IMMEDIATE RESPONSE ACTION MODIFICATION PLAN

Prepared for:
Eagle Gas, Inc., 131 Main Street, Carver, MA
DEP RTN 4-17825

Prepared by:
Decoulos & Company

Date: April 21, 2004

DECOULOS & COMPANY

ENVIRONMENTAL ENGINEERING & LAND PLANNING

Wednesday, April 21, 2004

Jonathan E. Hobill, Regional Engineer
Bureau of Waste Site Cleanup
20 Riverside Drive
Lakeville, MA 02347

RE: 131 Main Street, Carver; RTN 4-17825

Dear Mr. Hobill:

On behalf of Eagle Gas, Inc., Decoulos & Company is pleased to submit this modification to the Immediate Response Action (IRA) Plan for the above referenced property.

On January 21, 2004 an Immediate Response Action (IRA) Plan was submitted to the Department for this release. The IRA Plan was filed in response to NON-SE-03-3T-109.

The Department requested a modification of the IRA Plan on April 5, 2004. The purpose of this IRA Plan is to further assess and mitigate the discharge of oil and hazardous materials to the stormwater outfall into South Meadow Brook. The proposed scope of work follows the guidelines set forth in the April 5th request together with on-going discussions with Department representatives.

Eagle Gas is potentially responsible for two existing releases on record for the Site (RTNs 4-13333 and 4-17582). Over the next few weeks documentation will be provided to merge these two tracking numbers.

We appreciate your patience and cooperation on this matter. Please feel free to call or email if you have any questions or concerns. Thank you.

Very truly yours,

James J. Decoulos, PE, LSP
jamesj@decoulos.com

cc: Francis J. Casey, Carver Board of Selectmen
Robert C. Tinkham, Jr., Carver Board of Health
Sarah G. Hewins, Carver Conservation Commission
William A. Halunen, Carver Department of Public Works
Dana E. Harriman, Carver Fire Department
Donald P. Nagle, Esq.
Theodore J. Kaegael, Jr., Kaegael Environmental, Inc.
Theodore L. Bosen, Esq.
Najib Badaoui, Eage Gas, Inc.

3 ELECTRONICS AVENUE, DANVERS, MASSACHUSETTS 01923
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Massachusetts Department of Environmental Protection
Bureau of Waste Site Cleanup

BWSC105

IMMEDIATE RESPONSE ACTION (IRA) TRANSMITTAL FORM

Pursuant to 310 CMR 40.0424 - 40.0427 (Subpart D)

Release Tracking Number 4 - 17825

A. RELEASE OR THREAT OF RELEASE LOCATION:

1. Release Name/Location Aid: Eagle Gas, Inc.

2. Street Address: 131 Main Street

3. City/Town: Carver
4. ZIP Code: 02330-0000

☐ 5. Check here if a Tier Classification Submittal has been provided to DEP for this Disposal Site.
  ☐ a. Tier 1A ☐ b. Tier 1B ☐ c. Tier 1C ☐ d. Tier 2

☐ 6. Check here if this location is Adequately Regulated, pursuant to 310 CMR 40.0110-0114. Specify Program (check one):
  ☐ a. CERCLA ☐ b. HSWA Corrective Action ☐ c. Solid Waste Management
  ☐ d. RCRA State Program (21C Facilities)

B. THIS FORM IS BEING USED TO: (check all that apply)

1. List Submittal Date of Initial IRA Written Plan (if previously submitted): ______ (MM/DD/YYYY)

☐ 2. Submit an **Initial IRA Plan.**

☑ 3. Submit a **Modified IRA Plan** of a previously submitted written IRA Plan.

☐ 4. Submit an **Imminent Hazard Evaluation** (check one)
  ☐ a. An Imminent Hazard exists in connection with this Release or Threat of Release.
  ☐ b. An Imminent Hazard does not exist in connection with this Release or Threat of Release.
  ☐ c. It is unknown whether an Imminent Hazard exists in connection with this Release or Threat of Release, and further assessment activities will be undertaken.
  ☐ d. It is unknown whether an Imminent Hazard exists in connection with this Release or Threat of Release. However, response actions will address those conditions that could pose an Imminent Hazard.

☐ 5. Submit a request to **Terminate an Active Remedial System or Response Action(s) Taken to Address an Imminent Hazard**.

☐ 6. Submit an **IRA Status Report**.

☐ 7. Submit an **IRA Completion Statement**.

  ☐ a. Check here if future response actions addressing this Release or Threat of Release notification condition will be conducted as part of the Response Actions planned or ongoing at a Site that has already been Tier Classified under a different Release Tracking Number (RTN). When linking RTNs, rescoring via the NRS is required if there is a reasonable likelihood that the addition of the new RTN(s) would change the classification of the site.

  b. State Release Tracking Number of Tier Classified Site (Primary RTN): ☐ - ☐

These additional response actions must occur according to the deadlines applicable to the Primary RTN. Use the Primary RTN when making all future submittals for the site unless specifically relating to this Immediate Response Action.

☐ 8. Submit a **Revised IRA Completion Statement**.

(All sections of this transmittal form must be filled out unless otherwise noted above)

Massachusetts Department of Environmental Protection
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IMMEDIATE RESPONSE ACTION (IRA) TRANSMITTAL FORM Pursuant to 310 CMR 40.0424 - 40.0427 (Subpart D)

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C. RELEASE OR THREAT OF RELEASE CONDITIONS THAT WARRANT IRA:

1. Identify Media Impacted and Receptors Affected: (check all that apply)

☐ a. Air ☐ b. Basement ☐ c. Critical Exposure Pathway ☐ d. Groundwater ☐ e. Residence

☑ f. Paved Surface ☐ g. Private Well ☐ h. Public Water Supply ☐ i. School ☐ j. Sediments

☐ k. Soil ☑ l. Storm Drain ☑ m. Surface Water ☐ n. Unknown ☑ o. Wetland ☐ p. Zone 2

☐ q. Others Specify: ______

2. Identify Oils and Hazardous Materials Released: (check all that apply)

☑ a. Oils ☐ b. Chlorinated Solvents ☐ c. Heavy Metals

☐ d. Others Specify: ______

D. DESCRIPTION OF RESPONSE ACTIONS: (check all that apply. for volumes list cumulative amounts)

☐ 1. Assessment and/or Monitoring Only
☑ 3. Deployment of Absorbent or Containment Materials
☐ 5. Structure Venting System
☐ 7. Product or NAPL Recovery
☐ 9. Groundwater Treatment Systems
☐ 11. Bioremediation
☐ 13. Excavation of Contaminated Soils

☐ 2. Temporary Covers or Caps
☐ 4. Temporary Water Supplies
☐ 6. Temporary Evacuation or Relocation of Residents
☐ 8. Fencing and Sign Posting
☐ 10. Soil Vapor Extraction
☐ 12. Air Sparging

☐ a. Re-use, Recycling or Treatment ☐ i. On Site Estimated volume in cubic yards ______

☐ ii. Off Site Estimated volume in cubic yards ______

iia. Facility Name: ______ Town : ______ State: ______

iib. Facility Name: ______ Town : ______ State: ______

iii. Describe: ______

☐ b. Store ☐ i. On Site Estimated volume in cubic yards ______

ii. Off Site Estimated volume in cubic yards ______

iia. Facility Name: ______ Town : ______ State: ______

iib. Facility Name: ______ Town : ______ State: ______

D. DESCRIPTION OF RESPONSE ACTIONS (cont.): (check all that apply, for volumes list cumulative amounts)

☐ c. Landfill

☐ i. Cover Estimated volume in cubic yards ________

Facility Name: ________ Town : ________ State: ____

☐ ii. Disposal Estimated volume in cubic yards ________

Facility Name: ________ Town : ________ State: ____

☐ 14. Removal of Drums, Tanks or Containers:

a. Describe Quantity and Amount: ________

b. Facility Name: ________ Town : ________ State: ____

c. Facility Name: ________ Town : ________ State: ____

☐ 15. Removal of Other Contaminated Media:

a. Specify Type and Volume: ________

b. Facility Name: ________ Town : ________ State: ____

c. Facility Name: ________ Town : ________ State: ____

☐ 16. Other Response Actions:

Describe: ________

☐ 17. Use of Innovative Technologies:

Describe: ________

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BWSC105

Release Tracking Number
4 - 17825

E. LSP SIGNATURE AND STAMP :

I attest under the pains and penalties of perjury that I have personally examined and am familiar with this transmittal form, including any and all documents accompanying this submittal. In my professional opinion and judgment based upon application of (i) the standard of care in 309 CMR 4.02(1), (ii) the applicable provisions of 309 CMR 4.02(2) and (3), and 309 CMR4.03(2), and (iii) the provisions of 309 CMR 4.03(3), to the best of my knowledge, information and belief,

> *if Section B of this form indicates that an* ***Immediate Response Action Plan*** *is being submitted*, the response action(s) that is (are) the subject of this submittal (i) has (have) been developed in accordance with the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000, (ii) is (are) appropriate and reasonable to accomplish the purposes of such response action(s) as set forth in the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000 and (iii) complies(y) with the identified provisions of all orders, permits, and approvals identified in this submittal;

> *if Section B of this form indicates that an* ***Imminent Hazard Evaluation*** *is being submitted*, this Imminent Hazard Evaluation was developed in accordance with the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000, and the assessment activity(ies) undertaken to support this Imminent Hazard Evaluation complies(y) with the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000;

> *if Section B of this form indicates that an* ***Immediate Response Status Report*** *is being submitted*, the response action(s) that is (are) the subject of this submittal (i) is (are) being implemented in accordance with the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000, (ii) is (are) appropriate and reasonable to accomplish the purposes of such response action(s) as set forth in the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000 and (iii) complies(y) with the identified provisions of all orders, permits, and approvals identified in this submittal;

> *if Section B of this form indicates that an* ***Immediate Response Action Completion Statement*** *or a request to* ***Terminate an Active Remedial System or Response Action(s) Taken to Address an Imminent Hazard*** *is being submitted*, the response action(s) that is (are) the subject of this submittal (i) has (have) been developed and implemented in accordance with the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000, (ii) is (are) appropriate and reasonable to accomplish the purposes of such response action(s) as set forth in the applicable provisions of M.G.L. c. 21E and 310 CMR 40.0000 and (iii) complies(y) with the identified provisions of all orders, permits, and approvals identified in this submittal.

I am aware that significant penalties may result, including, but not limited to, possible fines and imprisonment, if I submit information which I know to be false, inaccurate or materially incomplete.

1. First Name: James
2. Last Name: Decoulos
3. Telephone: (617) 489-7795
4. Ext.:
5. FAX: (877) 842-9629
6. Signature:
7. Date: 4/21/04
8. LSP #: 9360
9. LSP Stamp: JAMES J. DECOULOS No. 9360

Massachusetts Department of Environmental Protection
Bureau of Waste Site Cleanup

IMMEDIATE RESPONSE ACTION (IRA) TRANSMITTAL FORM Pursuant to 310 CMR 40.0424 - 40.0427 (Subpart D)

BWSC105

Release Tracking Number
4 - 17825

F. PERSON UNDERTAKING IRA:

1. Check all that apply: ☐ a. change in contact name. ☐ b. change of address ☐ c. change in the person undertaking response actions

2. Name of Organization: Eagle Gas, Inc.

3. Contact First Name: Najib 4. Last Name: Badaoui

5. Street: 131 Main Street 6. Title: President

7. City/Town: Carver 8. State: MA 9. ZIP Code: 02347-0000

10. Telephone: (508) 866-9098 11. Ext.: 12. FAX:

G. RELATIONSHIP TO RELEASE OR THREAT OF RELEASE OF PERSON UNDERTAKING IRA:

☑ 1. RP or PRP ☑ a. Owner ☐ b. Operator ☐ c. Generator ☐ d. Transporter

☐ e. Other RP or PRP Specify:

☐ 2. Fiduciary, Secured Lender or Municipality with Exempt Status (as defined by M.G.L. c. 21E, s. 2)

☐ 3. Agency or Public Utility on a Right of Way (as defined by M.G.L. c. 21E, s. 5(j))

☐ 4. Any Other Person Undertaking IRA Specify Relationship:

H. REQUIRED ATTACHMENT AND SUBMITTALS:

☐ 1. Check here if any Remediation Waste, generated as a result of this IRA, will be stored, treated, managed, recycled or reused at the site following submission of the IRA Completion Statement. If this box is checked, you must submit one of the following plans, along with the appropriate transmittal form.

☐ A Release Abatement Measure (RAM) Plan (BWSC106) ☐ Phase IV Remedy Implementation Plan (BWSC108)

☐ 2. Check here if the Response Action(s) on which this opinion is based, if any, are (were) subject to any order(s), permit(s) and/or approval(s) issued by DEP or EPA. If the box is checked, you MUST attach a statement identifying the applicable provisions thereof.

☐ 3. Check here to certify that the Chief Municipal Officer and the Local Board of Heath have been notified of the implementation of an Immediate Response Action taken to control, prevent, abate or eliminate an Imminent Hazard.

☐ 4. Check here to certify that the Chief Municipal Officer and the Local Board of Heath have been notified of the submittal of a Completion Statement for an Immediate Response Action taken to control, prevent, abate or eliminate an Imminent Hazard.

