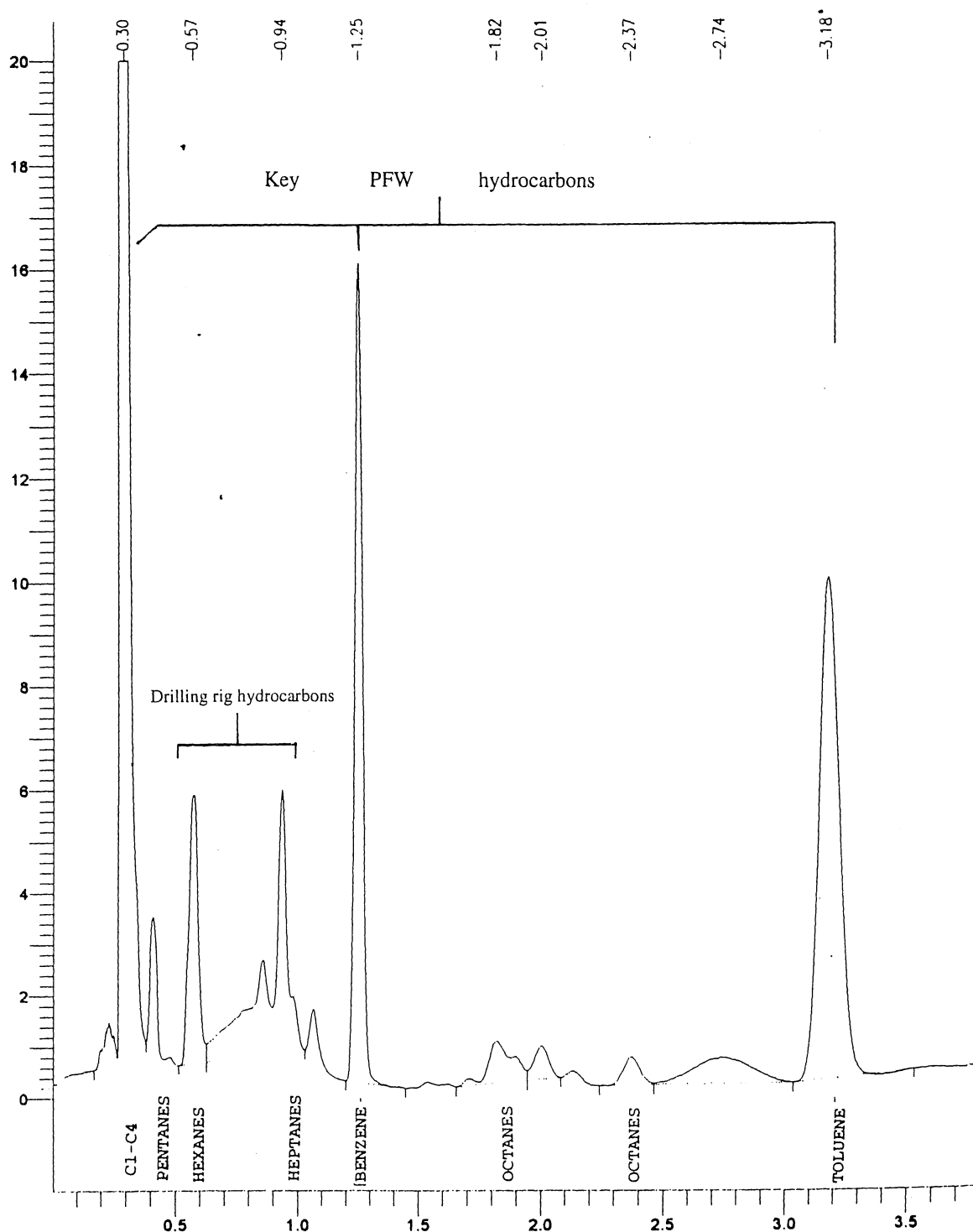


Figure 19. An example of a chromatogram of 'plume' hydrocarbons from both PFW and drilling rig derived sources on the 25.9.95

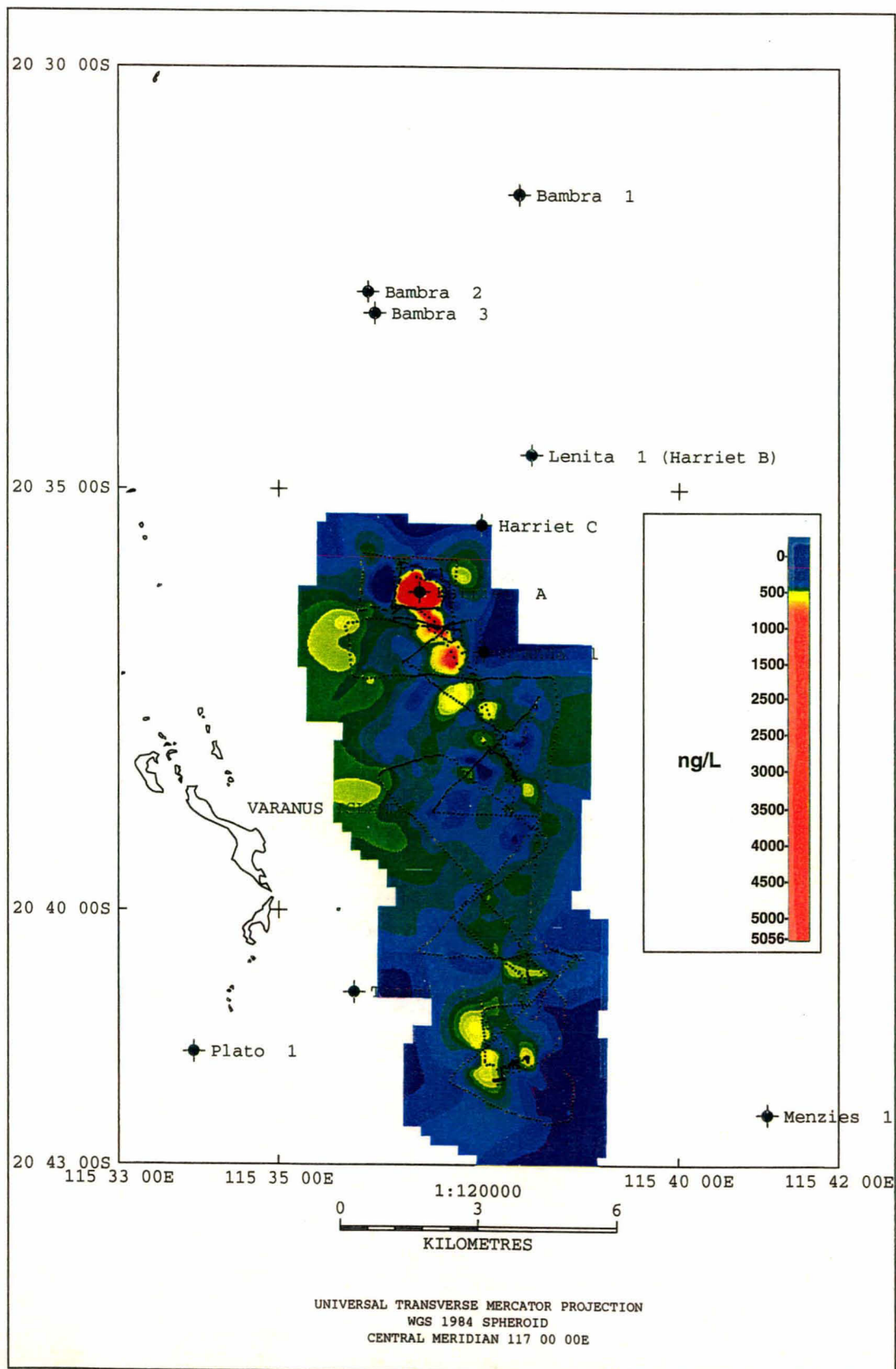


Figure 20. C1 to C6 combined dispersion contour map;
Lines 11 and 12

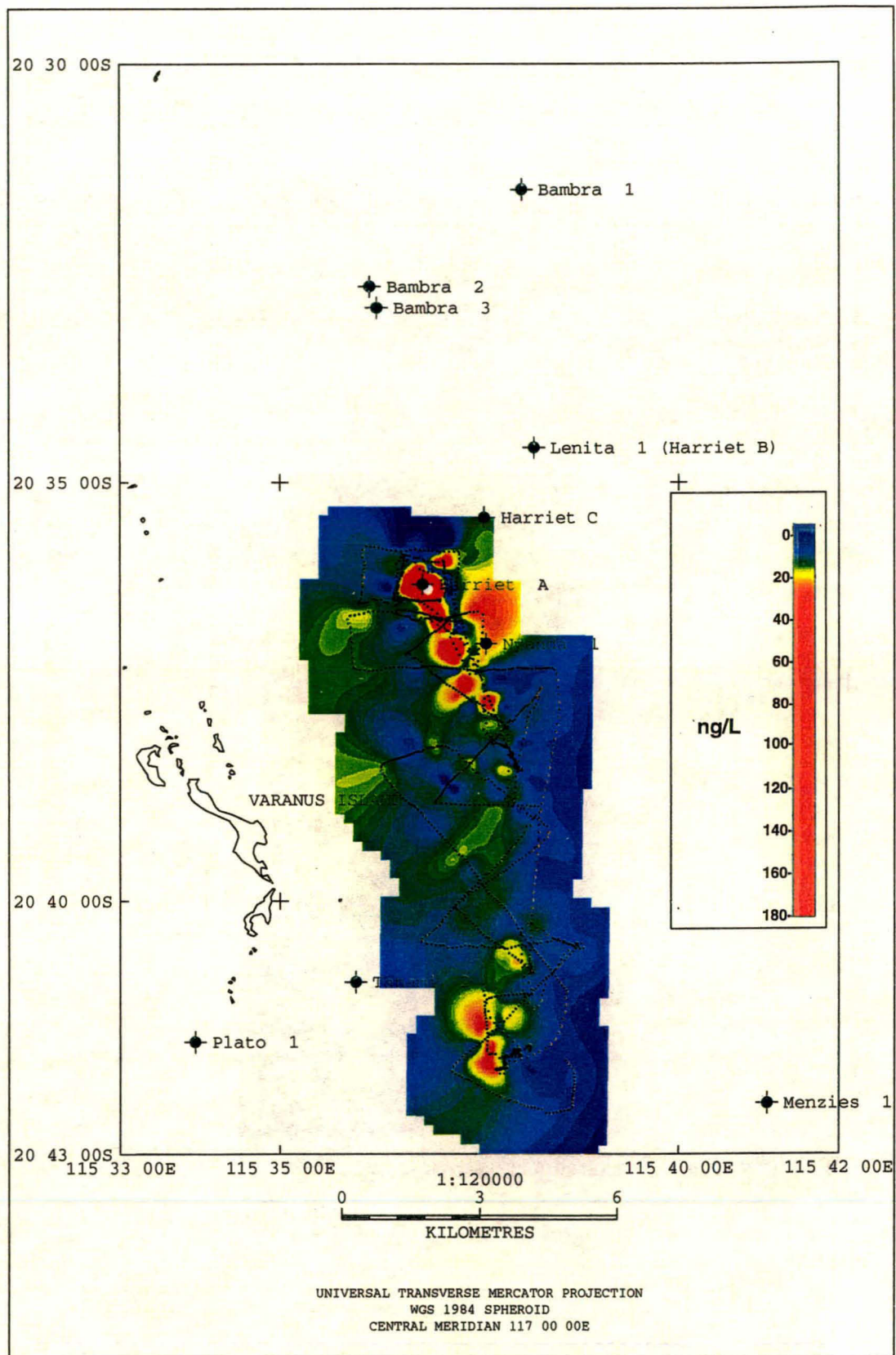


Figure 21. Toluene combined dispersion contour map;
Lines 11 and 12

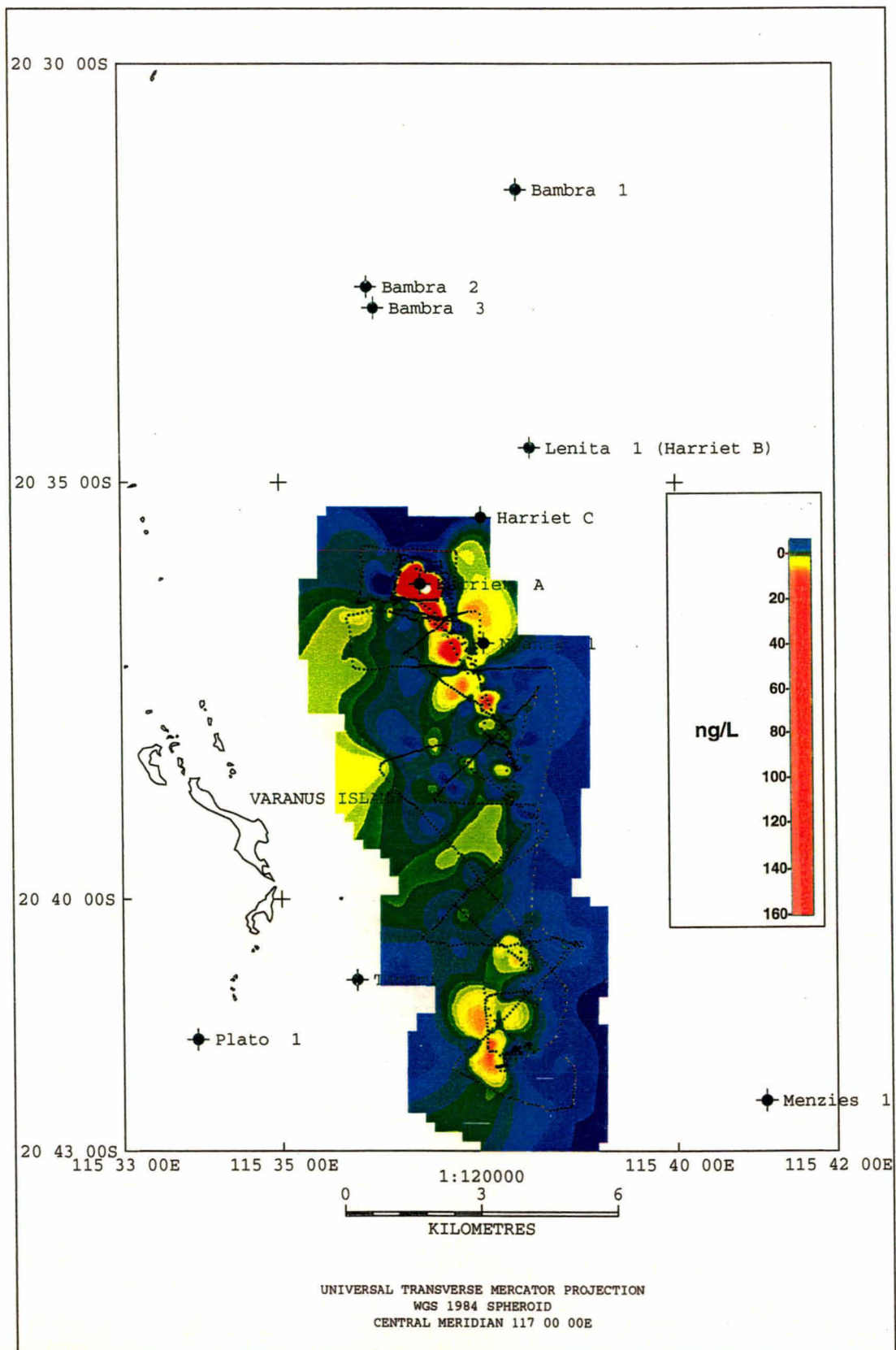


Figure 22. Benzene combined dispersion contour map;
Lines 11 and 12

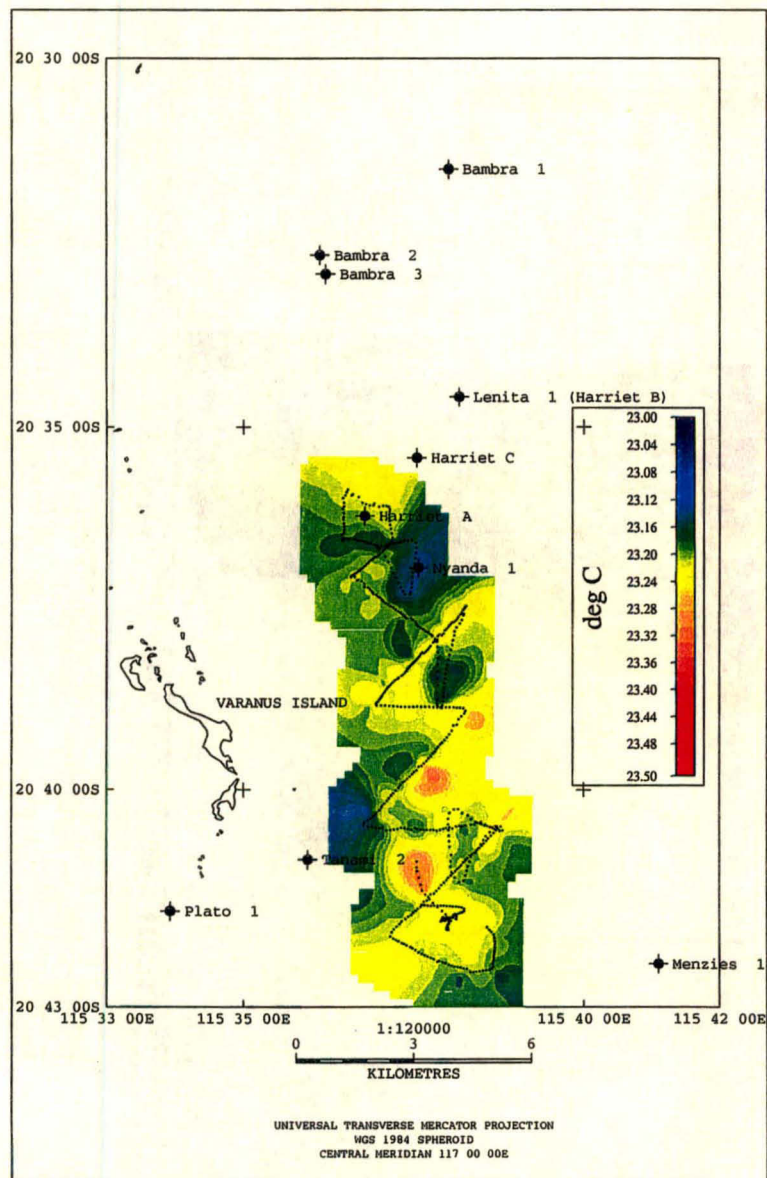


Figure 23. Temperature contour map; Line 12

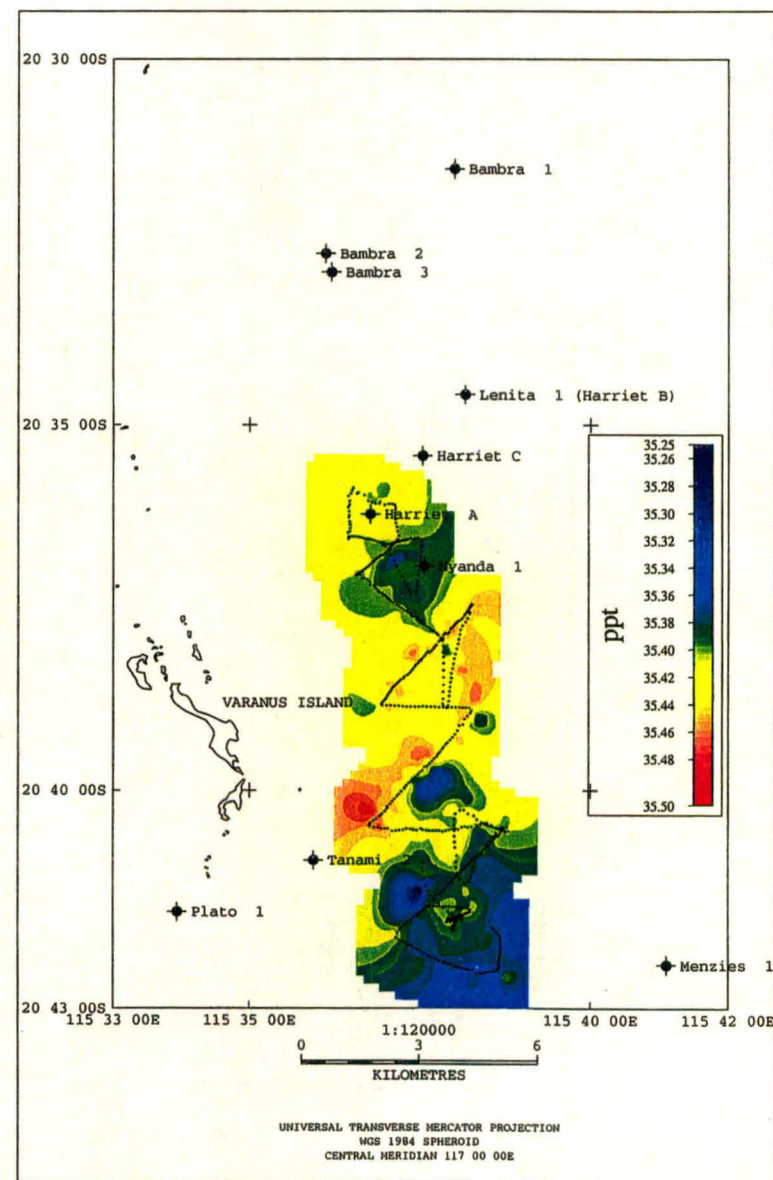


Figure 24. Salinity contour map; Line 12

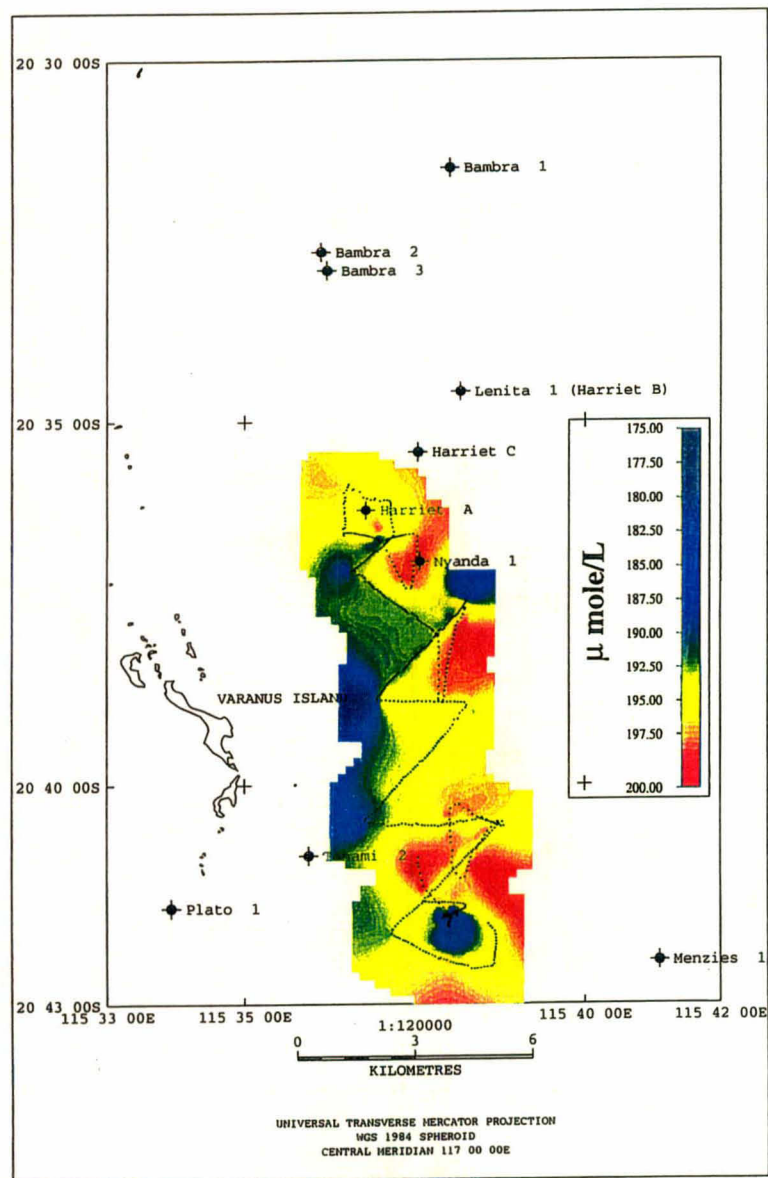


Figure 25. Dissolved Oxygen contour map; Line 12

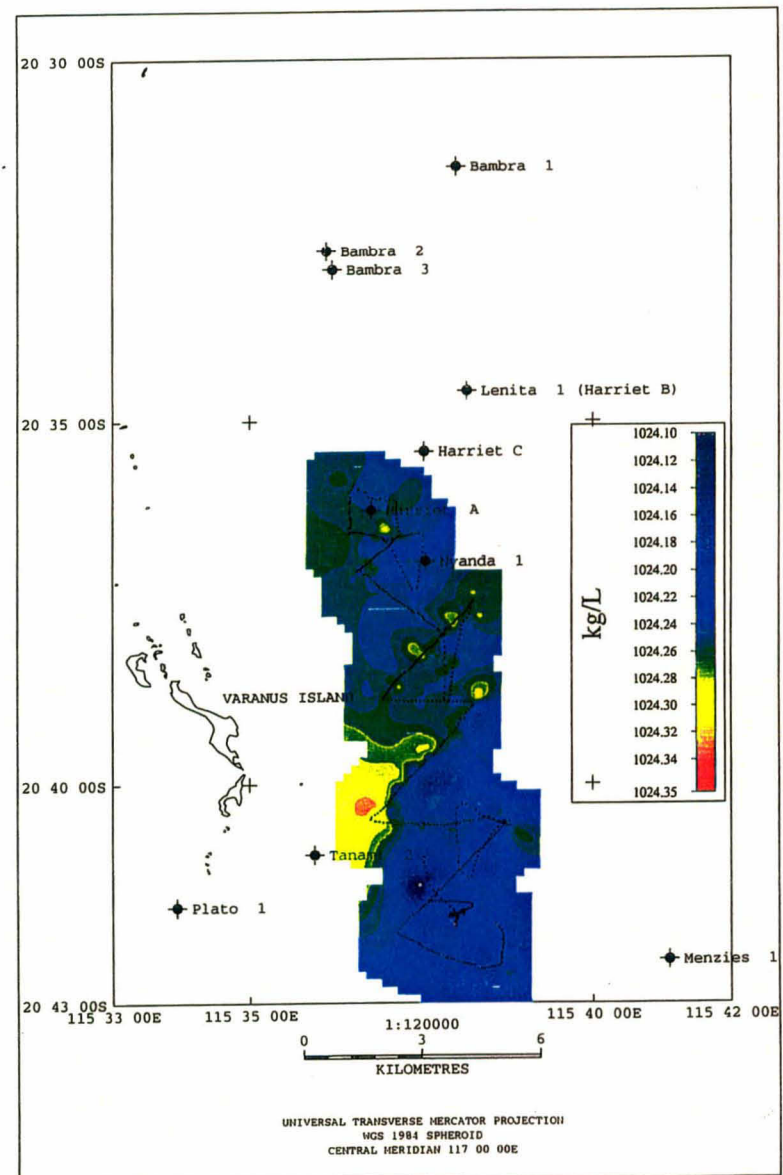
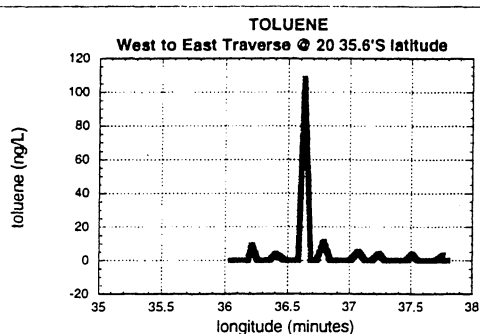
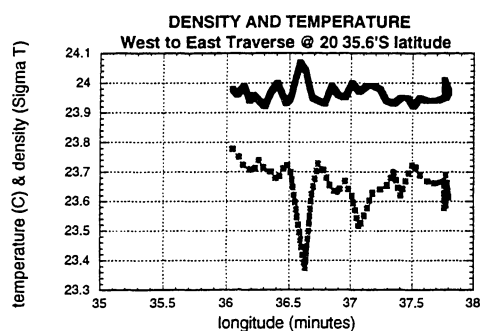


Figure 26. Density contour map; Line 12

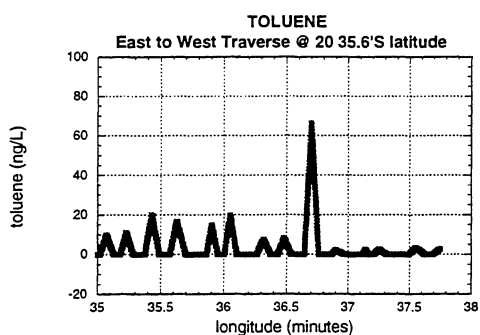


West to East

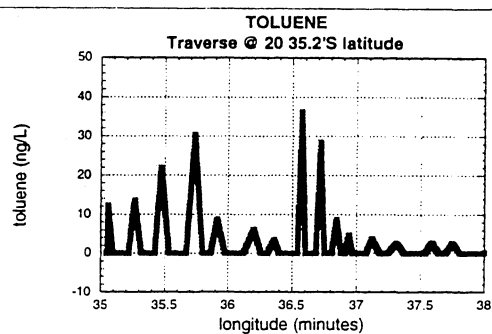
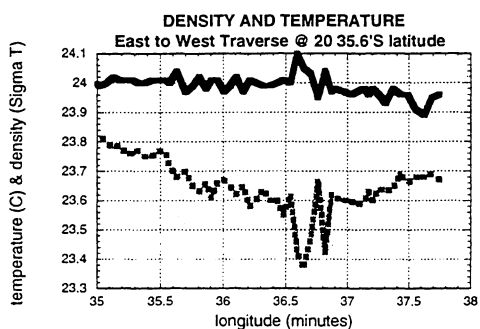


Near traverse

(1 km north of the platform)

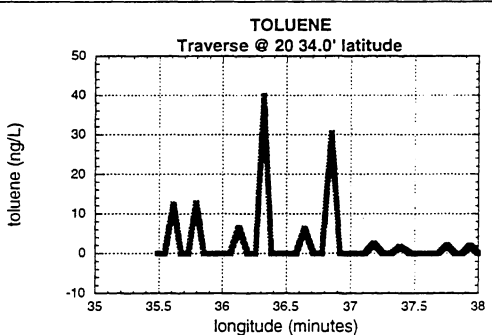
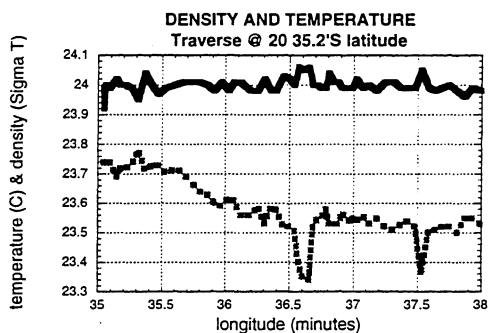


East to West



Intermediate traverse

(2.75 km north of the platform)



Far traverse

(4.25 km north of the platform)

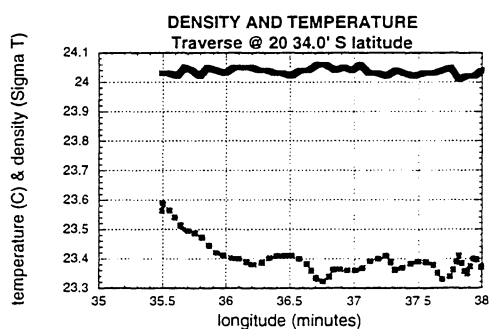


Figure 27. Hydrographic tracers of the plume; anomalous density and temperature profiles across the plume centre-line on Line 9

3. 3 Modelling of plume dispersion

We have used the mapped distributions of hydrocarbon concentrations shown in Figures 5 to 22 to examine other aspects of hydrocarbon dispersion from Harriet A. First, plots of hydrocarbon concentrations versus distance from the platform were constructed for select lines from those noted above, and all showed hydrocarbons decreasing systematically with increasing distance from the platform, although the hydrocarbon/distance relationships were scattered depending upon whether or not the data were collected within the hydrocarbon plume or normal to the plume. By choosing, at each distance, the highest hydrocarbon concentrations as being representative of the plume, a simple model can be developed to examine plume behaviour. This model is described below.

Hydrocarbon concentration-distance data have been fit to a solution of the equation:

$$D[d^2C/dX^2] = -W dC/dX$$

where: D is the diffusion coefficient in seawater, W is the advection, C is the hydrocarbon concentration and X is distance from Harriet A.

For the boundary conditions:

$$C = C_o \text{ at } X=0$$

$$C = C_m \text{ at } X=\infty$$

the solution is: $(C-C_m) = (C_o - C_m) (e^{-[W/D]X})$

Writing W/D as α (the dispersion coefficient), the equation describing hydrocarbon dispersion becomes:

$$(C-C_m) = (C_o - C_m) (e^{-\alpha X})$$

This equation is identical in form to a diffusion/reaction equation described by C. Maris (pers. communication). The term α therefore describes the dispersion

coefficient but does not discriminate if hydrocarbons are dispersed conservatively by diffusion and advection of by an unspecified chemical reaction described by a first order removal rate constant. The mathematical solutions to these two scenarios are equivalent for data described by an asymptotic concentration at an infinite distance from the hydrocarbon source.

The data-fits are shown for survey lines 7, 9, 11 and 12 and the 1994 pilot study in Figure 28. Projection of the concentration/distance plot to $X=0$ (at the platform) predicts a concentration C_0 of hydrocarbon in seawater at the platform. The ratio of PFW/ C_0 therefore is a measure of the initial dilution of the PFW in seawater at the platform. These calculations and the dispersion coefficient α (m^{-1}) are tabulated in Table 5. Values of the dispersion coefficient provide estimates of the distance over which the hydrocarbon concentration decreases by a factor of two, i.e. the characteristic half distance is $0.69/\alpha$. Also shown are model fits for the combined data collected during the 1994 survey.