☐ 5. Check here if any non-updatable information provided on this form is incorrect, e.g. Site Address/Location Aid. Send corrections to the DEP Regional Office.

☑ 6. Check here to certify that the LSP Opinion containing the material facts, data, and other information is attached.

Massachusetts Department of Environmental Protection
Bureau of Waste Site Cleanup

BWSC105

IMMEDIATE RESPONSE ACTION (IRA) TRANSMITTAL FORM

Pursuant to 310 CMR 40.0424 - 40.0427 (Subpart D)

Release Tracking Number
4 - 17825

I. CERTIFICATION OF PERSON UNDERTAKING IRA:

1. I, Najib Badaoui, attest under the pains and penalties of perjury (i) that I have personally examined and am familiar with the information contained in this submittal, including any and all documents accompanying this transmittal form, (ii) that, based on my inquiry of those individuals immediately responsible for obtaining the information, the material information contained in this submittal is, to the best of my knowledge and belief, true, accurate and complete, and (iii) that I am fully authorized to make this attestation on behalf of the entity legally responsible for this submittal. I/the person or entity on whose behalf this submittal is made am/is aware that there are significant penalties, including, but not limited to, possible fines and imprisonment, for willfully submitting false, inaccurate, or incomplete information.

2. By: ______________________ Signature

3. Title: President

4. For: Eagle Gas, Inc.
(Name of person or entity recorded in Section F)

04/21/2004
(mm/dd/yyyy)

☐ 5. Check here if the address of the person providing certification is different from address recorded in Section F.

6. Street: ______

7. City/Town: ______ 8. State: ______ 9. ZIP Code: ______

10. Telephone: ______ 11. Ext.: ______ 12. FAX: ______

YOU MUST LEGIBLY COMPLETE ALL RELEVANT SECTIONS OF THIS FORM OR DEP MAY RETURN THE DOCUMENT AS INCOMPLETE. IF YOU SUBMIT AN INCOMPLETE FORM, YOU MAY BE PENALIZED FOR MISSING A REQUIRED DEADLINE.

Date Stamp (DEP USE ONLY:)

2.0 BACKGROUND

On January 21, 2004 an Immediate Response Action (IRA) Plan was submitted to the Department for Release Tracking Number (RTN) 4-17825. The IRA Plan was filed in response to NON-SE-03-3T-109.

The Department requested a modification of the IRA Plan on April 5, 2004. The following proposed scope of work follows the guidelines set forth in the April 5th request together with on-going discussions with Department representatives.

2.1 Site Description

The property is identified as the Eagle Gas Station at 131 Main Street in Carver, Massachusetts and the deed for the property is recorded at the Plymouth Registry of Deeds in Book 15615, Page 160 (the Site) (see locus on Figure 1).

According to the U.S. Geological Survey (USGS) map of Plympton, Massachusetts dated 1990, the Site is located approximately 99 meters above the National Geodetic Vertical Datum of 1929 (NGVD) with horizontal coordinates within the Universal Transverse Mercator (UTM) system at coordinates 4,638,246 mN, and 190,353,296 mE.

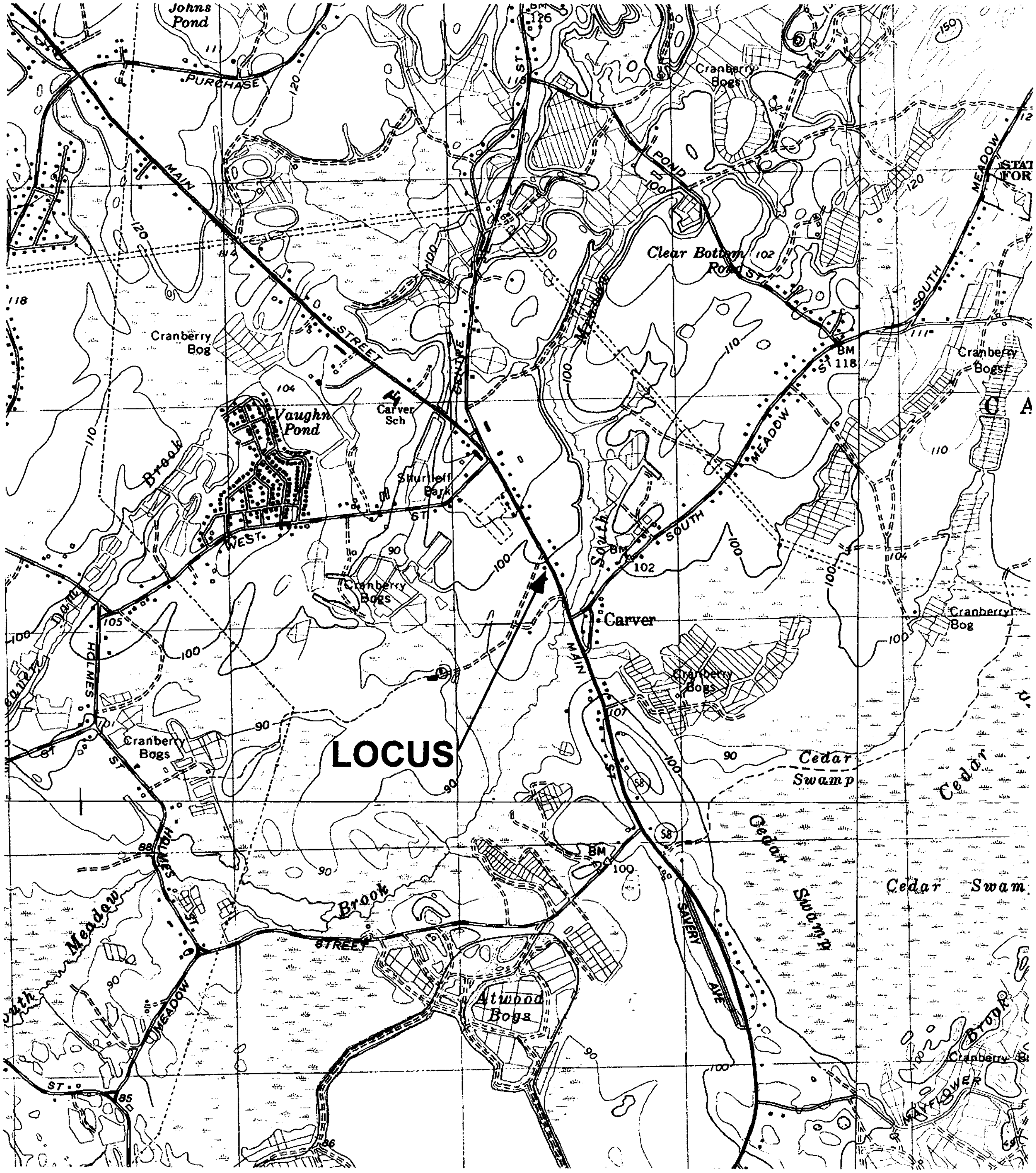
The Site has also been mapped by the Carver Department of Public Works (CDPW). The horizontal control for the mapping is the Massachusetts State Plane Coordinate System and vertical control is in NGVD. Mapping from the CDPW has been scanned and digitized into AutoCAD. The modified plan showing the Site overlayed on the CDPW mapping is provided on Sheet 1 (see Appendix A).

The Flood Insurance Rate Map (FIRM) for the Town of Carver from the Federal Emergency Management Agency (FEMA) shows vertical control in the Site area in the NGVD system on Community Panel Number 250262 0009 B. The closest vertical control is identified as RM 4 with an elevation of 101.87 on a concrete monument along South Meadow Road (see Appendix B).

Approximately 264.55 feet of frontage lies on Main Street. Main Street is a public right of way owned by the Town of Carver. Main Street is also known as Route 58, as it was once under the control of the Massachusetts Highway Department. Entrance onto the Site can be gained along most of the frontage on Main Street.

2.2 Current Use

Eagle Gas, Inc. (Eagle), the current operator of the gas station on Site, operates and maintains four double walled, underground storage tanks (USTs) on Site. Three of the USTs store gasoline; each have a capacity of 5,000 gallons; and, are located underneath the southerly portion of the existing concrete pad. The third UST, with a capacity of 4,000 gallons, stores diesel fuel and is located under the northerly portion of the concrete pad. The public gas station distributes fuel for automobiles and trucks.



REFERENCE:

USGS QUADRANGLES
PLYMPTON, MA 1990
PLYMOUTH, MA 1974
SNIPATUIT POND, MA 1990
WAREHAM, MA 0972
SCALE: 1:25,000

LOCUS MAP

FIGURE 1

DECOULOS & COMPANY

UST tightness tests have been periodically conducted on Site and the results have continued to demonstrate that the UST system is tight. The entire UST system is monitored and automatically gauged by a Veeder-Root TLS-350 Monitoring System. A remote diesel supply line (used to fill the diesel UST with product) was found to be insecure in May of 2003 and immediately taken out of service. Filling for the diesel UST now occurs directly over the UST.

Eagle Gas, Inc. also operates a general automotive repair business at the two story concrete and wood building on Site. One bay is located in the southern portion of the building for general vehicle repairs. No floor drains exist within the bay area.

An unoccupied apartment exists on the second floor of the gas station building. According to a septic system design plan by Webby Engineering Associates, Inc. of Plympton, MA dated June 27, 1998, the apartment contains two bedrooms and a potable drinking water supply well is located in the southwesterly corner of the building. The pump and storage tank for the well are accessed directly from within the vehicle repair shop.

2.3 Current Abutting Uses

A residence is located south of the Site and an access road to a rod and gun club abuts the triangular shaped Site to the north.

3.0 PROPOSED IMMEDIATE RESPONSE ACTION TASKS

Various tasks and a schedule for implementation of each task have been developed. See attached IRA Schedule. The schedule starts on May 6, 2004 and ends on August 26, 2004. The dates shown on the Gantt chart reflect the end dates of each task. The schedule will be updated on August 23, 2004 based upon progress of the proposed tasks. Details of each task are as follows:

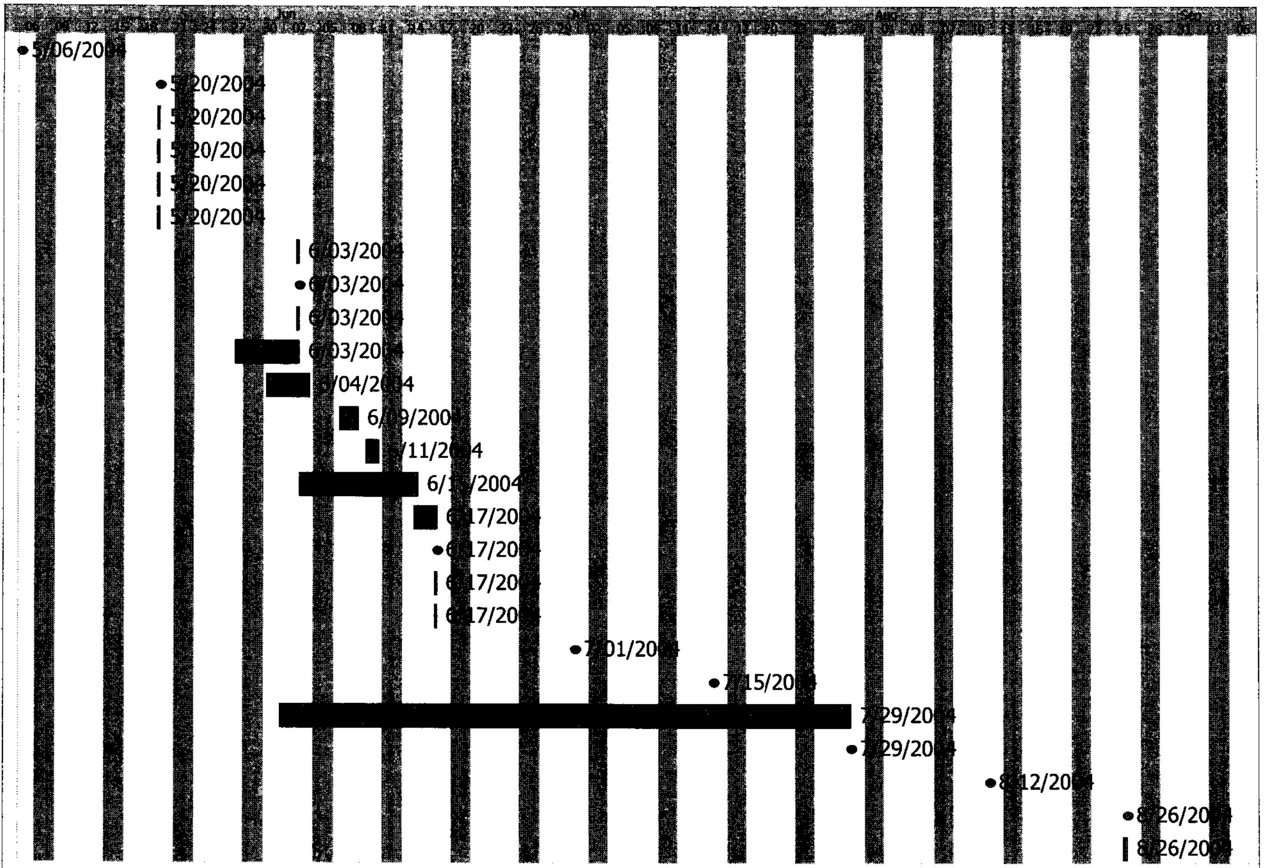
1. Continued inspection and replacement of absorbent booms and pads at the stormwater outfall discharge area to South Meadow Brook. Inspection and necessary replacement shall occur every two weeks on the dates specified in the schedule.