Throughout the following we compare the data from Line 7 (1.5 m tide) with that from lines 9,11 and 12 (3 m tides). We then compare the 1995 data with that collected during 1994. The characteristic half distance for the combined C_1 - C_6 hydrocarbons collected, during a neap tide, from Line 7 during 1995 was 1568 m. The characteristic half distance for dispersion over the 3 metre tides, for lines 9, 11, 12 for those same compounds is 3285 m. The characteristic half distance for dispersion of benzene from Line 7 is 958 m. Similarly the average half dispersion distance for lines 9, 11 and 12 is 3631 m. The characteristic half dispersion distance for toluene from Line 7 data is 945 m, while that for the average of lines 9,11 and 12 is 3285 m. The results indicate that for a doubling of the tidal range the characteristic half dispersion distances for all compounds measured increases by a factor of about 2-3.7.

When these data are compared to the half dispersion distances estimated from the 1994 survey i.e. methane is 156 m, benzene is 202 m and toluene is 191 m, the results suggest a more dynamic dispersion in 1994 than in 1995. However we note that the data from 1994 are fit only over a narrow range collected comparatively close to the platform at distances < 1.6 km, and as such must be considered an approximation to a

near-field dispersion only. Likewise if data less than 1 km from the platform on Line 7 is separated into a near-field dataset the estimated half dispersion distances begin to approach that of the 1994 survey. It is also clear from the distributions noted in Lines 9, 11 and 12, that hydrocarbons are dispersed to distances of up to 10 km at least, and at these distances there is an apparent concentration of hydrocarbons (note the elevated levels distances beyond 8 km). These data have not been included in the model fits. If they are included then the characteristic half distances are significantly increased although the statistical significance of the data-fit to the model is reduced. This suggests that the model does not adequately describe all data collected but when selected, for example, between 1 km and 8 kms distance from the platform gives a consistent model of the hydrocarbon dispersion. The characteristic half-distances estimated above thus provide a first-order approximation of how these hydrocarbons are dispersed in this area. The elevated concentrations beyond 8 kilometres although not included in our model are a consistent feature thought to be due to 'ponding' of the PFW discharge on the turn of the tide at the platform discharge outlet, and therefore related to the oscillatory nature of tidal flow.

Overall these findings suggest that the 'far-field' (distances beyond about 1 km) hydrocarbon concentrations decrease by a factor of two - depending on the tide - every 1.5 to 3.5 km for both total hydrocarbons and benzene and toluene. The 'near-field' (distances less than about 1 km) concentrations however show that benzene and toluene appear to be somewhat more reactive than the total C₁-C₆ hydrocarbons. Despite the uncertainties in the model fits, this type of analysis does provide empirical estimates of distances over which hydrocarbon levels are halved, estimates of which were not available prior to this study.

The model-estimating dilution values for the various hydrocarbons are shown in Table 5. These results were calculated by extrapolating the curve-fit of the data from each of the survey lines back to the origin, i.e. the platform. Values of PFW/Co shown in Table 5 vary between about 2500 and 8000 for total hydrocarbons on the 1.5 and 3 m tides respectively. Predicted dilutions for benzene and toluene are similarly greater on the 3 m tides than on the 1.5 m tides and these are of the order of 10,000 - 20,000 and more than 30,000 and 150,000 respectively. Thus the result confirms that both toluene

and benzene are preferentially removed from seawater relative to the total hydrocarbons close to the platform and provides quantitative estimates of initial dilution.

Another way of examining the comparative reactivities of the total hydrocarbons, benzene and toluene is to prepare cross-plots of all data from the survey lines and compare the results to the ratio of concentrations of these same compounds in the PFW. These plots are shown in Figure 29(a-d). The solid and broken 'PFW' trend lines on the figures represent the initial C_1 - C_6 to toluene ratio and C_1 - C_6 to benzene ratio of the PFW, at the platform respectively. Data from all lines show that both benzene and toluene concentrations in the samples collected in sea water are lower than predicted from the PFW concentrations and the benzene and toluene/total hydrocarbon ratios in PFW. Figure 29(e) is a plot of the benzene and toluene/total hydrocarbon ratios and total hydrocarbons for data from Line 7. Knowing that total hydrocarbon concentrations decrease with increasing distance away from the platform, the total hydrocarbon axis therefore is a proxy for distance away from the platform. The plot indicates that benzene and toluene total hydrocarbon ratios decrease with decreasing total hydrocarbon concentrations (or distance away from the platform). These results again illustrates that benzene and toluene are preferentially removed from seawater compared to the total hydrocarbons.

Table 5 Exponential curve parameters α and Co and dilution coefficients (PFW/Co) for survey lines 7, 9, 11 and 12.

| Compound | α | R (correlation coefficient) | Co (ng/L) | PFW (mg/L) | Dilution (PFW/Co) |
|-------------------------------|----------------------|-----------------------------------|--------------|---------------|----------------------|
| Line 7 | | | | | |
| C ₁₋₆ | 4.4×10^{-4} | 0.81 | 1511 | 3.75 | 2480 |
| Benzene | 7.2×10^{-4} | 0.83 | 99 | 1.59 | 16060 |
| Toluene | 7.3×10^{-4} | 0.83 | 191 | 1.72 | 9000 |
| Line 9 | | | | | |
| C ₁₋₆ | 2.1×10^{-4} | 0.92 | 469 | 3.75 | 8020 |
| Benzene | 2.6×10^{-4} | 0.99 | 46 | 1.59 | 34510 |
| Toluene | 3.2×10^{-4} | 0.95 | 113 | 1.72 | 15260 |
| Line 11 | | | | | |
| C ₁₋₆ | 2.4×10^{-4} | 0.95 | 500 | 3.75 | 2480 |
| Benzene | 1.1×10^{-4} | 0.87 | 11 | 1.59 | 144500 |
| Toluene | 1.3×10^{-4} | 0.90 | 25 | 1.72 | 68800 |
| Line 12 | | | | | |
| C ₁₋₆ | 1.9×10^{-4} | 0.96 | 471 | 3.75 | 7960 |
| Benzene | 2.0×10^{-4} | 0.99 | 14 | 1.59 | 113570 |
| Toluene | 1.9×10^{-4} | 0.97 | 29 | 1.72 | 59300 |
| 1994 composite dataset | | | | | |
| Methane | 4.4×10^{-3} | 0.99 | 17534 | 1.17 | 66 |
| Benzene | 3.4×10^{-3} | 0.99 | 1610 | 2.55 | 1580 |
| Toluene | 3.6×10^{-3} | 0.99 | 3799 | 2.67 | 700 |

Additional Modelling

The PFW discharge data supplied by Apache and the PFW chemical analysis conducted by AIMS and AGSO, together with hydrographic and meteorological information gathered during the survey period, have been examined by AIMS with an advanced computer based dispersion model called MUDMAP. The algorithms and methodology used by MUDMAP build on formulation by Koh and Chang, (1973) and extended by Brandsma and Sauer, (1983) in the Offshore Operators Committee (OOC) model for convective descent and dynamic collapse of plume motion. MUDMAP has been integrated into an environmental management system called OILMAP, which incorporates OILTRAK, a fully three dimensional hydrodynamic

modelling system that allows high resolution current modelling. This work is covered in detail by AIMS (King and McAllister, 1996).

3.4 Vertical Profiles

Four vertical hydrocarbon profiles were completed during the field work. The locations are shown in Figure 1 and recorded below;

VP 1 was located at 20° 36.1 S / 115° 36.5 E (400-560 metres NW of the platform);

VP 2 at 20° 35.7 S / 115° 36.6 E (1040-1180 metres NNW);

VP 3 at 20° 37.0 S / 115° 37.4 E (1830-1920 metres SE); and

VP 4 at 20° 36.6 S / 115° 37.0 E (700- 825 metres SSE of the platform).

Total C₁-C₆ hydrocarbons, benzene and toluene concentrations were determined at several depths, ranging from 2 metres to a maximum depth of 24 metres. Data from VP 1 were collected only during the downcast, while data from all other profiles were collected first on the downcast and then repeated as the instrument was returned from the seafloor to the surface. Approximately 1 hour elapsed during the VP's. The ship was not anchored during the VP data collections and the positions noted are nominal; the vessel moving approximately 100 metres from the reported position during the occupation of a VP station. All vertical distributions of hydrocarbons are shown in Figure 30. The average concentration is plotted, and a horizontal bar shows the range of concentrations measured during deployment and retrieval of the tow-fish.

The VP 1 (480 metres north of Harriet on the ebb tide) results show high concentrations on the surface; C₁-C₆ levels were in excess of 600 ng/L (28 nM); benzene 25 ng/L (0.32 nM) and toluene 45 ng/L (0.49 nM). Concentrations rapidly decrease with increasing water depth to values of 260 ng/L (12 nM), 4 ng/L (0.05 nM) and 10 ng/L (0.11 nM) respectively for total hydrocarbons, benzene and toluene (ie. near background levels) near the seafloor.

The VP 2 profile (1110 metres to the north on the ebb tide) shows less depth-variation, with hydrocarbon values increasing from the surface to depths of about 8 m, and then remaining constant to the seafloor, with concentrations clearly above background levels. The hydrocarbon concentrations in VP 2 at depth are about twofold those levels measured at VP 1 nearer the platform.

The VP 3 (1880 metres SE of Harriet), results indicate nearly constant hydrocarbon levels at all depths in the water column, and as noted for VP 2, concentrations at depth are significantly above detectable 'background' levels.

The VP 4 profile (760 metres SSE of Harriet) shows high levels of all hydrocarbons in surface waters which systematically decrease with increasing depth to the seafloor. The hydrocarbon concentrations near the seafloor are near detectable 'background' limits and similar to those measured in VP 1. The concentrations measured during retrieval of the tow-fish were significantly lower at the surface; a result which indicates the plume of PFW has moved relative to the ship as the tide has changed direction.

A comparison of all VP data suggest that at distances of less than about 1 km from the platform, there is a distinct surface plume. At distances greater than about 1 km, the various hydrocarbons are apparently mixed vertically throughout the water column as the significant concentration gradients in surface waters, noted closer to the platform, disappear.

Hydrocarbon data from the VP's are plotted in Figure 31 (a)-(d) and show consistent ratios of total hydrocarbons to benzene and toluene at different depths, suggesting little detectable fractionation between these hydrocarbons as they are mixed vertically throughout the water column. Figure 31(e) is a cross-plot of benzene / total light hydrocarbons and toluene / total light hydrocarbon ratios against total light hydrocarbons (C_1 - C_6). As for the surface data of Figure 29(e), these data show decreasing benzene and toluene to C_1 - C_6 hydrocarbon ratios with increasing distance away from the platform. Thus benzene and toluene are apparently removed from

seawater more rapidly than total C₁-C₆ hydrocarbons near the platform, and are thus more reactive than the saturated hydrocarbons.

3.5 PFW Analyses

PFW samples gathered from Harriet 'A' on the 20.9.95 and 29.9.95 were analysed using the CGT equipment. There were two purposes for these analyses. Firstly, to determine the PFW hydrocarbon concentrations at the point of discharge by conducting headspace measurements as described in the field methods. Secondly, to determine hydrocarbon partition coefficients and allow conversion of concentrations measured with the CGT gas extractors to seawater concentrations, from a knowledge of the partition coefficients and the total dissolved gas load in seawater.

Two headspace extractions were conducted for each sample of PFW collected. These are noted in Table 6. From these results the highest values for P - the partitioning coefficient - for each hydrocarbon have been selected on the basis that the gas extractor (which works under a vacuum) is likely to be at least as efficient as the highest calculated coefficient. For each determination, the agreement between partition coefficients calculated from each sample was consistent and values of the partition coefficient (P) were chosen as; total hydrocarbons P=0.94; benzene, P=0.70 and toluene, P=0.71. A description of Harriet 'A' PFW is tabulated below (Table 6.) using both AGSO and NIWA derived data and information supplied by the oil field operator. (Apache Energy Report, 1996).

Table 6. Harriet Alpha treated produced formation water discharge parameters derived from survey data and Apache Energy records

| Parameter | PFW 1994 | PFW 1995 | | | | Background Seawater |
|--------------------------------------|----------------------------|----------------------------|---------------|----------------|-----------------|----------------------------|
| | | Sample 1 | Sample 2 | Average | | |
| <u>Sample 1</u> | | | | | | |
| C ₁ -C ₆ (sum) | | 2.50 116962 | 5.00 33644 | 3.75 175327 | mg/L nmole/L | < 200 ng/L < 10 nm/L |
| Methane | 1.18 mg/L 73687 nmole/L | | | | | <100 ng/L < 5 nm/L |
| Benzene | 2.55 mg/L 32679 nmole/L | 1.14 14564 | 2.04 26141 | 1.59 20354 | mg/L nmole/L | < 0.75 ng/L < 0.01 nm/L |
| Toluene | 2.67 mg/L 28978 nmole/L | 1.37 14847 | 2.08 22630 | 1.72 18740 | mg/L nmole/L | < 1.5 ng/L < 0.02 nm/L |
| DIC | 154.92 mg/Kg | 160.35 mg/Kg | | | | 23.5 mg/Kg |
| $\delta^{13}\text{C}$ in DIC | -3.11 ppt | -4.39 ppt | | | | 0.8 ppt |
| ^{14}C in DIC | 0.94 pMC | 37.04 pMC (mixed?) | | | | 110 to 115 pMC |
| Methane | 357 ppmv | | | | | < 3.4 ppmv |
| $\delta^{13}\text{C}$ in methane | -36.4 ppt | | | | | -44.8 ppt |
| ^{14}C in methane | 1.3 pMC | | | | | > 93.0 pMC |
| Salinity - Apache | 37 ppt | 37 ppt | | | | 35.3 |
| - AGSO | 27 | 28/27 | | | | |
| Temperature | 70°C | 70°C | | | | 23.5°C |
| SG | 1.026 | 1.026 | | | | |
| Av. Flow Rate | >6000 m ³ / day | >6000 m ³ / day | | | | ----- |

Three PFW samples were analysed; one from 1994 and two from the 1995 survey. The 1995 samples show a variation by a factor of two in concentration for all hydrocarbons, e.g. 2.50 mg/L and 5.00 mg/L for C₁₋₆. The benzene analysis yielded 1.14 mg/L and 2.04 mg/L and toluene 1.37 mg/L and 2.08 mg/L. The 1994 results for benzene and toluene are slightly higher again than the second 1995 sample - 2.55 mg/L and 2.67 mg/L respectively. The cause of this variation is unknown but is assumed to be a result of fluctuations in PFW concentration rather than a change in sampling position on the platform or sampling methodology. AGSO salinity measurements for all samples were in the range 27-28 ppt compared with a background of 35.2 for seawater.

Benzene and toluene concentrations for Harriet PFW thus vary in the range 3.5 to 5.5 mg/L. (Table 6) Total BTEX including ethylbenzene and xylenes from an inspection

of AGSO 1994 data is approximately 5 to 8 mg/L. This compares with concentrations of benzenes from Bass Strait platforms of between 8 to 34 mg/L (Terrens and Tait, 1994), and results from the Brent platform in the North Sea (Somerville et al, 1987) and Gulf of Mexico (Sauer, 1981) where 36 mg/L and 12 mg/L have been recorded for BTEX and BTX respectively.