2. Spent booms and pads shall be placed in 55 gallon drums located in close vicinity to the outfall. The disposal and replenishment of clean drums has been scheduled for June 17, 2004 and August 26, 2004.

3. The sampling of surface water at the outfall basin and within South Meadow Brook shall occur on or about May 20, 2004. The surface water shall be field screened for temperature, conductivity and pH and laboratory analyzed for Extractable Petroleum Hydrocarbons (EPH) and semi-volatile organic compounds by EPA method 8270. Two surface water samples shall be collected in the outfall basin and two surface water samples shall be collected within South Meadow Brook. One of the samples within the Brook shall be collected at the intersection of the Brook centerline and the projected outfall line. The other brook sample shall be collected at the centerline of the Brook just east of Main Street.

Immediate Response Action Schedule - DEP RTN 4-17825

Description	
Inspect and Replace Booms and Pads at Outfall	5/06/2004
Inspect and Replace Booms and Pads at Outfall	5/20/2004
Surface Water Sampling @ South Meadow Brook	5/20/2004
Sediment Sampling @ Outfall and within Brook	5/20/2004
Soil Sampling of BVW to South Meadow Brook	5/20/2004
Groundwater Mon Well Sampling @ Eagle plus	5/20/2004
Stabilize Sediment Discharge from Outfall Basin	6/03/2004
Inspect and Replace Booms and Pads at Outfall	6/03/2004
Level Survey Traverse from FEMA Benchmark	6/03/2004
App to Buzzards Bay Estuary Program	6/03/2004
App to CZM for CPR Grant	6/04/2004
Forensic Assessment of Soil, Sediment and Water Data	6/09/2004
ZBA App to Permit Canopy and Oil/Water Separator	6/11/2004
Imminent Hazard Evaluation	6/1[illegible]/2004
Preparation of NOI to Carver Con Com	6/17/2004
Inspect and Replace Booms and Pads at Outfall	6/17/2004
Video Inspection Survey of Stormwater System	6/17/2004
Disposal of 55 gal Drums of Spent Pads/Booms	6/17/2004
Inspect and Replace Booms and Pads at Outfall	7/01/2004
Inspect and Replace Booms and Pads at Outfall	7/15/2004
Remediation Plan to Eliminate Stormwater Contamination	7/29/2004
Inspect and Replace Booms and Pads at Outfall	7/29/2004
Inspect and Replace Booms and Pads at Outfall	8/12/2004
Inspect and Replace Booms and Pads at Outfall	8/26/2004
Disposal of 55 gal Drums of Spent Pads/Booms	8/26/2004



4. The sampling of sediment at the outfall basin shall occur on or about May 20, 2004. The sediment shall be screened for grain size distribution and laboratory analyzed for EPH; semi-volatile organic compounds by EPA method 8270; RCRA 8 metals; poly-cholorinated biphenyls (PCBs); and, total organic carbon (TOC). Three sediment samples shall be collected in the outfall basin and two sediment samples shall be collected within South Meadow Brook. One of the sediment samples within the Brook shall be collected at the intersection of the Brook centerline and the projected outfall line. The other brook sediment sample shall be collected at the centerline of the Brook just east of Main Street.

5. The sampling of soil within the bordering vegetated wetland (BVW) in proximity to the outfall shall occur on or about May 20, 2004. Two composite soil samples shall be collected at depths between 6 and 12 inches and laboratory analyzed for EPH; semi-volatile organic compounds by EPA method 8270; RCRA 8 metals; PCBs; and, TOC.

6. The sampling of groundwater monitoring wells KEI-4, KEI-5, BP-1, BP-2, BP-3, BP-4, DCW-1, DCW-2 and DCW-3 shall occur on or about May 20, 2004. All of the samples shall be analyzed for EPH and volatile petroleum hydrocarbons (VPH). Wells DCW-2 and BP-4 shall also be analyzed for semi-volatile organic compounds by EPA method 8270 and RCRA 8 metals.

7. The stabilization of contaminated sediment from traveling into South Meadow Brook shall occur no later than June 3, 2004. This work will involve placing sand bags at the intersection of the outfall basin with South Meadow Brook. A silt curtain shall also be laid adjacent to the sand bags, on the outfall basin side, to prevent contaminated suspended particles from migrating into South Meadow Brook.

8. A level survey traverse shall be run from FEMA benchmark RM-4, as shown on FIRM panel number 250262 0009 B, to the Site locus to allow for elevation data to be tied into the NGVD system. This work shall be conducted no later than June 3, 2004.

9. An application shall be submitted to the Buzzards Bay Project National Estuary Program for the Buzzards Bay Watershed, Wetlands and Open Space Protection Grant Program. The deadline for filing is June 3, 2004. The application shall be filed by the Town of Carver and Eagle shall provide support for Town representatives in preparing the application. See program information in Appendix C.

10. An application shall be submitted to the Massachusetts Coastal Zone Management for the Coastal Pollutant Remediation Grant Program. The deadline for filing is June 4, 2004. The application shall be filed by the Town of Carver and Eagle shall provide support for Town representatives in preparing the application. See program information in Appendix D.

11. A forensic geochemistry assessment of water, sediment and soil data shall be conducted. "Peak Area Reports" shall be provided from the laboratory, based on the EPH and VPH data, that present the normal alkanes, isoprenoids (IPs) and unresolved complex mixtures (UCMs) of the petroleum hydrocarbons. Information on these assessment techniques are presented in papers compiled in Appendix E.

12. An application shall be filed to the Carver Zoning Board of Appeals (ZBA) to permit the construction of an overhead canopy and the installation of an oil/water separator that discharges into the Town's municipal stormwater collection system. Information on the separator is provided in Appendix F. The application shall be filed no later than June 11, 2004. The oil/water separator shall be designed to collect all runoff from the easterly portion of the Site. The outlet for the separator shall be fitted with an alarm that will activate if oil is detected flowing into the Town's drain manhole.

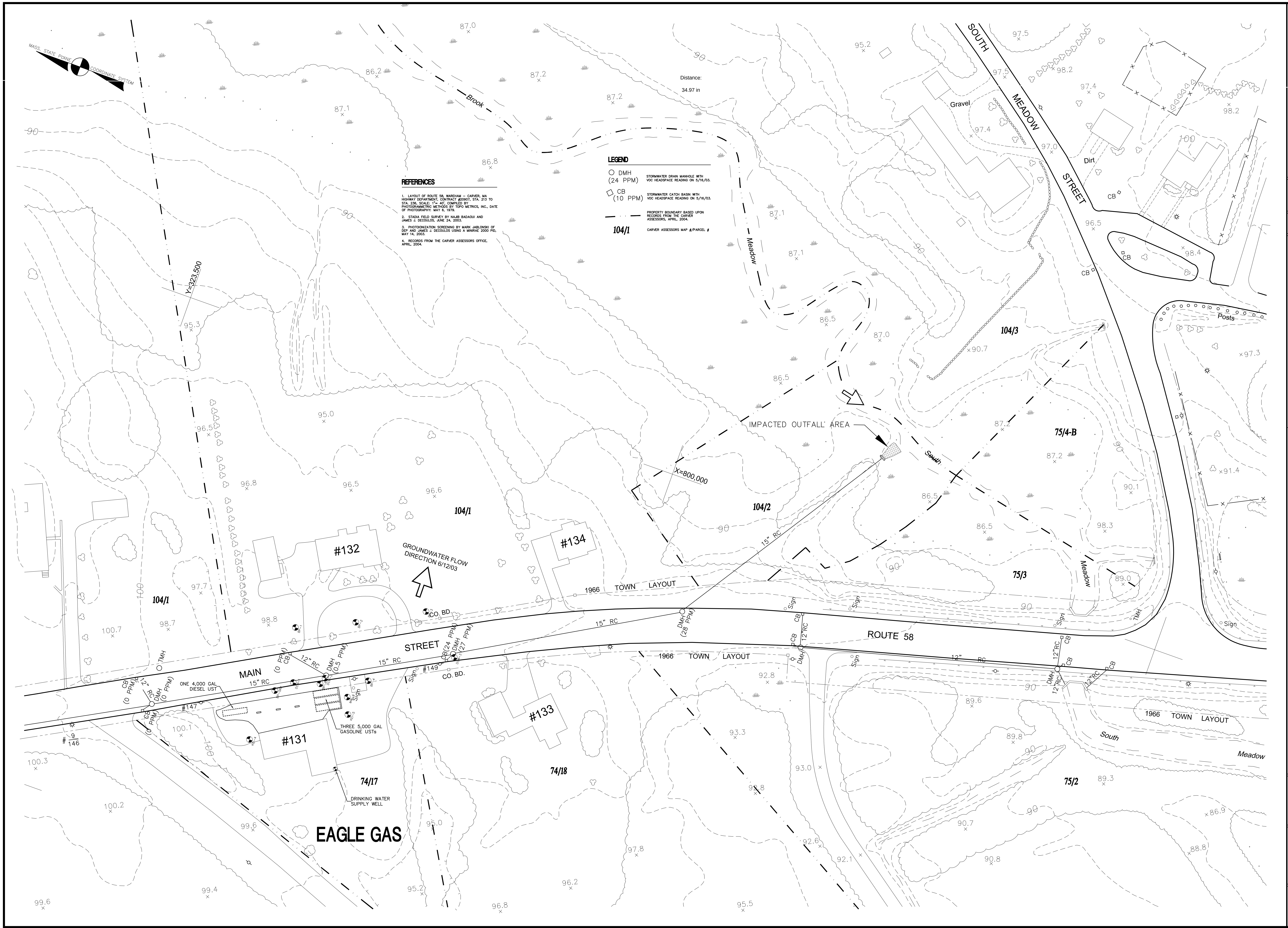
13. An Imminent Hazard Evaluation shall be conducted and submitted to the Department no later than June 15, 2004.

14. Conceptual remediation plans to eliminate the stormwater contamination to South Meadow Brook shall begin on June 1, 2004 and continue through the end of July. The planning will seek input from Department personnel, Town officials and representatives of the Cape Cod Cranberry Growers' Association.

15. A Notice of Intent (NOI), under the provisions of G.L. c. 131, § 40 and the Carver Wetland Bylaws, shall be filed with the Carver Conservation Commission and the Department no later than June 17, 2004. The NOI shall describe all anticipated actions within the regulated wetland areas that will eliminate the source of contamination and restore the utilities and environment to a suitable condition.

16. A video inspection of the stormwater collection system shall be conducted on or about June 17, 2004. The inspection shall begin at the outfall and video tape the entire collection system up to the drain manhole just south of the entrance to the Rod and Gun Club.

APPENDIX A
EXISTING CONDITIONS PLAN, SHEET 1



REFERENCES

1. LAYOUT OF ROUTE 58, WAREHAM – CARVER, MA HIGHWAY DEPARTMENT, CONTRACT #20907, STA. 213 TO STA. 236, SCALE: 1"= 40', COMPILED BY PHOTOGRAMMETRIC METHODS BY TOPO METRICS, INC., DATE OF PHOTOGRAPHY: MAY 6, 1979.

2. STADIA FIELD SURVEY BY NAJIB BADAOUI AND JAMES J. DECOULOS, JUNE 24, 2003.

3. PHOTOIONIZATION SCREENING BY MARK JABLONSKI OF DEP AND JAMES J. DECOULOS USING A MINIRAE 2000 PID, MAY 14, 2003.

4. RECORDS FROM THE CARVER ASSESSORS OFFICE, APRIL, 2004.

LEGEND

○ DMH (24 PPM)	STORMWATER DRAIN MANHOLE WITH VOC HEADSPACE READING ON 5/16/03.
◇ CB (10 PPM)	STORMWATER CATCH BASIN WITH VOC HEADSPACE READING ON 5/16/03.
— · —	PROPERTY BOUNDARY BASED UPON RECORDS FROM THE CARVER ASSESSORS, APRIL, 2004.
104/1	CARVER ASSESSORS MAP #/PARCEL #

REVISION	DATE	NO.

DECOULOS & COMPANY
3 ELECTRONICS AVE, DANVERS, MA 01923
WWW.DECOULOS.COM
617 489 7795

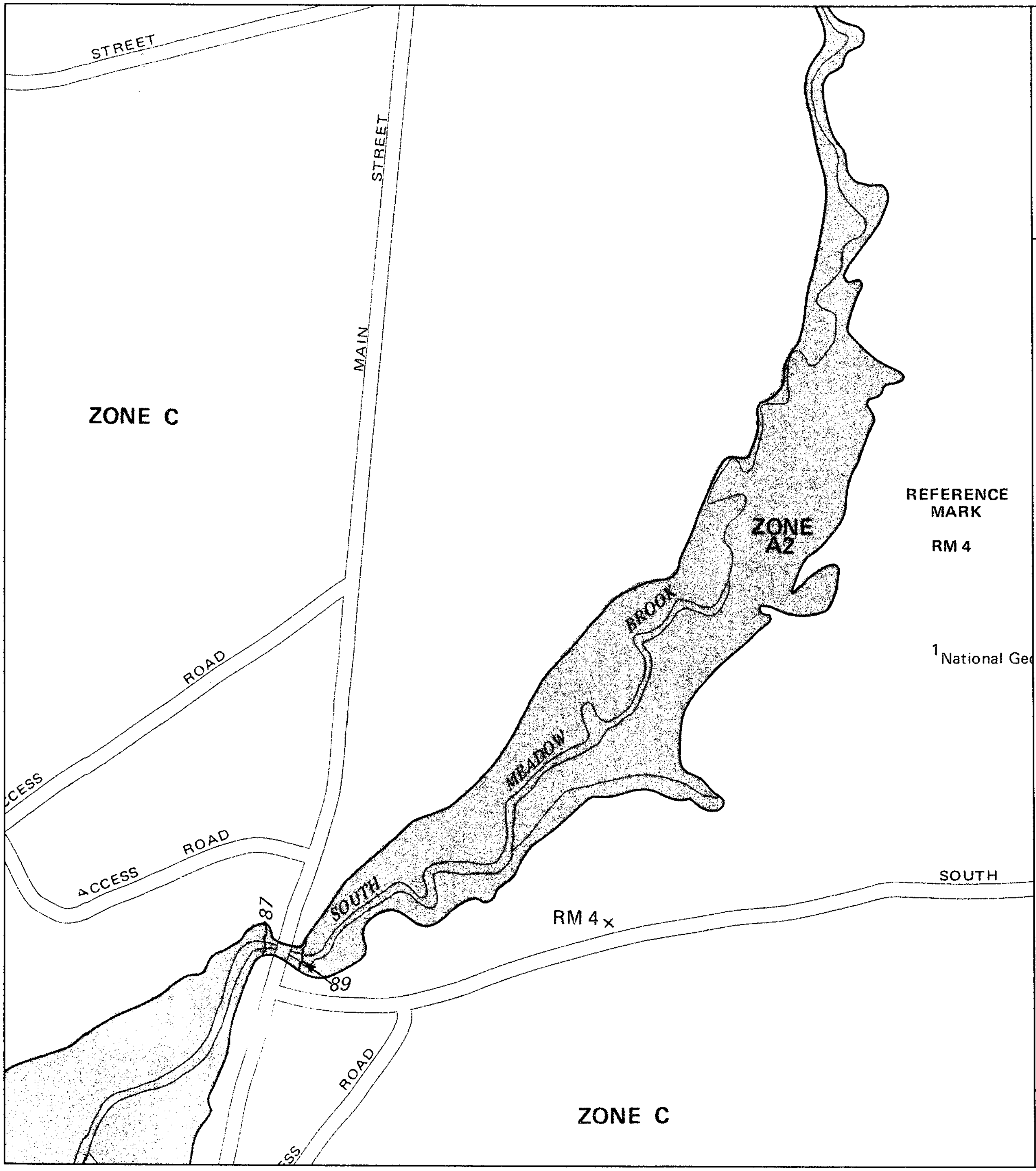
EXISTING CONDITIONS
EAGLE GAS STATION
CARVER, MASSACHUSETTS

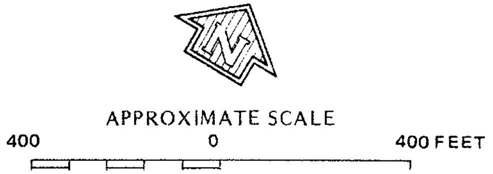
DATE
APR 2004
SCALE
1"= 40'

DRWN TCM
DES JJD
CHKD JJD
APRVD JJD

SHEET NO.
1

APPENDIX B
FLOOD INSURANCE RATE MAP





NATIONAL FLOOD INSURANCE PROGRAM

FIRM
FLOOD INSURANCE RATE MAP

TOWN OF
CARVER,
MASSACHUSETTS
PLYMOUTH COUNTY

PANEL 9 OF 20
(SEE MAP INDEX FOR PANELS NOT PRINTED)

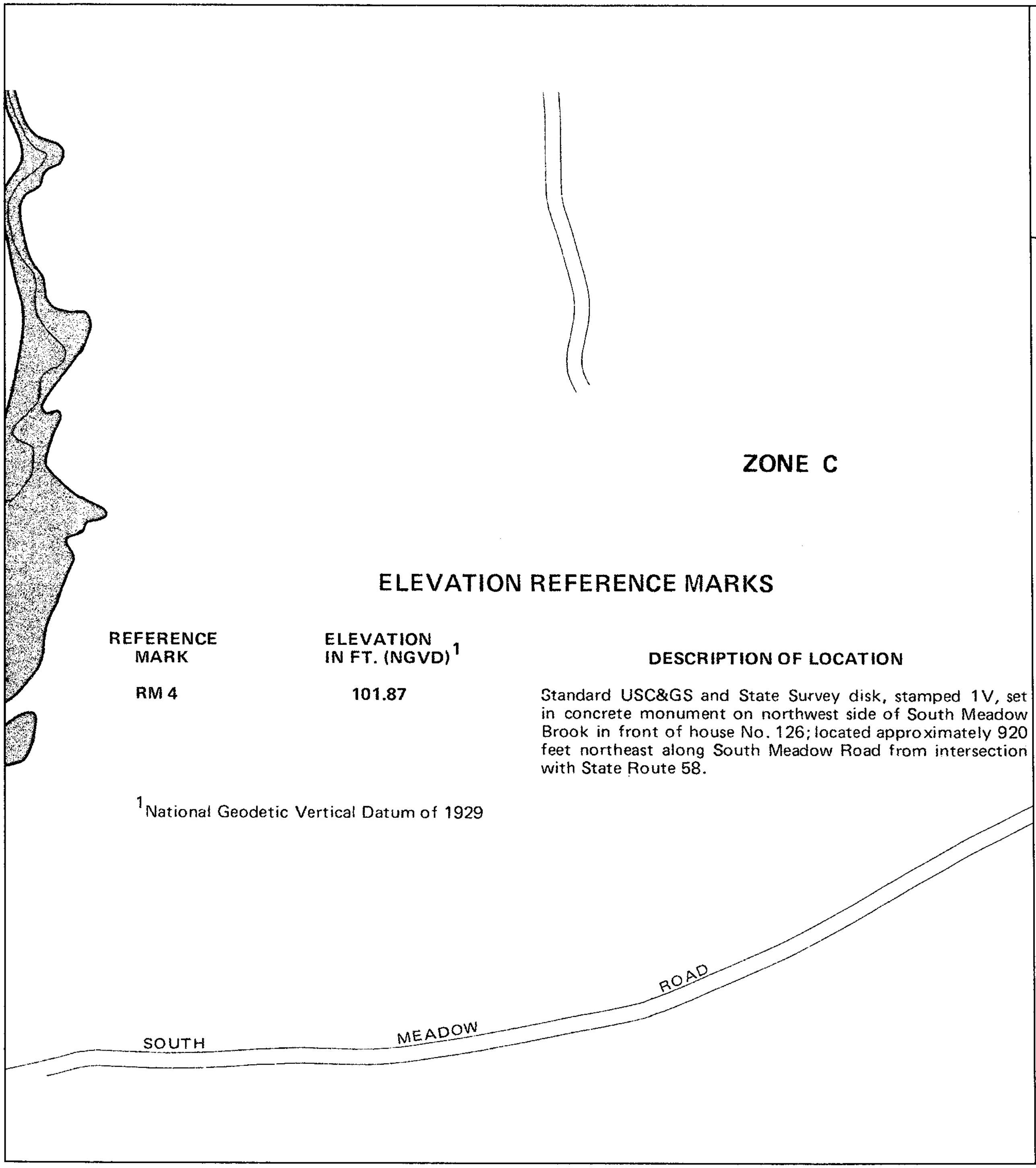
COMMUNITY-PANEL NUMBER
250262 0009 B

EFFECTIVE DATE:
JULY 19, 1982

Federal Emergency Management Agency

This is an official copy of a portion of the above referenced flood map. It was extracted using F-MIT Version 1.0. This map does not reflect changes or amendments which may have been made subsequent to the date on the title block. Futher information about National Flood Insurance Program flood hazard maps is available at www.fema.gov/mit/tsd.

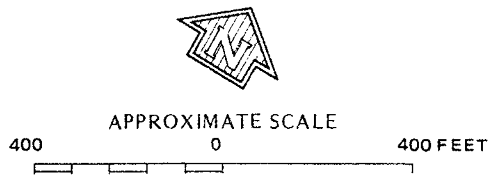
Print Date: 5/4/2004 (printed at scale and type A)



ELEVATION REFERENCE MARKS

REFERENCE MARK	ELEVATION IN FT. (NGVD)[1]	DESCRIPTION OF LOCATION
RM 4	101.87	Standard USC&GS and State Survey disk, stamped 1V, set in concrete monument on northwest side of South Meadow Brook in front of house No. 126; located approximately 920 feet northeast along South Meadow Road from intersection with State Route 58.

[1] National Geodetic Vertical Datum of 1929



NATIONAL FLOOD INSURANCE PROGRAM

FIRM
FLOOD INSURANCE RATE MAP

TOWN OF
CARVER,
MASSACHUSETTS
PLYMOUTH COUNTY

PANEL 9 OF 20
(SEE MAP INDEX FOR PANELS NOT PRINTED)

COMMUNITY-PANEL NUMBER
250262 0009 B

EFFECTIVE DATE:
JULY 19, 1982

Federal Emergency Management Agency

APPENDIX C

BUZZARDS BAY WATERSHED, WETLANDS AND OPEN SPACE PROTECTION GRANT PROGRAM

Buzzards Bay Project
National Estuary Program

April 14, 2004

Distribution: Boards of Selectmen, Buzzards Bay Action Committee Representatives, Shellfish Officers, Conservation Commissions, Planning Boards, Boards of Health, Oil Spill Coordinators

Re: 2004 Municipal Mini-Grants available

Dear Municipal Official:

In accordance with a Cooperative Agreement with the US EPA, the Buzzards Bay Project National Estuary Program is providing interested Buzzards Bay watershed municipalities with $125,000 of its federal funds to assist eligible Buzzards Bay watershed municipalities implement environmental restoration and protection projects. Municipalities can use these funds to protect open space or rare and endangered species habitat, conduct land surveys in support of those activities, restore freshwater and saltwater wetlands including tidally restricted salt marshes, purchase oil spill containment equipment, restore fish runs, and to remediate stormwater discharges threatening water quality. The funds will be distributed in the following categories:

- Oil Spill containment boom and oil spill response supplies: $15,000 total dollar amount will be divided equally among all interested municipalities However, because of the small dollar amount in this category, the Buzzards Bay Project is seeking one municipality to be the sole applicant to act as a clearing house for all interested municipalities. Such a single application will need a letter of endorsement from a representative from each participating municipality.
- Stormwater Remediation or Management: $40,000 total, no more than $20,000 per municipality
- Herring Run Restoration: $20,000 total in category, no more than $20,000 per municipality
- Wetland and open space habitat restoration/preservation/acquisition: $50,000 total in category, no more than $20,000 per municipality

Enclosed is the complete application package. Only projects located principally in the Buzzards Bay watershed are eligible for funding. For land acquisitions and restoration projects, we encourage partnerships with land trusts and other not for profit organizations.

Grant applications, and questions about the application must be submitted in writing to Sarah Williams, Municipal Grant Coordinator, Buzzards Bay Project National Estuary Program, 2870 Cranberry Highway, East Wareham, MA 02538. For your convenience, questions about the solicitation can be emailed to sarah.williams@state.ma.us.

Sincerely,

Joseph E. Costa

Joseph E. Costa, Ph.D.
Executive Director

RECEIVED
4-20-04

2870 Cranberry Highway, East Wareham, Massachusetts 02538 (508) 291-3625 Facsimile (508) 291-3628 http://www.capecod.net/~menviron

The Buzzards Bay Project is sponsored by the U.S. Environmental Protection Agency and the Massachusetts Executive Office of Environmental Affairs through the Coastal Zone Management Office.

EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS
OFFICE OF COASTAL ZONE MANAGEMENT
BUZZARDS BAY PROJECT NATIONAL ESTUARY PROGRAM

REQUEST FOR RESPONSES (RFR)

MUNICIPAL GRANT PROGRAM
BUZZARDS BAY WATERSHED WETLANDS & OPEN SPACE PROTECTION GRANTS

FISCAL YEAR 2005
April 14, 2004

ENV 04 CZM 09

Post Date: April 14, 2004 Close Date: June 3, 2004 Value: $125,000

Contact Person: Sarah Williams, Municipal Grant Coordinator
Address: Buzzards Bay Project National Estuary Program
2870 Cranberry Highway
East Wareham, MA 02538
fax: 508-291-3628
email: sarah.williams@state.ma.us

Summary

The Executive Office of Environmental Affairs, through the Buzzards Bay Project National Estuary Program in the Office of Coastal Zone Management, announces that funding is available to assist eligible Buzzards Bay watershed municipalities in the protection of open space, rare and endangered species habitat, and freshwater and saltwater wetlands, and to help restore tidally restricted salt marshes, to purchase oil spill containment equipment, to restore fish runs, and to remediate stormwater discharges threatening water quality. This work is being conducted in accordance with a Cooperative Agreement with the US EPA using federal funds.