3.5 Isotopic Analysis

A variety of seawater samples, mixed seawater /PFW samples and PFW alone were collected for isotopic analyses of PFW components during both the 1994 pilot survey and again in the 1995 survey. The purpose of gathering these samples was to investigate possible isotopic tracers of PFW in seawater and to help define dispersion and separation processes of PFW that might be operating in the water column. If conservative tracers of the PFW plume can be identified then these can be used to assess the non-conservative behaviour of hydrocarbons in seawater.

The samples were analysed by NIWA/INGRS (NZ) for the following:-

$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and ^{14}C in Dissolved Inorganic Carbon (DIC)
 $\delta^{13}\text{C}$ and ^{14}C in methane (CH_4)
salinity.

DIC Isotopes

We have included here the preliminary results obtained on the 1994 pilot survey for information and completeness although these results are not bound by the terms and conditions of the ERDC contract. We collected 7 samples during the 1994 pilot survey for analyses of isotopes in DIC. The locations of these samples are summarised in Table 7. The isotopic DIC results are shown in Table 8. The DIC content and the isotopic contents of DIC show a contrast between DIC in the PFW and DIC in background seawater. Thus these are potential useful tracers of the PFW, and DIC in

background seawater. Two samples collected at 2 m depth (from the shipboard pump) at distances of < 1 km from Harriet A show tracer values which are indicative of small proportions of PFW. For example the dissolved inorganic carbonate levels from the 1994 samples vary from a minimum of 23.5 mg/Kg in 'background' clean seawater to 154.9 mg/Kg in the PFW sample. Typical 'mixed' seawater and hydrocarbon samples have DIC values between 23.8 and 24.3 mg/Kg indicating large dilutions of PFW in seawater. Also four samples collected from a vertical profile suggest small proportions of PFW mixed throughout the water column. These observations and the underlying rationale resulted in further samples being collected during the 1995 survey for DIC analyses.

Table 7. Water samples collected on the 1994 pilot study for isotopic analysis

| Sample Numbers | CGT Methane conc. (ng/L) | (nmole/L) | Date | Location |
|---|--------------------------------------|---|---------|--|
| GS001 - GS007 | 21 | 1.3 | 10.9.94 | Transit - Passage Is. to Harriet 'A' |
| GS008 - GS014 | 26-36 | 1.6-2.2 | 10.9.94 | 0.5 nm grid around Harriet 'A' |
| GS015 - GS018; BTEX001 -BTEX003; CO001 | 34-95 | 2.1-5.9 | 10.9.94 | 'in plume' 1 km downstream from Harriet 'A' |
| GS019, GS020; BTEX004, BTEX005; CO002 | 710 (GS019); 36-497 (other) | 44.3 (GSO19); 2.2-31.1 (other) | 10.9.94 | 'in plume' 0.5 km downstream from Harriet 'A' |
| GS021,GS022; CO003 | 38-290 | 2.4-18.1 | 12.9.94 | VP to south-east of Harriet 'A'; (surface water samples 0-2.5 m) |
| GS023 (may have surface sample included), GS024 - GS027; CO004 | 43- 53 | 2.7-3.3 | 12.9.94 | VP at 15 m water depth |
| CO005 | | | 12.9.94 | VP at 10 m water depth |
| GS028 - GS030; CO006 | 44-50 | 2.7-3.1 | 12.9.94 | VP at 0.5 m water depth |
| GS031 - GS036; CO007, CO008 | 22 | 1.8 | 12.9.94 | 'Station clean' approx. 6 nm south-east of Harriet 'A' |
| GS037, GS028 | 22 | 1.8 | 12.9.94 | In transit 'station clean' to anchorage at Varanus Island |

Table 8. NIWA DIC analysis, 1994 survey

| AGSO Sample No. | Total DIC (mg/Kg) | $\delta^{13}\text{C}$ (ppt) | ^{14}C (pMC) | ^{18}O (ppt) | Depth (metres) | Latitude/ Longitude | Comments |
|--------------------|-------------------------|--------------------------------|--------------------------|--------------------------|-------------------|------------------------|---------------------|
| CO001 | 23.80 | 0.50 | 105.42 | -0.09 | 2.0 | | 0.5 km d/s from rig |
| CO002 | 24.20 | 0.49 | 105.14 | 0.12 | 2.0 | | 1 km d/s from rig |
| CO003 | 24.34 | 0.41 | 104.24 | -0.03 | 0 to 2.5 | 20 36.55 115 37.23 | VP 148001 |
| CO004 | 24.34 | 0.75 | 107.81 | 0.08 | 15.0 | 20 36.55 115 37.23 | VP 148002 |
| CO005 | 23.62 | 0.75 | 113.41 | 0.02 | 10.0 | 20 36.55 115 37.23 | VP 148002 |
| CO006 | 23.39 | 0.87 | 113.55 | 0.17 | 0.5 | 20 36.55 115 37.23 | VP 148002 |
| CO007 | 23.76 | 0.80 | 115.85 | 0.10 | 2.0 | 20 40.53 115 40.06 | Ocean station clean |
| CO008 | 23.50 | 0.67 | NO | -0.12 | 2.0 | 20 40.53 115 40.06 | Ocean station clean |
| COHA | 154.92 | -3.11 | 0.94 | -0.95 | | | Harriet PFW |

A total of twenty-four 1 litre surface water samples were collected during the 1995 fieldwork. These included two PFW samples taken from the platform on the 20.9.95 and 29.9.95; clean seawater samples at background levels from distant locations on the 21.9.95 and 25.9.95; and a range of intermediate samples collected in the PFW plume (Table 9). These results are summarised in table 10. Similar results were obtained for the 1995 survey, with DIC content of PFW of about 160 mg/Kg. DIC values of seawater/hydrocarbon mixtures varied between 23.3 and 24.2 mg/Kg. Despite an approximate seven-fold difference in DIC contents of ambient seawater and PFW, DIC alone is not a sensitive tracer of PFW dilution.

The carbon isotopic compositions of ambient seawater ($\delta^{13}\text{C}$ = 0.85, 0.92 ppt; samples CO/003, 004) is markedly different to that in PFW ($\delta^{13}\text{C}$ = -3.11, -3.52 and -4.36 ppt). Values of $\delta^{13}\text{C}$ for seawater / hydrocarbon mixtures (Tables 9 & 10) vary between 0.95 and 1.11, and these are apparently indistinguishable from seawater; suggesting very small proportions of PFW isotopes in these samples. Similar observations can be

made of the ^{14}C data (although we note that the ^{14}C of the 1995 PFW end-member is 0.37, a result which indicates apparent contamination with contemporary seawater), i.e. distinct differences occur between the 'clean' seawater and PFW end-members (based upon 1994 observations). However seawater/hydrocarbon mixtures do not show significant deviations from the seawater end-member (Tables 9 & 10), suggesting very small PFW isotopic components in these samples. Some of these relationships are illustrated in the carbon-14, carbon-13 and oxygen-18 versus DIC graphs of Figure 32.

The data of Table 10 show that, based upon a comparison of the toluene concentrations only in PFW and those collected for isotopic analyses, there is an apparent dilution of the PFW of the order of 10,000. The observations on DIC isotopes indicate that despite the sensitivity and high precision analyses of the isotope data, at these large dilutions of the PFW in seawater it is difficult to infer anything about the conservative/non-conservative behaviour of the hydrocarbons. More specific laboratory-base experiments whereby PFW was mixed with various proportions of seawater, would be required to examine the reactivity of PFW in seawater using a variety of isotopic data.

Table 9. Water samples collected on the 1995 survey for isotopic and salinity determinations

| Sample | Adjacent CGT Shotpoint | CGT Toluene (ng/L) | CGT Toluene (nmole/L) | Date | Location |
|---------------|------------------------------|--------------------------|-----------------------------|---------|------------------------|
| Harriet PFW-1 | at platform | 1365721 | 14844 | 20.9.95 | 20 36.10S / 115 36.70E |
| Harriet PFW-2 | at platform | 1365721 | 14844 | 20.9.95 | 20 36.10S / 115 36.70E |
| 152CO.001 | 152006/442 | 3 | 0.03 | 21.9.95 | 20 22.04S / 115 33.93E |
| 152CO.002 | 152006/442 | 3 | 0.03 | 21.9.95 | 20 22.04S / 115 33.93E |
| 152CO.003 | 152009/105 | 1 | 0.55 | 25.9.95 | 21 01.19S / 115 49.82E |
| 152CO.004 | 152009/105 | 1 | 0.55 | 25.9.95 | 21 01.19S / 115 49.82E |
| 152CO.005 | 152009/1132 | 14 | 0.15 | 25.9.95 | 20 34.70S / 115 35.93E |
| 152CO.006 | 152009/1144 | 14 | 0.15 | 25.9.95 | 20 34.62S / 115 35.40E |
| 152CO.007 | 152010/1059 | 56 | 0.61 | 26.9.95 | 20 36.01S / 115 36.84E |
| 152CO.008 | 152010/1169 | 412 | 4.48 | 26.9.95 | 20 35.49S / 115 36.69E |
| 152CO.009 | 152010/1140 | 194 | 2.10 | 26.9.95 | 20 35.78S / 115 36.65E |
| 152CO.010 | 152010/1169 | 78 | 0.84 | 26.9.95 | 20 35.49S / 115 36.69E |
| 152CO.011 | 152010/1188 | 17 | 0.18 | 26.9.95 | 20 35.19S / 115 36.69E |
| 152CO.012 | 152010/1207 | 83 | 0.90 | 26.9.95 | 20 35.14S / 115 36.60E |
| 152CO.013 | 152010/1239 | 83 | 0.90 | 26.9.95 | 20 35.25S / 115 36.64E |
| 152CO.014 | 152010/1260 | 70 | 0.77 | 26.9.95 | 20 34.76S / 115 36.68E |
| 152CO.015 | 152010/1295 | 62 | 0.67 | 26.9.95 | 20 34.72S / 115 36.61E |
| 152CO.016 | 152010/1319 | 6 | 0.06 | 26.9.95 | 20 34.14S / 115 36.67E |
| 152CO.017 | 152010/1351 | 4 | 0.04 | 26.9.95 | 20 34.09S / 115 37.49E |
| 152CO.018 | 152010/1097 | 56 | 0.61 | 26.9.95 | 20 35.78S / 115 36.70E |
| 152CO.019 | 152010/1105 | 20 | 0.22 | 26.9.95 | 20 35.76S / 115 36.73E |
| 152CO.020 | 152010/1129 | 20 | 0.22 | 26.9.95 | 20 35.79S / 115 36.76E |
| Harriet PFW-3 | at platform | 2082360 | 22634 | 29.9.95 | 20 36.10S / 115 36.70E |
| Harriet PFW-4 | at platform | 2082360 | 22634 | 29.9.95 | 20 36.10S / 115 36.70E |

Note: the methane and toluene concentrations of Tables 7 and 9 are derived from CGT data recorded as the water sample was being collected, and these may vary over a wide range as the vessel transits the PFW plume. As such these levels are indicative only of sample hydrocarbon concentrations.

Table 10. NIWA DIC analysis, 1995 survey

| Sample | Toluene (ng/L) | DIC (mg/Kg) | $\delta^{13}\text{C}$ (ppt) | ^{14}C (pMC) | Salinity (ppt) | Comments |
|-----------|-------------------|----------------|--------------------------------|--------------------------|-------------------|-------------------------------|
| 152CO.001 | 2.67 | 23.87 | 1.12 | | 35.36 | For locations see Table 9. |
| 152CO.002 | 2.67 | 23.90 | 1.10 | | 35.34 | |
| 152CO.003 | 1.07 | 24.37 | 0.92 | | 35.34 | |
| 152CO.004 | 1.07 | 24.50 | 0.85 | | 35.33 | |
| 152CO.005 | 13.76 | 23.96 | 1.11 | | 35.33 | |
| 152CO.006 | 13.76 | 23.85 | 1.10 | | 35.38 | |
| 152CO.007 | 55.90 | 24.11 | 1.12 | 109.90 | 35.33 | |
| 152CO.008 | 412.23 | 24.15 | 1.03 | 105.32 | 35.32 | |
| 152CO.009 | 193.57 | 24.06 | 1.03 | 105.44 | 35.32 | |
| 152CO.010 | 77.75 | 24.16 | 1.04 | 108.52 | 35.35 | |
| 152CO.011 | 17.00 | 23.27 | 1.04 | 104.82 | 35.33 | |
| 152CO.012 | 82.59 | 23.84 | 1.04 | 105.75 | 35.31 | |
| 152CO.013 | 82.59 | 24.24 | 1.03 | 105.42 | 35.25 | |
| 152CO.014 | 70.48 | 23.99 | 1.04 | 107.60 | 35.34 | |
| 152CO.015 | 61.57 | 23.81 | 1.04 | 104.61 | 35.35 | |
| 152CO.016 | 5.67 | 23.99 | 1.14 | 106.99 | 35.33 | |
| 152CO.017 | 4.07 | 23.97 | 1.10 | | 35.42 | |
| 152CO.018 | 55.90 | 23.89 | 0.95 | | 35.42 | |
| 152CO.019 | 20.25 | 24.11 | 1.09 | | 35.4 | |
| 152CO.020 | 20.25 | 24.09 | 1.08 | | | |
| HA PFW-1 | 1365768.75 | 162.30 | -3.52 | | | |
| HA PFW-3 | 2082432.32 | 160.35 | -4.36 | 37.04? | | |

Methane Isotopes

Methane isotopic data are summarised in Table 11. Background seawater values of methane, measured in several places on the northern Australian continental margin and shelf are about 2-3 ppmv with pMC values of 100 or greater. Methane in the Harriet PFW sample has a pMC values of 1.3. A sample collected about 0.5 km from Harriet, with a methane content about 10-20 fold ambient levels, has a pMC of 8.3, indicating that most methane in this sample is PFW sourced.