Introduction

The Buzzards Bay Project National Estuary Program[1] has allocated $125,000 of federal grants, to assist interested Buzzards Bay watershed municipalities in the protection of open space, rare and endangered species habitat, and freshwater and saltwater wetlands, and to help restore tidally restricted salt marshes, to purchase oil spill containment equipment, to restore fish runs, and to remediate stormwater discharges threatening water quality. These funds have been made available in accordance with US EPA National Estuary Program Cooperative Agreements and are part of an ongoing Buzzards Bay Watershed Municipal Grant Program implemented by the Buzzards Bay Project National Estuary Program.

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[1] The Buzzards Bay Project is an advisory and planning unit of the Massachusetts Office of Coastal Zone Management within the Executive Office of Environmental Affairs. Information about the Buzzards Bay Project is available at www.BuzzardsBay.org.

Eligible Respondents
Eligible towns include Fall River, Westport, Dartmouth, New Bedford, Acushnet, Fairhaven, Rochester, Mattapoisett, Marion, Wareham, Middleborough, Carver, Plymouth, Bourne, Falmouth, and Gosnold. **However, specific restoration and protection projects must lie principally within the Buzzards Bay watershed (see attached map).**

Eligible uses of funds
Projects eligible for funding include but are not limited to:
1) Oil spill containment boom and oil spill response supplies of any type to minimize water quality and habitat impacts of water and land born spills.

2) Stormwater remediation projects, particularly those that treat stormwater to improve water quality in order to open or protect shellfish beds or protect public bathing beaches

3) Herring and anadramous or catadramous fish restoration including, but not limited to, fish ladder improvements and debris or obstruction removal.

4) Wetland and habitat restoration, preservation, acquisition and protection, and upland open space acquisition for habitat protection, conservation and passive recreation purposes, including, but not limited to:

a) Startup or seed money for restoration of wetlands, including development of designs.

b) Appraisals, site evaluations, or professional land surveys of any parcels where wetlands, wetland buffer zones, or endangered species habitats are a major feature. These evaluations are intended for parcels that are expected to be available for public land purchases, permanent conservation restrictions or easements, or purchase by Lands Trust organizations.

c) Appraisals or professional land surveys on any parcels to support the potential purchases of land for wetland habitat restoration, exclusive of projects required by wetland enforcement orders or relating to a wetlands violation under ajudicatory review.

d) Outright municipal purchase of parcels where wetlands, wetland buffer zones, or endangered species habitats are a major feature, and the purchase price of the parcel is $4,000 per acre or less.

e) Municipal acquisition of Conservation Restrictions to permanently protect a parcel from development, particularly on those parcels where wetlands, wetland buffer zones, or endangered species habitat are a major feature. Work may be conducted in partnership with Lands Trusts.

f) Restoration of tidally restricted salt marshes or impaired freshwater wetlands.

Note: Funds may be used to match state grants in any of the aforementioned categories as part of another grant application.

The Buzzards Bay Project recognizes that this level of funding represents a modest contribution to local needs, however, the intent of this grant program is to enable towns to quickly proceed with either appraisals, professional surveys or conservation restriction purchases, or designs, when it is not feasible to wait for Town Meeting funding, or to provide seed funds or match[2] for larger projects. To ensure that the minigrants are directed to a wide range of projects, a minimum dollar

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[2] These are federal funds and can be used to match state funded projects.

amounts and dollar limits will be targeted to the grant categories as follows:

1) Oil Spill containment boom and oil spill response supplies: $15,000 total dollar amount will be divided equally among all interested municipalities However, because of the small dollar amount in this category, the Buzzards Bay Project is seeking one municipality to be the sole applicant to act as a clearing house for all interested municipalities. Such a single application will need a letter of endorsement from a representative from each participating municipality.

2) Stormwater Remediation or Management: $40,000 total, no more than $20,000 per municipality

3) Herring Run Restoration: $20,000 total in category, no more than $20,000 per municipality

4) Wetland and open space habitat restoration/preservation/acquisition: $50,000 total in category, no more than $20,000 per municipality

If insufficient qualifying eligible proposals are submitted to any of the above categories, funds will be directed to the category or categories where there is the greatest need and interest. If their are insufficient qualifying eligible proposals to utilize all funds, remaining funds will be directed to the next Buzzards Bay Project Municipal Minigrant round

Required Match
A match is required, equal to 33% of the grant award. This match can be provided either as cash or in-kind services (e.g., DPW labor, in kind permitting or design work, fees waived, installation, etc.). Match expenditures in support of the project made after January 1, 2004 can be credited toward meeting the match requirement for the proposed project. A statement of final match amount must be provided to receive final payment. However, grant funds may not be used to reimburse any work that may have been done on the project before the actual contracted period.

Inquiries about the RFR
Questions about this RFR can be submitted **in writing** by mail, fax, or email to the Municipal Grant Coordinator through Monday May 17, 2004. Responses to questions, if any, will be sent in writing and posted on the Buzzards Bay Project website www.buzzardsbay.org/funding by May 21, 2004, as well as on www.Comm-Pass.com. These answers are for clarification purposes only and do not constitute an amendment to the RFR unless expressly stated as such.

Proposal Submission
Interested municipalities must submit one copy of the attached two-page application. The application form must be received by the Buzzards Bay Project at 2870 Cranberry Highway, East Wareham, MA 02538 by 4:00 P.M at the above-listed address by Thursday, June 3, 2004.

Municipalities may submit up to one application in each of the four funding areas: 1) oil spill containment, 2) stormwater remediation, 3) Herring or anadramous fish restoration, 4) wetland and habitat protection and restoration and open space protection or acquisition.

Municipalities are also encouraged to consult with or form partnerships with area Lands Trusts to help identify local needs wetland and open space habitat protection. Incomplete or incorrectly submitted applications will be disqualified. Qualified applications will be judged on a competitive basis according to the selection criteria.

Selection Criteria

Grants will be competitively selected based on these criteria:

- Cost effectiveness
- For wetland and habitat protection and acquisition projects: Presence of rare and endangered species, and partnerships formed with other municipalities or Lands Trusts to achieve goals more cost effectively will receive additional weight in the ranking.
- Documented impairments demonstrated by water quality data, closed shellfishing beds, filled wetlands, declining herring catch or counts, etc.
- For salt marsh restoration projects only: Site ranking identified in the report published by the Commonwealth's "Atlas of Tidally Restricted Salt Marshes In Buzzards Bay" dated June 2002 final, available at www.buzzardsbay.org/smatlasmain.htm and previously provided to all eligible municipal conservation commissions, Public Works Departments, and Boards of Selectmen. The applicant may propose a new site not included in the Atlas and justify its proposed priority.
- For stormwater remediation projects only: Site ranking identified in the report published by the Commonwealth's "Atlas of Stormwater Discharges in the Buzzards Bay Watershed" dated August 2003 will represent 15% of the score. The Atlas available at www.buzzardsbay.org and previously provided to all eligible municipal conservation commissions, Public Works Departments, and Boards of Selectmen or requested on CD). The applicant may propose a new site not included in the Atlas and justify its proposed priority.
- Match provided

A review committee composed of Buzzards Bay Project staff will evaluate all proposals on a competitive basis. The review committee may include a non-governmental representative to serve in an advisory role to the committee. The review committee reserves the right to reject any or all proposals that they deem do not meet the intent of the federal Cooperative Agreement under which the funds have been provided.

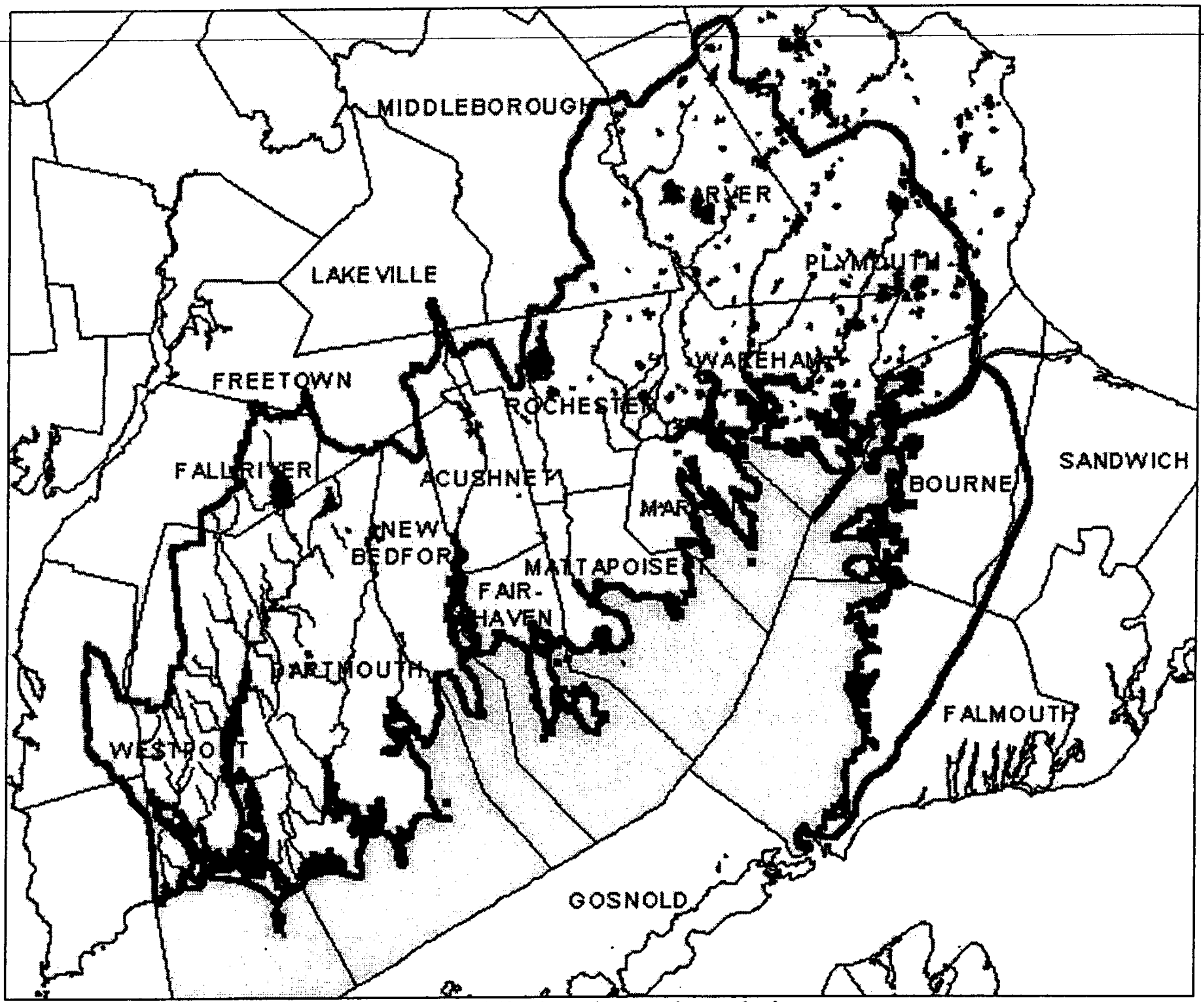
Contract Awards and Administration

After awards are announced, each applicant will receive a written notification from the Buzzards Bay Project. Shortly after the grant announcement, a contract will be executed between the municipality and the Commonwealth. A municipal contact must be identified for contract administration. Selected municipalities will enter into a standard Terms and Condition Contract with the Commonwealth of Massachusetts Executive Office of Environmental Affairs. Contracts must be signed by the appropriate municipal legal authority. Contract funds are awarded on a reimbursement basis for expenditures made during the period of the contract. Payments are wired electronically to municipal accounts by the state Comptroller. All work must be completed by June 30, 2005.

Program Schedule

RFR Release Date:	April 14, 2004
Written inquiries deadline:	May 17, 2004
Application Deadline:	June 3, 2004, 4:00pm
Grant Awards:	After July 1, 2004
Completion/Termination:	June 30, 2005

A copy of this RFR is available from the Buzzards Bay Project website at http://www.buzzardsbay.org and posted on the Comm-PASS website at: http://www.comm-pass.com. The attached Supplemental Terms and Conditions are incorporated into this RFR.



Buzzards Bay watershed boundary (bold line) and town boundaries.

Buzzards Bay Watershed Wetlands and Open Space Protection Grants
Municipal Grant Application
RFR CZM 04-xx

PART I- Proposal Overview

Proposal title: ____

Participating municipality (-ies): ___________________________________

Municipality to administer grant: ___________________________________

Proposal contact: _____________________________ Title: ____________

Phone: _____________ Fax: ____________________

Amount requested: __________ Total Match: __________ (>1/3 of requested)

Location of Proposed Work: _____________________________________

____

Check if true: ___ The town/city of ____________ has previously received grants from DEP, EOEA, CZM, or the Buzzards Bay Project and the necessary signed contract forms[3] are, to the best of our knowledge, on file. (Note: If a form cannot be found on file, it must be completed before a contract can be initiated. These forms are not used in the selection process. A new "Standard Contract Form" and "Contractor Authorized Signature Verification Form" must be completed for each new contract execution.

PART II- Proposal Detail

Proposed Work: (Provide a succinct summary and tasks to be accomplished. Identify the individual/position who will coordinate this work effort. You may attach maps or other information.)

Implementation Strategy: (Describe how the municipality proposes to implement the proposed work (town meeting appropriations, etc.)

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[3] 1. Commonwealth Terms and Conditions. 2. Affirmative Action Plan Form (For Procurements of $50,000 or more), 3. Contractor Mandatory Submissions Form, and 4. Northern Ireland Notice and Certification

Proposed budget for awarded funds (Break down budget by category (materials and supplies, contractual, etc.). If more than one task is proposed, include costs for each task. Proposed contractual services need not be broken down here.

Proposed Match: (Note: Any match expenditures made by the town after January 1, 2004 can be credited to the town's match requirement). Please note that any match claimed below will be considered estimates and not a commitment at this time. Final match will be documented in awarded contracts between the Commonwealth and the municipality.

Cash: ________(a)

In kind: ________(b)

i: Materials and supplies: ________

ii: Administrative and Direct Costs ________

iii. Personnel (list by title, hourly rate, etc.) ________

	Hours	Rate	Total
1)________________	_______	_______	_________
2)________________	_______	_______	_________
3)________________	_______	_______	_________
4)________________	_______	_______	_________
5)________________	_______	_______	_________

TOTAL MATCH (Cash+In kind): ________(a+b)

Explanations, if any:

Any additional supporting information may be attached.

Notes on RFR Mandatory Attachments

In addition to any forms specific to this RFR, we require signed originals of the following Commonwealth of Massachusetts forms before contracts can be initiated. All the forms mentioned below are available for download on the state's web site at the following location: http://www.comm-pass.com/comm-pass/forms.asp. If your municipality has previously received a contract from the Commonwealth, these documents may be on file and need not be submitted by the deadline. If contracts are not on file, they must be completed before a contract is initiated.

1. **Commonwealth Terms and Conditions.** If the Bidder has already executed and filed the **Commonwealth Terms and Conditions,** please indicate this in your Response. The Commonwealth Terms and Conditions shall be incorporated by reference into any Contract executed pursuant to this RFR. A Bidder is required to execute the Commonwealth Terms and Conditions only once. *Please note, in addition to the* ***Commonwealth Terms and Conditions****, upon execution of a final contract the* ***EOEA Supplemental Terms and Conditions*** *are in effect.*

2. All Bidders must also complete, execute and return the **Standard Contract Form upon selection for Contract negotiation and execution**. By executing the Standard Contract Form, the Contractor certifies under the pains and penalties of perjury that it has submitted a Response to a Request for Response (RFR) issued by the Department and that this Response is the Contractor's offer as evidenced by the execution by the Contractor's authorized signatory, that the Contractor's Response may be subject to negotiation by the Department, and that the terms of the RFR, the Contractor's Response and any negotiated terms shall be deemed accepted by the Department and included as part of the Contract upon execution of the Standard Contract Form by the Department's authorized signatory.

3. **W-9 Request for Verification of Taxation Reporting Information** must be completed by all new vendors who wish to conduct business with the Commonwealth and each time a vendor change occurs, including address, vendor name, etc.

4. **Contractor Authorized Signature Verification Form**
5. **Affirmative Action Plan Form** (For Procurements of $50,000 or more)
6. **Northern Ireland Notice and Certification**
7. **Business Reference Form** (For bidder's completion if references are required by the RFR)
8. **Affirmative Action Market Form**

The attached Supplemental Terms and Conditions are incorporated into this RFR.

Request for Responses (RFR) Supplemental Terms and Conditions

1. For the purposes of these *Supplemental Terms and Conditions*, Department shall mean the Executive Office of Environmental Affairs (EOEA) and the office requesting Responses as identified within this RFR.
2. These *Supplemental Terms and Conditions* are incorporated by reference into this RFR. If any amendment, attachment [not including the Commonwealth's *Standard Terms and Conditions, Standard Form Contract*, or any other form jointly published by the Executive Office for Administration and Finance (EOAF), the Office of the Comptroller (CTR) and the Operational Services Division (OSD), or any provision or form required by State or Federal law] or other part of this RFR deletes, modifies, ~~replaces or otherwise contains language that conflicts with these *Supplemental Terms and Conditions*, these *Supplemental*~~ *Terms and Conditions* shall supersede and control to the extent necessary to accomplish these conditions. The remaining provisions of this RFR shall remain in effect and enforced to the fullest extent permitted.
3. The Commonwealth's *Standard Terms and Conditions* [as currently and jointly issued by EOAF, CTR, and OSD] are incorporated by reference into this RFR. To the extent that any amendment, attachment, condition or other part of this RFR deletes, modifies, replaces or otherwise contains language that conflicts with the Commonwealth's *Standard Terms and Conditions*, the official printed language of the Commonwealth's *Standard Terms and Conditions* shall supersede and control to the extent necessary to accomplish its conditions. The remaining provisions of this RFR shall remain in effect and enforced to the fullest extent permitted.
4. The terms of 801 CMR 21.00: Procurement of Commodities and Services (and 808 CMR 1.00: Compliance, Reporting and Auditing for Human and Social Services, if applicable) are incorporated by reference into this RFR. Words used in this RFR shall have the meanings defined in 801 CMR 21.00 (and 808 CMR 1.00, if applicable). Additional definitions may also be identified in this RFR. Unless otherwise specified in this RFR, all communications, Responses, and documentation must be in English, all measurements must be provided in feet, inches, and pounds and all cost proposals or figures in U.S. currency. All Responses must be submitted in accordance with the specific terms of this RFR. No electronic Responses may be submitted in Response to this RFR.
5. Bidder Communication. Bidders are prohibited from communicating directly with any employee of EOEA except as specified in this RFR, and no other individual Commonwealth employee or representative is authorized to provide any information or respond to any question or inquiry concerning this RFR. Bidders may contact the contact person for this RFR in the event this RFR is incomplete or the Bidder is having trouble obtaining any required attachments electronically through Comm-PASS.
6. Reasonable Accommodation. Bidders with disabilities or hardships that seek reasonable accommodation, which may include the receipt of this RFR information in an alternative format, must communicate such requests in writing to the contact person. Requests for accommodation will be addressed on a case by case basis. A Bidder requesting accommodation must submit a written statement which describes the Bidder's disability and the requested accommodation to the contact person for the RFR. The Department reserves the right to reject unreasonable requests.

   The Department may require the Contractor to provide all materials, software, maps, studies, reports, and other products or data in alternative formats upon request.
7. Public Records. All Responses and information submitted in response to this RFR are subject to the Massachusetts Public Records Law, M.G.L. Chapter 66, section 10 and Chapter 4, section 7(26). Any statements in submitted Responses that are inconsistent with the Public Records Law shall be void and disregarded.
8. All materials, software, maps, studies, reports, and other products or data, regardless of physical form or characteristics, produced in furtherance of the Contract and funded, in whole or in part, under the Contract shall be considered in the public domain and available to EOEA or its agencies at the reasonable cost of reproduction in any of the formats in which it is stored or maintained. The Contractor shall not obtain, attempt to obtain or file for a patent, copyright, trademark or any other interest in any such materials, software, maps, reports, and other products or data without the express, written consent of the Department and subject to any other approvals required by state or federal law.
9. Best Value Selection and Negotiation. The Department may select the Response(s) which demonstrates the best value overall, including proposed alternatives, that will achieve the procurement goals of the Department. The Department and a Selected Bidder, or a Contractor, may negotiate a change in any element of contract performance or cost identified in the original RFR or the Selected Bidder's or Contractor's Response which results in lower costs or a more cost effective or better value than was presented in the Selected Bidder's or Contractor's original Response.
10. The Department reserves the right to fund a portion, change the scope, and/or delete tasks of any Response to more closely meet the purposes of the program or to obtain the best procurement value for the Department. Selected Bidders may decide not to enter into a contract if the revised scope does not meet its approval. The Department does not guarantee that any Contract will be awarded under the RFR. Any potential Contract with a Selected Bidder shall be subject to the appropriation and availability of funds.
11. Costs. Costs which are not specifically identified in the Bidder's Response, and accepted by a Department as part of a Contract, will not be compensated under any contract awarded pursuant to this RFR. The Commonwealth will not be responsible for any costs or expenses incurred by Bidders responding to this RFR.
12. Comm-PASS. This RFR has been distributed electronically using the Comm-PASS system, RFR attachments that are referenced will be found either as a separate .pdf file along with the RFR, or are found in the "Forms and Information" section at: **(http://www.comm-pass.com/comm-pass/forms.html)**. Bidders are solely responsible for obtaining and completing required attachments that are identified in this RFR and for checking Comm-PASS for any addenda or modifications that are subsequently made to this RFR or attachments. The Commonwealth and its subdivisions accept no liability and will provide no accommodation to Bidders who fail to check for amended RFRs and submit inadequate or incorrect Responses. Bidders are advised to check the "last change" field on the summary page of RFRs for which they intend to submit a Response to ensure that they have the most recent RFR files. Bidders may not alter (manually or electronically) the RFR language or any RFR

component files. **Modifications to the body of the RFR, specifications, terms and conditions are prohibited and may disqualify a Response.** Bidders having difficulty obtaining any required attachments electronically through Comm-PASS should seek assistance from the Comm-PASS "Help Desk" by calling 1-800-MA-STATE.

If the Department is also distributing this RFR directly to Bidders, those Bidders, that requested and received a copy of this RFR directly from the Department, will be sent a copy of any modifications or amendments to the RFR by the Department.

13. Northern Ireland Notice and Certification. All Bidders must complete the "Northern Ireland Notice and Certification" form to satisfy M.G.L. Chapter 7, section 22C.

14. Subcontracting. Prior written approval of the Department is required for any subcontracted service (which includes consultants) of the contract. Contractors are responsible for the performance and oversight of its subcontractors. Subcontractors are required to meet the same state and federal financial and program reporting requirements and are held to the same reimbursable cost standards as contractors.

15. Affirmative Market Program. Massachusetts Executive Order 390 established a policy to promote the award of state contracts in a manner that develops and strengthens Minority and Women Business Enterprises (M/WBEs). As a result, M/WBEs are strongly encouraged to submit Responses to this RFR, either as prime vendors, as joint venture partners, or as subcontractors.

    Non-M/WBE Bidders are strongly encouraged to develop creative initiatives to help foster *new business relationships* with M/WBEs within the primary industries affected by this RFR. The highest number of points will be awarded for Responses that clearly illustrate how the proposed business relationship(s) will result in the development and growth of M/WBEs within these primary industries. A lesser number of points will be awarded for traditional subcontracting relationships. The least number of points will be awarded for ancillary uses of M/WBEs.

    In order to satisfy this section, the Bidder must submit: the names, addresses, phone numbers and contact persons of each M/WBE firm; a description of each business relationship to be established; and the actual dollar amounts, or percentages, to be awarded to each M/WBE firm. MBE and WBE firms must submit a copy of their SOMWBA certification letter for the current period. A directory of SOMWBA certified firms is available via the internet at **http://www.magnet.state.ma.us/somwba.**

    A Minority Business Enterprise (MBE) or a Woman Business Enterprises (WBE) is defined as a business that has been certified as such by the State Office of Minority and Women Business Assistance (SOMWBA). Minority and women-owned firms that are not currently SOMWBA-certified but would like to be considered as an M/WBE for this RFR should apply for certification. A fast track application is available, and will be considered for the purposes of this RFR. For further information on SOMWBA certification contact the State Office of Minority and Women Business Assistance at (617) 727-8692 or via the internet at **http://www.magnet.state.ma.us/somwba.**

    All Bidders must complete and sign the "Affirmative Action Plan Form" for any RFR from which a Contract may result that has a potential financial benefit of $50,000 or more.

16. The Commonwealth makes no guarantee that any commodities or services will be purchased from any contract resulting from this RFR. Any estimates or past procurement volumes referenced in this RFR are included only for the convenience of Bidders, and are not to be relied upon as any indication of future purchase levels.

17. Unless otherwise specified in this RFR, any reference to a particular trademark, trade name, patent, design, type, specification, producer or supplier is not intended to restrict this RFR to any manufacturer or proprietor or to constitute an endorsement of any commodity or service, and the Department may consider clearly identified offers of substantially equivalent commodities and services submitted in response to such reference.

18. Alternatives. A Response which fails to meet any material term or condition of the RFR, including the submission of required attachments, may lose points or be deemed unresponsive and disqualified. Unless otherwise specified, Bidders may submit Responses proposing alternatives which provide equivalent, better or more cost effective performance than achievable under the stated RFR specifications. These alternatives may include related commodities or services that may be available to enhance performance during the period of the contract. The Response should describe how any alternative achieves substantially equivalent or better performance to that of the RFR specifications. The Department will determine if a proposed alternative method of performance achieves substantially equivalent or better performance. The goal of this RFR is to provide the best value of commodities and services to achieve the procurement goals of the Department. Bidders that propose discounts, uncharged commodities and services or other benefits in addition to the RFR specifications may receive a preference or additional points under this RFR as specified.