Four other samples in Table 11 were collected during a vertical profile of hydrocarbons in seawater. One sample (an integrated one collected between the surface and 2.5 metres depth) has a methane content about 10 fold ambient levels, and pMC and carbon isotopic compositions which reflect a significant PFW component. Another sample collected from 'surface waters' at 2 m depth is only slightly elevated

above ambient levels with a pMC close to background; this sample has only a small component of PFW methane. Interestingly, a sample collected at 15 m water depth has a methane content about twice ambient levels and a pMC and isotopic composition which reflects a significant proportion of PFW sourced methane. The result indicates that PFW sourced methane is being mixed throughout the water column to the seafloor.

Methane has a concentration of 255 $\mu\text{L/L}$ in PFW compared to 339nL/L in clean seawater whereas DIC has concentrations of 162.3 mg/Kg and 23.27 mg/Kg respectively. Thus, the levels of $\delta^{13}\text{C}$ and ^{14}C in methane show considerable overall contrast between PFW/seawater concentrations and end-member background levels (Figures 32 and 33) and $\delta^{13}\text{C}$ and ^{14}C in methane, are therefore both good tracers of the plume despite the high dilution experienced by the PFW in seawater.

The ^{14}C and $\delta^{13}\text{C}$ concentrations are presented in Figures 33(c) as a cross-plot which indicates an inverse linear relationship from background seawater through PFW end-member concentrations. Lowe (1988) used similar plots to show the various proportions of biogenic and fossil fuel sourced methanes in the atmosphere.

Table 11. INGS Gas (CH_4) Analysis

| AGSO Sample No. | NZA No. | CH_4 (ppmv) | $\delta^{13}\text{C}$ (%PDB) | ^{14}C (pMC) | Depth (metres) | Latitude / Longitude | Comments |
|--------------------|------------|-------------------------|---------------------------------|--------------------------|-------------------|-------------------------|---|
| 016-018 148A | 4923 | 8.0 | -40.0 | nd | 2 | 20 35.53 115 36.59 | 1km from Harriet 'A' |
| 019-020 148B | | 66.2 | -39.0 | 8.3 | 2 | 20 35.31 115 36.54 | 0.5 km from Harriet 'A' |
| 021-022 148C | 4942 | 29.6 | -37.0 | 14.9 | 0 to 2.5 | 20 36.55 115 37.23 | VP 148001 |
| 024-027 148D | 4960 | 7.2 | -41.5 | 58.4 | 15 | 20 36.55 115 37.23 | VP 148002 |
| 028-030 148F | 4940 | 7.2 | -41.3 | 55.1 | 0.5 | 20 36.55 115 37.23 | VP 148002 |
| 031-038 148E | 4952 | 3.4 | -44.8 | 93.0 | 2 | | 'Ocean station clean' approx 6 nm Se of Harriet |
| Fm. Water 148G | 4961 | 357 | -36.4 | 1.3 | | | Harriet PFW |

CONCLUSIONS

A Continuous Geochemical Tracer system measured a variety of PFW hydrocarbons in seawater by gas chromatography, collected hydrographic data and samples for isotopic chemistry, to provide a detailed understanding of the dispersion of PFW around the Harriet 'A' platform under local tidal conditions. Hydrocarbon measurements for C₁-C₆ hydrocarbons, benzene and toluene were made about every 180 metres, and hydrographic datapoints recorded every 60 metres using a repeatable tide-dependent strategy which involved commencing a profile around the platform at the turn of tide and then completing a series of lines progressively further away in the direction of tidal flow. The key findings were:

1. Two samples of Produced Formation Water taken from the platform for analysis indicated average values of 3.75 mg/L for C₁-C₆, 1.59 mg/L for benzene and 1.72 mg/L seawater for toluene. This compared with an analysis of 1.18 mg/L for methane, 2.55 mg for benzene and 2.67 mg/L for toluene from a 1994 pilot survey. Benzene and toluene in particular, proved to be excellent tracers of the Produced Formation Water discharge in seawater. Maximum seawater concentrations > 1500 ng/L (70 nM) were determined for C₁-C₆, at 600 metres from the platform and benzene and toluene levels were about 100 fold higher than detectable background levels. Benzene concentrations varied from > 140 ng/L (1.78 nM) to < 0.7 ng/L (0.01 nM) and toluene from 250 ng/L (2.72 nM) to 1.6 ng/L (0.02 nM) respectively.
2. During September 1995, the PFW plume was mapped NNW of the platform to a distance of 10 km on a 3 metre ebb tide, and to a similar distance on the flood tide to the SSE. The net effect of the tidal action appears to promote a westerly drift of the plume toward Varanus Island and the Montebello Island group, rather than toward the east and the mainland.
3. A simple model was used to estimate the dispersion characteristics of the various hydrocarbons from the platform. The C₁-C₆ hydrocarbons were found to have characteristic half-dispersion distances of approximately 3500 m on the spring (3 m)

tide between 800 metres and 8 km from the platform. Benzene and toluene have a similar half distance indicating similar dispersion characteristics. Measurements taken on the neap tide (1.5 metre) between 500 metres and 3.5 km show a half dispersion distance of about 1500 metres for C₁-C₆ and 950 metres for benzene and toluene.

4. The modelling data and vertical profiles indicate that within 1 km of the platform the estimated dilution for C₁-C₆ is 8000 times and for benzene and toluene dilution rates are up to 150000 and 70000 times respectively. Thus benzene and toluene are both more 'reactive' than the C₁-C₆ saturated hydrocarbons close (< 1 km) to the platform. We also find that within 1 km of the platform, the PFW plume appears to be confined to the surface layers but are mixed vertically throughout the water column with increasing distance from the platform.

5. The isotopic compositions of dissolved inorganic carbon and methane in produced formation water and 'background' seawater are markedly different suggesting that both species could be useful tracers of produced water. However, comparatively low contrasts between DIC concentrations in end-member PFW and seawater suggest that at the apparent dilutions in this area, DIC alone is not a practical tracer of PFW discharge. In contrast, the comparatively high concentration of methane in PFW, compared to background seawater, indicates that methane and its carbon isotopic signatures are potential tracers of the PFW plume, and the reactivity of a PFW hydrocarbon in seawater.

6. Hydrographic parameters temperature, salinity, dissolved oxygen and seawater density were measured continuously at 1.5 metre depth during the survey. These data show no direct correlation with plume hydrocarbons and therefore are not useful tracers of the Produced Formation Water discharge.

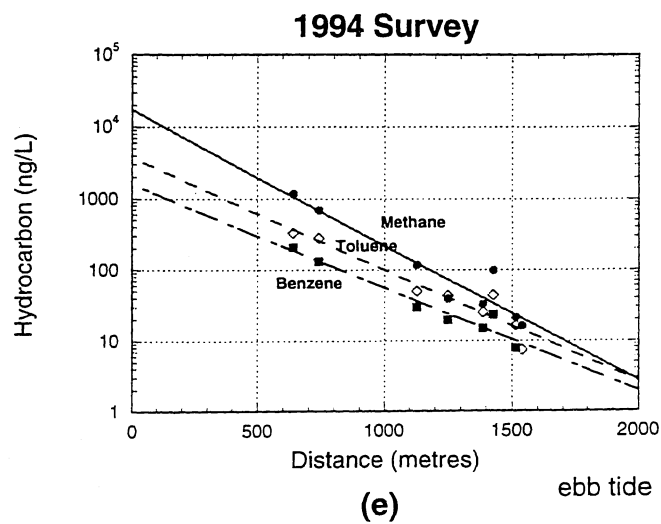
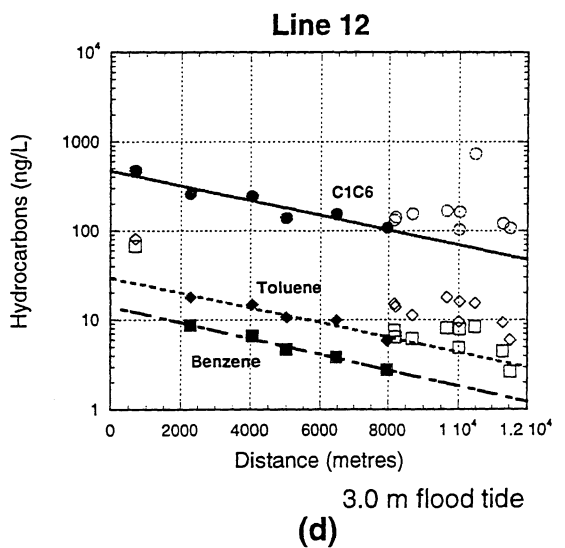
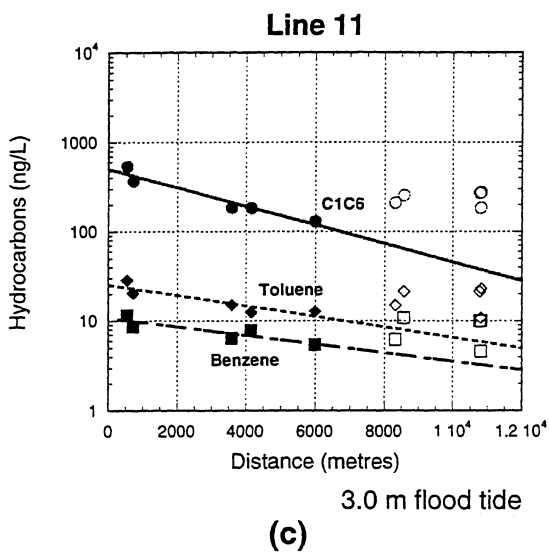
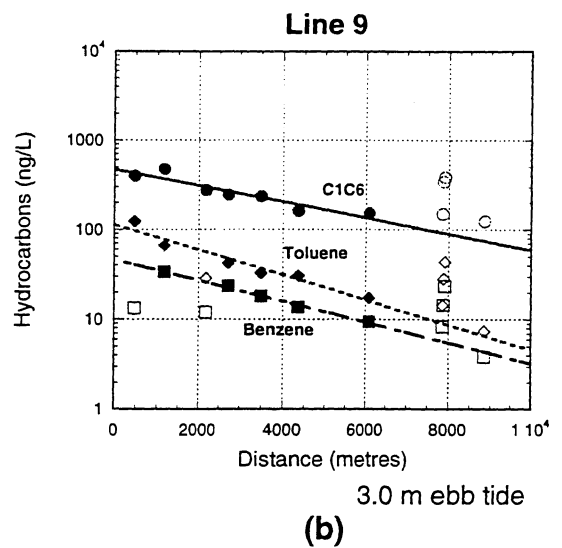
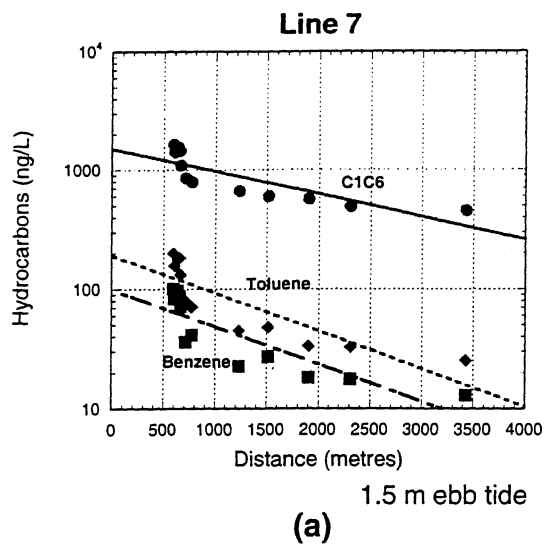


Figure 28. Plume centreline hydrocarbon concentrations as a function of distance from the platform

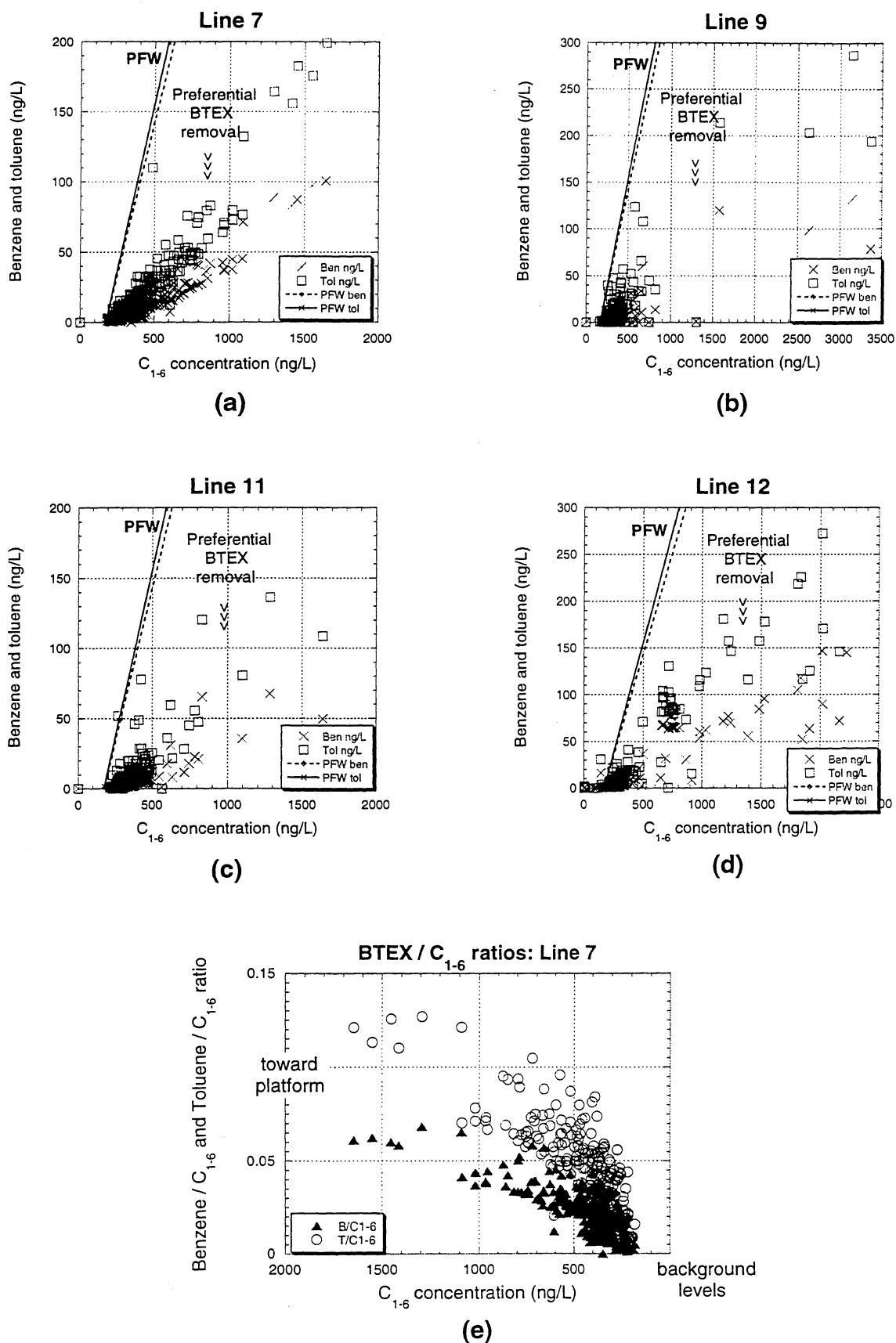


Figure 29. Benzene and toluene / C_{1-6} X-plots for Lines 7, 9, 11 and 12 and BTEX / C_{1-6} ratios as a function of plume concentration

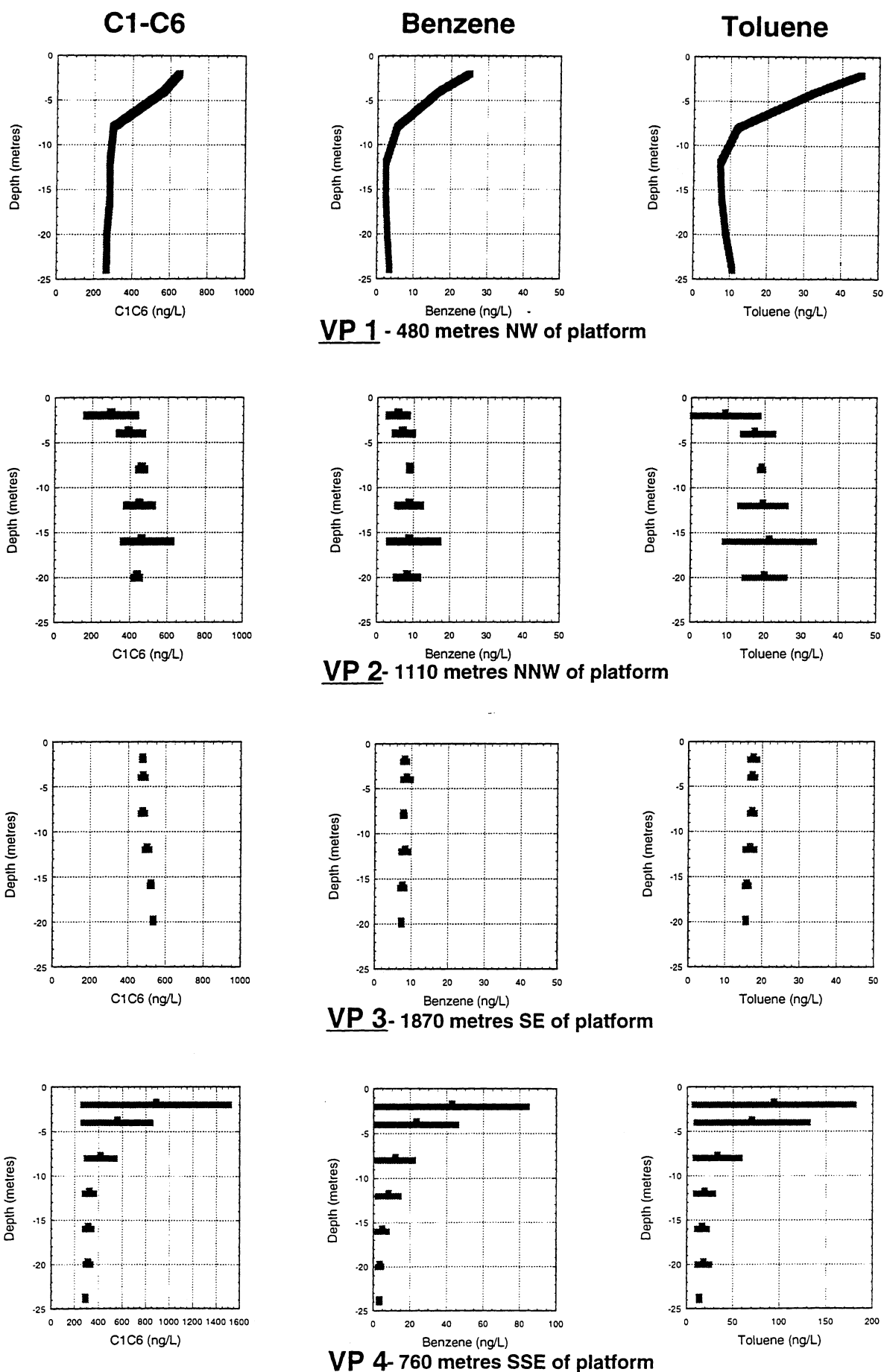


Figure 30. C_1 to C_6 , benzene and toluene vertical profiles for VP's 1 to 4

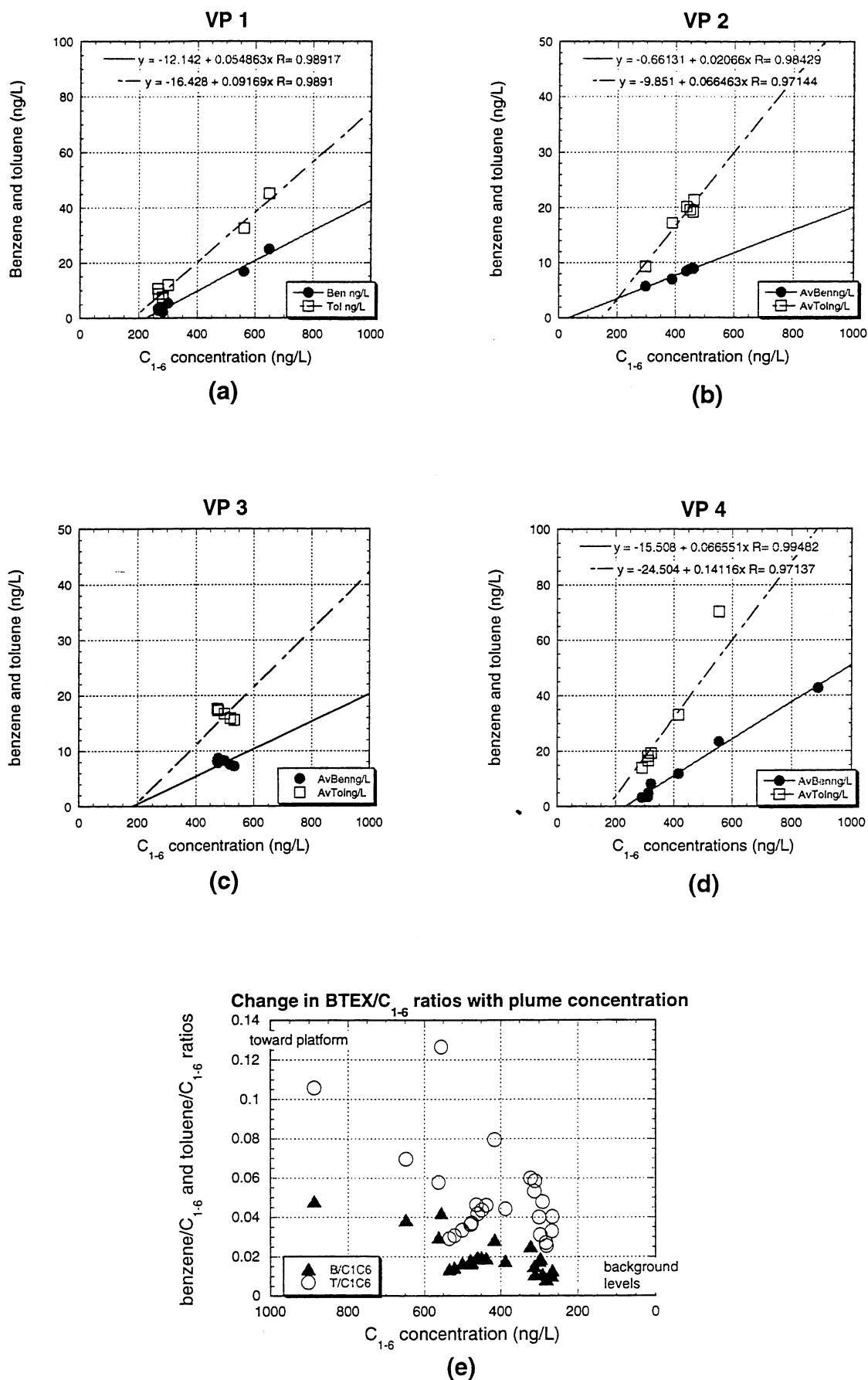
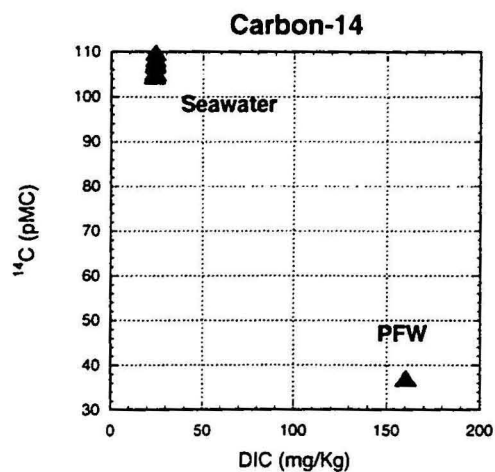
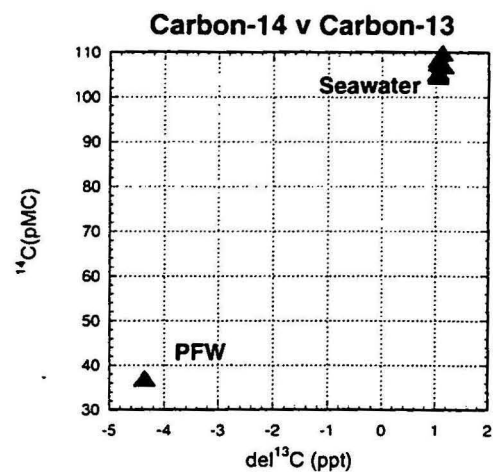