19 Contract Expansion. If additional funds become available during the contract duration period, the Department reserves the right to increase the maximum obligation to some or all contracts executed as a result of this RFR or to execute contracts with contractors not funded in the initial selection process, subject to available funding, satisfactory contract performance and service or commodity need.

20. Year 2000 Compliance. The contractor warrants that all systems, interfaces to such systems, or information technology produced in furtherance of this Contract and funded, in whole or in part, under this Contract must be year 2000 compliant. Year 2000 compliant means information technology that accurately processes date/time data (including but not limited to calculating, comparing and sequencing) from, to and between the twentieth and twenty-first centuries and the years 1999 and 2000 including leap year calculations. Furthermore, year 2000 compliant information technology, when used in combination with other information technology, shall accurately process date/time data if the other informational technology properly exchanges date/time data with it. This warranty shall survive the expiration or termination of this contract.

21. Environmentally Preferable Products and Services. At the Department's sole discretion, the Department and contractor may negotiate during the contract term to permit the substitution or addition of Environmentally Preferable Products (EPPs) when such products become available at a competitive cost and satisfy the Department's performance needs. Unless otherwise specified in the RFR, during evaluation of Responses, an EPP may be considered best value even when the price is greater than (but does not exceed 10% in price) that of a non-EPP. Bidders are encouraged to submit appropriate information to identify important environmental attributes of items being procured, even when such attributes are not being required. Information or

technical assistance regarding EPPs may be obtain from OSD at 617-727 7500 ext. 351 or via the internet at **http://www.magnet.state.ma.us/osd/enviro/enviro.htm.**

22. Selected respondents will be required to execute the Commonwealth's *Standard Terms and Conditions, Standard Contract*, W-9 form, Signature Verification, and any other forms specified in this RFR.

23. GIS Standards. All GIS (Geographic Information System) data collected, compiled or created under this RFR shall conform to standards developed or established by the Office of Geographic and Environmental Information (a/k/a MassGIS) within EOEA. Such GIS data shall be made available to MassGIS upon request and at the reasonable cost of reproduction (cost to copy and/or transmit the data to MassGIS).

24. Nothing in this RFR authorizes or purports to grant the right to any Bidder, governmental entity or other person to enter or remain on any public or private property. If access to any property is necessary in any way for any purpose, such as responding to this RFR (e.g. surveying), that Bidder, governmental entity or other person must obtain appropriate permission authorizing such access from the person or governmental agency that has lawful control of the property.

25. **Anti-Collusion**. In reviewing responses to the RFR and awarding a contract, the Department will strictly interpret all provisions of the RFR, response and contract and other state regulations to ensure that collusion or the appearance of collusion has not occurred at any stage of the contracting process. Any attempt to secure information about this procurement through procedures other than those outlined in this RFR will be considered in violation of this provision and will result in disqualification of the Bidder.

Bidders must provide a statement with their responses certifying that all parties to this response, including members of teaming arrangements agree that:

- A contract has not been solicited or secured, directly or indirectly, in a manner contrary to the laws of the Commonwealth of Massachusetts and that said laws have not been violated as they related to the procurement or the performance of the contract by any conduct, including the paying or giving of any fees, commission, compensation, gift, gratuity, or consideration of any kind, directly or indirectly, to any State employee, agent, officer or official; and

- Unless otherwise required by law, any information quoted in this response, including prices, has not knowingly been disclosed by the respondent directly or indirectly to any other respondent or to any competitor and will not knowingly be disclosed by the respondent prior to award of a contract. Respondents are further advised that the contractor, including any of its employees, agents or representatives, is prohibited from paying or giving any fee, commission, compensation, gift, gratuity or consideration of any kind or amount, directly or indirectly, to any person connected with this procurement during the term of the procurement and subsequently through the term of the contract as governed by the State Ethics Commission and the provisions of Chapter 268 of the General Laws.

APPENDIX D
COASTAL POLLUTANT REMEDIATION GRANT PROGRAM

THE COMMONWEALTH OF MASSACHUSETTS
EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS
OFFICE OF COASTAL ZONE MANAGEMENT
251 Causeway Street, Suite 900, Boston, MA 02114-2136
(617) 626-1200 fax: (617) 626-1240

Upcoming Grant Opportunity
Coastal Pollutant Remediation Grant Program

The Massachusetts Office of Coastal Zone Management (CZM) will issue a Request for Response (RFR) for the Coastal Pollutant Remediation (CPR) grant program in **May of 2004**. The RFR, with an enclosed application, will be posted on the Commonwealth of Massachusetts' Procurement Access & Solicitation System at: http://www.comm-pass.com. **A Pre-RFR informational meeting** will be held on **Thursday, April 8 from 10:00 a.m. to 12:00, at the CZM Office: 251 Causeway Street, 8th Floor, Boston**. Potential respondents are strongly encouraged to attend this meeting to discuss the details of proposed projects, particularly since CZM can only offer general information to respondents after the RFR is posted. In addition, it is important for applicants to receive comments from CZM technical staff in advance regarding project design.

CZM administers two grant programs: the Coastal Pollutant Remediation grant program, and the Coastal Nonpoint Source grant program. The primary goal of both of CZM's grant programs is to improve coastal water quality by reducing or eliminating nonpoint sources of pollution through measures and strategies consistent with the Coastal Nonpoint Source Control Program. In addition, the CPR grant program compliments the Commonwealth's *Stormwater Management Volume I: Stormwater Policy Handbook and Volume II: Stormwater Technical Handbook*, as one source of funding available to communities to assist in remediating existing discharges from municipal roadways and parking lots.

CPR, funded through State legislative appropriations from Environmental Bonds, funds projects that address stormwater discharges from municipal roads, highways, or parking areas or for municipal boat sewage management efforts. The primary goal of the CPR program is to improve coastal water quality by implementing best management practices for managing roadway runoff and by constructing boat pumpouts to collect and hold sewage generated by marine vessels in areas where pumpouts are insufficient or inoperable. Proposals must clearly demonstrate that the source of pollution is either stormwater runoff from a roadway, bridge, parking lot or from vessel discharges. The funding available for CPR is typically $600,000, on average. The Coastal NPS grant program was developed to complement CPR and to address more general areas of nonpoint source control. Funding available for CNPS is approximately $250,000, and proposals are solicited in the fall.

The CPR grant program is open to any cities and towns located within the boundaries of the Massachusetts coastal watershed[1]. CZM administers the grants on a reimbursement basis, and projects selected for funding must be completed by June 30, 2005. Additional information can be found on the CZM web page at: http://www.state.ma.us/czm/cprgp.htm. Answers to specific questions regarding the program are listed on the FY 2004 Frequently Asked Questions document, which can be found on the Comm-pass website at: http://www.comm-pass.com/Comm-PASS/Scripts/xdoc_view.idc?doc_id=015095&dept_code=ENV&cp_xx=. If you would like to discuss a potential project, contact Julie Keane, Coastal Pollutant Remediation Grants Coordinator, at: (617) 626-1235, or e-mail: julie.keane@state.ma.us.

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[1] Cities and towns that are located within the following coastal watersheds: Boston Harbor (Mystic, Neponset, and Weymouth & Weir), Buzzards Bay, Cape Cod (Bay and Nantucket Sound), Charles, Concord, Ipswich, Islands, Merrimack, Mount Hope (Lower Mt. Hope), Narragansett (Upper Mt. Hope), Nashua, North Coastal, Parker, Shawsheen, South Coastal, Taunton, and the Ten Mile are eligible. Please refer to the CZM website to check specific city/town boundaries: http://www.state.ma.us/czm/twnscws.htm.

Massachusetts Office of
COASTAL ZONE MANAGEMENT

Communities I
CPR Grants

List of CPR-Fu
Projects

Coastal Nonpc
Pollution Gran
(Formerly CPR

The Coastal Pollutant Remediation Grant Program

The Coastal Pollutant Remediation (CPR) grant program, which is administered by the Massachusetts Office of Coastal Zone Management (CZM), allows the Commonwealth to assist communities in their coastal nonpoint source (NPS) pollution control efforts. Established by the State Legislature and funded through the Environmental Bond Bill, the CPR grant program serves to implement portions of the Massachusetts Coastal Nonpoint Source Control Plan. In addition, the CPR grant program complements the Commonwealth's Stormwater Management Policy, serving as a significant source of funding available to communities. Since 1996, more than $4 million in CPR grants have been awarded.

A Request for Responses for the current CPR grant round is now posted. Click here for the RFR.

The primary goal of CPR is to improve coastal water quality by reducing or eliminating NPS pollution, specifically transportation-related sources. Within this goal are four main objectives:

- Characterize and treat urban runoff from municipal roadways.
- Improve coastal resources such as shellfish beds and fish habitat.
- Demonstrate traditional and innovative best management practices.
- Educate the public about stormwater runoff problems.

Eligible Projects

Eligible municipalities are those located in the Greater Massachusetts Coastal Watershed, which encompasses 220 cities and towns in eastern Massachusetts.

Grant funds can be used to construct stormwater remediation systems or marine pumpout facilities, or to sample existing stormwater discharges to identify the pollution source and propose a solution. Example projects include filtering runoff through subsoil leaching galleys, utilizing new technologies for particle separation and filtration, and treating runoff through a water quality swale, as well as many assessment projects to determine water quality problems so that solutions can be devised.

CPR Projects

For the complete list of projects that have been funded through CPR, click here. For the press release announcing the 2004 CPR projects, click here. Below is a list of some representative CPR projects.

- In 1998, the Town of Bourne was awarded $45,350 for the installation of two vessel pumpout facilities at the Parker and Kingman Marinas that helped to reduce the discharge of sewage to Buzzards Bay. The availability and use of vessel pumpout facilities such as these were a factor in the recent designation of Buzzards Bay as a No Discharge Area (NDA).

- In 1999, the Town of Rockport was awarded $34,800 for the installation of two proprietary technology Best Management Practices (BMPs) to remove sediment from stormwater that was being discharged to the Saratoga Creek Marsh. Deposit of sediment in the marsh, the only one in Rockport, was leading to the invasion of Phragmities (common reed), which was crowding out the native vegetation and degrading the habitat. This municipal habitat protection initiative has dramatically reduced the impact of stormwater to the marsh.
- In 2001, the City of Revere was awarded $30,000 to investigate the sources of stormwater pollution to Trifone Brook, a tributary to the Rumney Marsh Area of Critical Environmental Concern (ACEC). This pollution has been responsible for shellfish closures in the estuary. As part of this project, a preliminary engineering design is being developed. When finalized, the design will be used to support a subsequent application to install a structure that will reduce or eliminate this pollution, directly benefiting water quality, habitat, and economic potential of the area.

Grant Cycle

Each spring, eligible municipalities will receive an announcement of the next grant round. Proposals are due to CZM in mid-spring, and grants are awarded in the summer. The grants are reimbursable upon project completion and pays for 75 percent of the total project cost. Municipalities are strongly encouraged to solicit input from CZM on proposal development prior to the release of applications.

Contact Information

For additional information about the program, please refer to Coastal Pollution Remediation (CPR) Program Questions and Answers (PDF, 142K) or contact Julie Keane, CPR Coordinator, at (617) 626-1235, email julie.keane@state.ma.us.

More on Massachusetts Coastal Nonpoint Source Control Plan

Grants issued under the Coastal NPS Grant Program, as well as the Coastal Pollutant Remediation grant program (CPR), serve to implement portions of the Massachusetts Coastal Nonpoint Source Control Plan (PDF Version). The Plan includes measures to address nonpoint source pollution problems from each of the following sources: urban areas, marinas and recreational boating, agriculture, forestry, hydromodification, wetlands, and riparian areas. The primary goal of both of CZM's grant programs is to improve coastal water quality by reducing or eliminating nonpoint sources of pollution through measures and strategies consistent with the Coastal Nonpoint Source Control Program.

Mitt Romney, Governor
Kerry Healey, Lieutenant Governor
Ellen Roy Herzfelder, Secretary

Tom Skinner, Director
Susan Snow-Cotter, Assistant Director
Deerin Babb-Brott, Assistant Director

251 Causeway Street, Suite 800
617-626-1200 617-626-1240 (fax)
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Boston, MA 02114-2136
czm@state.ma.us
Updated: 05/05/2004

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Summary:
The Massachusetts Office of Coastal Zone Management (CZM) within the Executive Office of Environmental Affairs (EOEA) announces a grant program Request for Responses (RFR) for fiscal year 2005 (FY05-July 1, 2004 through June 30, 2005). The Coastal Pollutant Remediation (CPR) grant program is administered by CZM under the Coastal Nonpoint Source Pollution Controll Program. The grants are dedicated to municipalities on a reimbursement basis for specific projects to improve coastal water quality. Projects eligible for funding include, but are not limited to, the treatment of stormwater polltion from roadways, assessment to identify the source(s) of pollution and design remediation systems, and the construction of boat pumpout facilities. The primary goal of the program is to improve coastal water quality by implementing Best Management Practices (BMPs) for managing roadway runoff by constructing boat pumpouts to collect and hold sewage generated by recreational marine vessels in areas where pumpouts are either effectively inoperable or do not exist.