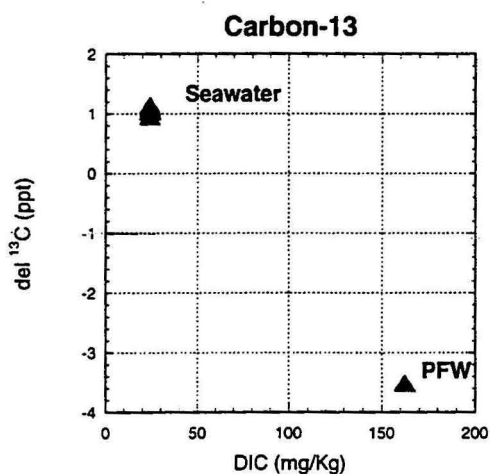
Figure 31. Benzene and toluene / C_1 - C_6 concentration X-plots for VP's 1 to 4 and BTEX / C_1 - C_6 ratios as a function of plume concentration



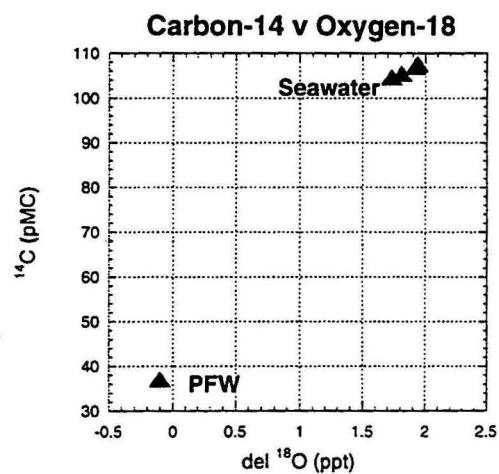
(a)



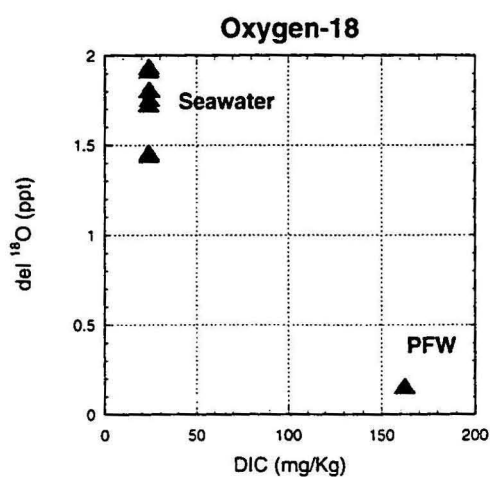
(b)



(c)



(d)



(e)

Figure 32. Carbon-14, carbon-13 and oxygen-18 isotopic compositions of DIC for PFW and seawater

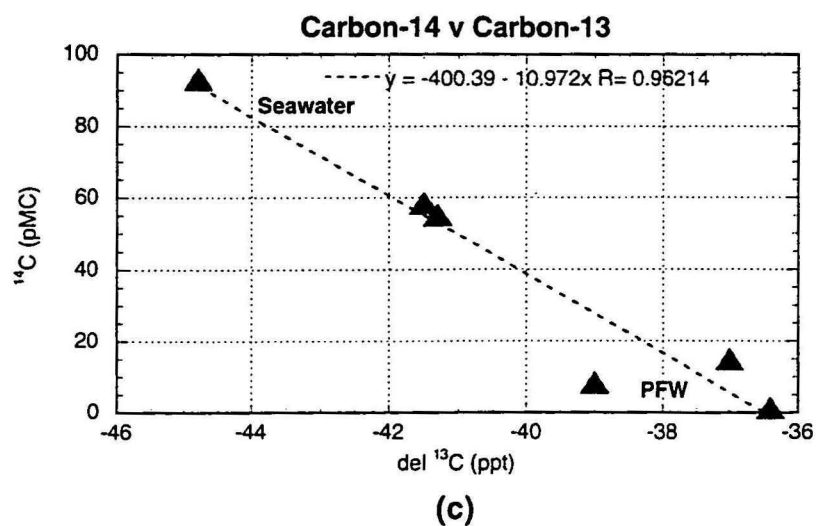
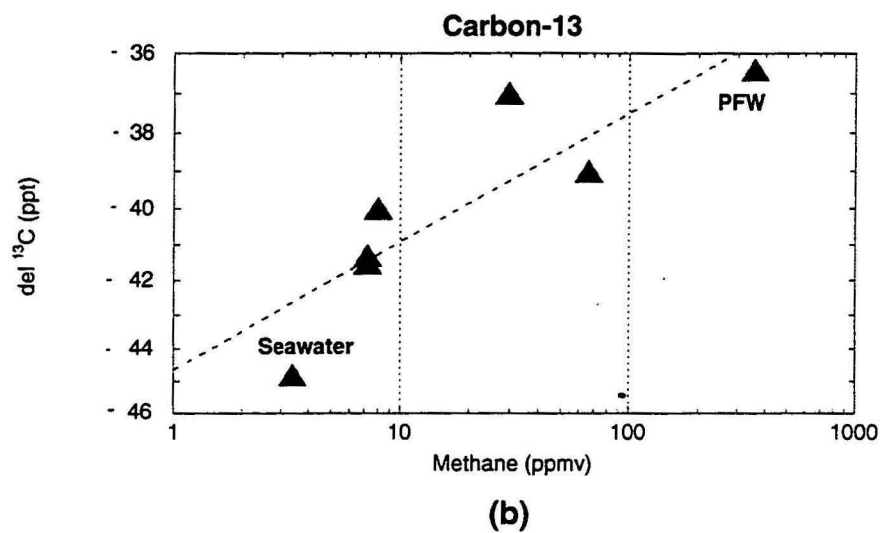
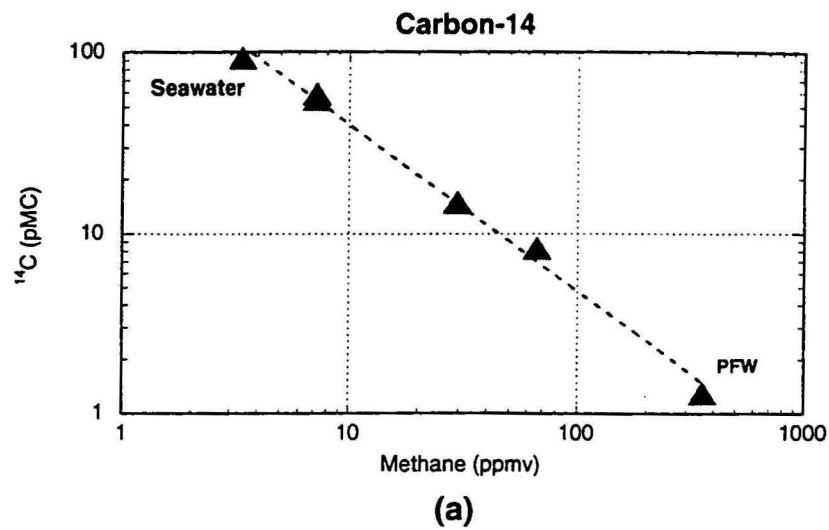


Figure 33. Carbon-14 and carbon-13 isotopic compositions of methane as potential tracers of the PFW plume

REFERENCES

- Albarede, F. 1995. Introduction to Geochemical Modelling. *Cambridge University Press*.
- Brand, G.W., Gibbs, C.F., Monahan, C.A., Palmer, D.H., Murray, A.J., Fabris, G.J., Chamberlain, T. & Nicholson, G.J. 1989. Production Waters from the Bass Strait Oil and Gas Field: Chemical characterisation and toxicity to marine organisms. *Department of Conservation, Forests and Lands; Fisheries Division. Internal Report, No. 186*.
- Brandsma, M.G., & Sauer, T.C., 1983. The OOC model: prediction of short term fate of drilling mud in the ocean, Part I model description and Part II model results. *Proceedings of Workshop on an Evaluation of Effluent Dispersion and Fate Models for OCS Platforms, Santa Barbara, California, 7-10 February, 1983*.
- Burke, R. A., Reid, D.F., Brooks, J.M., & Lavoie, D.M., 1983. Upper Water Column Methane Geochemistry in the Eastern Tropical North Pacific. *Limnology and Oceanography, Vol. 28 No.1 Jan. 1983*
- Furnas, M., & Burns, K. 1995. Preliminary Results of Oceanographic and Geochemical Measurements made in the Vicinity of the Harriet 'A' Production Platform September, 1994. *Australian Institute of Marine Science Report*
- Hubbert, G.D., 1993. Oil spill trajectory modelling with a fully three-dimensional ocean model. *Proceedings of the 11th Australasian Conference on Coastal and Ocean Engineering, Townsville, July 1993*.
- King, B.A., 1994. 'OILMAP: Application for BHP Petroleum's operations on the Australian North West Shelf'. *Australian Institute of Marine Science Report to BHP Petroleum, August, 1994*.
- King, B.A. & McAllister, F., 1996. The Application of 'MUDMAP' for Investigating the Dispersion of Produced Water Discharge from the 'Harriet A' on Australia's Northwest Shelf. *Australian Institute of Marine Science. Report to APPEA*.
- Koh, R.C.Y. & Chang, Y.C., 1993. Mathematical model for barged ocean disposal of waste. *Environmental Protection Technology Series EPA 660/2-73-029, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi*.
- Lowe, D., & Brailsford, G., 1996. The NIWA Automated DIC Extraction System. *National Institute of Water and Atmospheric Research, NZ. <http://www.niwa.cri.nz.co2extract.html>*
- Lowe, D., Brenninkmeijer, C.A.M., Manning, M.R., Sparks, R., Wallace, G., 1988. Radiocarbon Determination of Atmospheric Methane at Baring Head, New Zealand. *IGNS . Nature, 332, 522-525*.

Sauer, T.C., 1981. Volatile Liquid Hydrocarbon Characterisation of Underwater Hydrocarbon Vents and Formation Waters from Offshore Production Operations. *Environmental Science and Technology*, 15, 917-923

Somerville, H.J., Bennet, D., Davenport, J.N., Holt, M.S., Lynes, A., Maheiu, A., McCourt, B., Parker, J.G., Stephenson, R.R.,Watkinson, R.J. & Wilkinson, T.G., 1987. Environmental Effect of Produced Water from North Sea Oil Operations. *Marine Pollution Bulletin*, 10, 549-558.

Swan, J.M., Neff, J.M., & Young P.C., 1992. Environmental Implications of Offshore Oil and Gas Development in Australia. *Findings of an Independent Scientific Review*, APPEA & ERDC ,

Terrens, G.W. & Tate, R.D., 1994. Effects on the marine environment of produced formation water discharges from offshore development in Bass Strait, Australia. *Proceedings of the Second International Conference on Health, Safety & Environment in Oil and Gas Exploration & Production. Society of Petroleum Engineers publication*, #SPE 27149.

Terrens, G.W. & Tate, R.D., 1996. Monitoring Ocean Concentrations of Aromatic Hydrocarbons from Produced Formation Water Discharges to Bass Strait, Australia. *SPE 36033 (Society of Petroleum Engineers)*

Weiss, R.F., 1970. The Solubility of Nitrogen, Oxygen and Argon in Water and Seawater. *Deep Sea Research*, 17, 721-735.