PLEASE NOTE: Changes to the CPR RFR have been made. Please read carefully through the RFR, particularly noting the CPR Grant Program Conditions section, Selection Criteria and Preference Criteria section, and the Application.

Reference No: ENV 04 CZM 10 **Value(U.S.$):** 600000.00 maximum total

Related Files:
The following is a list of files for downloading. Files can be viewed and printed using the Adobe Acrobat® viewer, which can be downloaded FREE from the internet. You may wish to view and print our instructions by clicking here before you attempt to download.

Title	Date	Size
Coastal Pollutant Remediation (CPR) Grant Program RFR (pdf file) (Main Document)	04/15/04	298.21 KB
Coastal Pollutant Remediation (CPR) Grant Program RFR (word file) (Main Document)	04/15/04	211.5 KB
Coastal Pollution Remediation (CPR) Program Questions and Answers- FY05 (pdf file)	04/15/04	125.7 KB
Coastal Pollution Remediation (CPR) Program Questions and Answers- FY05 (word file)	04/15/04	57 KB

Americans with Disabilities Act (ADA) Policy:
In the event you experience difficulty accessing any document posted here, please contact the person listed below, who is solely responsible for providing alternate access.

Contact Information:

Contact Person: Julie Ann Keane , CPR Grant Coordinator
Address: MA Office of Coastal Zone Management
251 Causeway St., Suite 800
Boston, MA 02114
Email: julie.keane@state.ma.us

Interested In Bidding? - Indicate your interest in bidding on this RFR as a prime contractor, subcontractor or both.

Interested Business List - View a list of businesses who have indicated in Comm-PASS an interest to bid, or desire to subcontract.

Jump to SOMWBA - Obtain a listing of state certified minority or women-owned companies.

Document History - View a summary of the document changes and change dates.

NOTICE

It is the responsibility of every bidder to check Comm-PASS for any addenda or modifications to a solicitation for which they intend to bid. The Commonwealth of Massachusetts and its subdivisions accept no liability and will provide no accommodation to vendors who submit a bid based upon an out-of-date solicitation document. Potential bidders are advised to check the "last change" field on the summary page of solicitations they intend to bid upon to ensure that they have the most recent solicitation files.

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APPENDIX E
FORENSIC GEOCHEMISTRY ASSESSMENT PAPERS

[redacted] Method for Determining the Age of Diesel Oil Spills in the Soil

by Lars Bo Christensen and Thomas Hauerberg Larsen

Abstract

This study evaluates the changes in the composition of diesel oil as a function of the time during which the oil has been present in the vadose zone. The study also develops a reliable method for determining the age of diesel oil in the subsurface soil environment at service stations, oil terminals, and similar locations where the diesel is protected from direct exposure to factors increasing the rate of microbial activity.

Analyses demonstrate that n-alkanes are the dominant components of fresh diesel oil and isoprenoids the dominant components of degraded diesel oil. The analyses also show that the composition of fresh diesel oil produced in 1992 and that produced in 1974 is basically the same.

The difference in composition between fresh and degraded oil is the basis for defining a degradation ratio or rate of alteration in the composition of the diesel oil expressed in terms of a ratio between n-alkanes and isoprenoids. At 12 test locations where the date of property damage was known, the C_{17}/pristane ratio had by far the highest correlation factor (.89) with the residence time of the diesel based on the average degradation ratio for each location. Based on this high correlation factor, the C_{17}/pristane ratio can be used to estimate the age of a diesel oil spill. The standard error of such an estimate is approximately two years.

Introduction

In the subsoil, several processes may change the composition of petroleum products such as diesel oil. The most important of these processes are evaporation, leaching, and microbial action. Evaporation results in loss of the more volatile components; leaching causes removal of the more water soluble components; and microbial action results in transformation of components with specific configurations, e.g., the unbranched alkanes.

In some environments, these processes have only a minor influence on oil composition, and the oil will largely be preserved. In other environments, however, the processes strongly affect the composition of the oil and remove it completely in a short period of time (Atlas 1981). An example of an environment that preserves oil is the environment in underground storage tanks. Evaporation is extremely low, there is no leaching, and the proportions of water, oxygen, nutrients, and the free oil phase largely inhibit any microbial action.

In contrast, the environment in agricultural topsoil favors rapid degradation. In general, the conditions in such soil promote a rapid change in the composition of the oil, which in some cases will result in an almost complete removal of oil within a few months. The oil is exposed to evaporation, especially close to the surface, and to leaching, depending on the actual precipitation. The most significant process, however, is microbial action, which is generally high due to the high con-

Pages 142 - 149

centrations of oxygen and nutrients usually present in agricultural topsoil. Environmental conditions vary considerably in oil-affected soil: the soil environment may include both zones in which conditions resemble the situation in an oil tank and zones with conditions resembling those found in the topsoil.

Most research has focused on the alteration of oil under conditions favoring microbial action. It is generally accepted that environmental conditions favoring microbial action in oil-affected soil are found in the top layer of soil, e.g., agricultural topsoil, in the fringe of the oil-affected soil body, and in the plume that contains dissolved oil components (see Figure 1). It is also generally accepted that the conditions inside an oil-affected soil body inhibit microbial action due to factors such as low concentrations of nutrients and oxygen, high concentrations of components that may become toxic to microbes, and low biological availability of the oil components. Although microbial activity is inhibited in the oil-affected soil body, a long-term presence in the subsoil will nevertheless alter the composition of diesel oil.

It has previously been stated that "estimation of the length of time liquid hydrocarbons have been in the subsurface is possible from interpretation of gas chromatograms" (Senn and Johnson 1987). The degree of change in diesel oil within the subsurface environment may be measured by comparing ratios of components with different physical, chemical, or biological properties. Some of the most commonly used ratios for measuring biodegradability are n-C_{17}/pristane, n-C_{18}/phytane, and pristane/phytane (Glaser 1991; Flathman et al. 1991). Isoprenoids, such as pristane and phytane, are more resistant to biodegradation than the n-alkanes C_{17} and C_{18}. As biodegradation proceeds, the ratios of n-alkanes to isoprenoids will decrease, in this study from more than 2.2 for fresh diesel oil to less than 0.2 for diesel oil present within the soil for more than 20 years. Thus, the reduction in the values of such ratios can be used to measure the degree and rate of alteration of diesel oil in soil.

Table 1
Location, Type of Installation, and Age of Known Diesel Oil Spills

Location Name	Type of Installation	Age from Historical Records (Years)
Provestenen, DK	Oil Terminal	22
Hengelo, depot, NL	Oil Terminal	19
Fredericia, DK	Oil Terminal	18
Ishoj, DK	Service Station	18
Haarlem, NL	Service Station	17
Vanlose, DK	Service Station	14
Horsholm, DK	Service Station	12
Nieuwesluis, NL	Oil Terminal	11
Brunnik, NL	Service Station	9
Hengelo, loading rack, NL	Oil Terminal	9
Thisted, DK	Service Station	8
Ejby, DK	Heating Oil Tank*	0.5

*The site was included because the location was in all respects similar to the other locations. Heating and diesel oils are basically the same, except for additives.

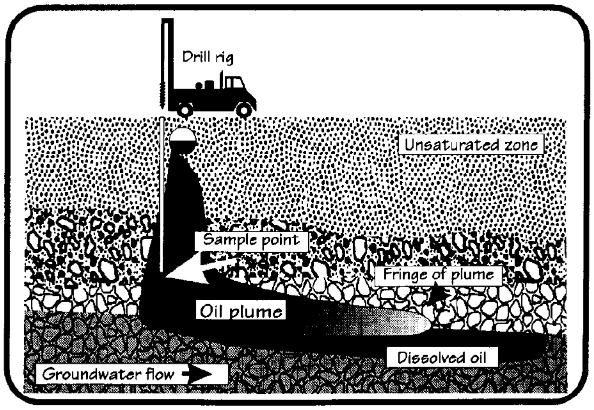

Figure 1. Sketch of an oil-affected soil body and placement of sample point for evaluating the age of a spill.

The objectives of this study are to evaluate the changes in diesel oil composition as a function of the length of time the diesel oil has been present in the subsurface and to develop a method which can be used to determine the age of a spill using data from commonly used analytical methods. The study is restricted to subsurface soil environment under service stations, oil terminals, and similar facilities, evaluating the oil-affected soil body located underneath paved areas and above the ground water table. This environment is to a large degree protected from direct exposure to factors increasing the rate of the microbial activity; it can also be named the vadose zone containing Lighter-than-water Non-Aqueous Phase Liquids (LNAPL) present in concentrations up to residual saturation.

Methodology

Data Collection from Service Stations and Oil Terminals Where the Age of the Diesel Oil Is Known

The study is based on previously made environmental reports from service stations and oil terminals, which in some cases underwent additional sampling and analysis, and on a more thorough investigation of a 22-year-old diesel spill located at Provestenen, Denmark, in order to examine factors affecting the degradation and to follow the future progress of degradation processes. More than 200 environmental reports from Denmark and the Netherlands were reviewed and examined for the relationship between the degree of degradation and the age of the diesel spills.

In many reports, historical records indicate the date of a sudden release of diesel oil into the natural environment. In 12 of the cases, the historical records gave not only precise information on the date of the spill, but also made clear that no diesel could have entered the environment at the location at a later time. This provided 12 "test cases" for accurately observing changes in the composition of diesel oil in a subsurface environment over a period of more than two decades. Table 1 lists these 12 cases.

In these 12 cases in which the precise time of the spill was known, we also required soil samples to meet the following criteria:

- The diesel oil concentration in the samples had to exceed 100 mg/kg.
- The samples had to be collected at least 1 m below ground level.
- The samples had to be collected from the unsaturated zone underneath a paved area.
- The analyses had to include information on single components such as C_{17}, C_{18}, pristane, and phytane.

The first two criteria ensured that the samples were representative of the oil-affected soil in the vadose zone. Samples with more than 100 mg diesel oil/kg provide a high degree of certainty that the proportions of oxygen, nutrients, and oil present would not promote microbial action. The third criterion, that soil samples be collected from the unsaturated zone underneath a paved area, limited the effect of leaching caused by rain water and flowing ground water, which might cause changes in the diesel oil composition. The last criterion, that analysis was to provide information on individual components like C_{17}, C_{18}, pristane, and phytane, was met through the use of GC-FID in all the environmental reports and in the additional analyses.

The alteration ratios were calculated based on gas chromatographic analyses for samples taken from locations where the age of the spill was known. The advantages of using gas chromatographic analysis instead of other analytical methods are that it is in wide use, the results are simple to evaluate, and it offers an acceptable level of reproducibility. Use of this analytical method was preferred because of the ability to gain access to a larger data pool, and because further applications of the method and results revealed by this study will benefit from the widespread availability and ready applicability of the gas chromatographic analytical method.

In general, we can describe the cases in which data were collected as follows. The main part of the oil-affected soil was situated above the water table between 1 and 5 m below the ground level. The soil temperature regime was mesic approximately constant, 10 C (USDA), and the sites examined were all service stations or oil terminals (except for Ejby). Gas chromatographic analysis was performed on samples taken from the oil-affected soil, and little or no remedial action had been taken prior to the time of the soil sampling. However, the sites were permitted to vary in local geology, the presence of other oil products, and the size and volume of the oil-affected soil.

In cases with insuffcent data, additional sampling was undertaken at sites that permitted supplementary drillings. The additional sampling and analyses were reported by one Danish and three Dutch consulting firms.

Description of the Provestenen Site

A detailed investigation was made at the Provestenen site, an oil terminal located on an island in the eastern part of Copenhagen, Denmark. On January 14, 1970, a major diesel oil spill occurred at the terminal. The spill had not been remediated and the oil was still located below the oil tanks without having mixed with other products at the terminal. The geology at the site was characterized by homogenous sand deposits, with the ground water table generally located 2 m below the surface. Five drillings were made at different distances from the source. Soil samples from different depths were analyzed for the following four factors: (1) the concentration of diesel oil and oil components; (2) the total number of microorganisms (CFU); (3) the number of oil-degrading microorganisms; and (4) the concentration of the nutrients of nitrogen and phosphorus.

Chemical and Microbial Analyses

The soil samples were extracted with pentane or hexane and measured by a gas chromatograph equipped with capillary column and a flame ionization detector (GC-FID). The analyses were conducted with a temperature program, which ensured all relevant diesel oil components were resolved. For practical reasons, including consistency, simplicity of analysis, and the limitations imposed by older gas chromatograms, we chose to base our calculations of the ratios between different components on the peak heights. The use of peak area, which represents the true value of the mass, is an alternative and may ultimately be a more suitable analytical method. However, the use of peak height also allows consistent and accurate analysis, which is shown by the low average deviation of -10 percent between the n-C_{17}/pristane ratio measured by peak height and the mass (unpublished data). We calculated the following ratios: n-C_{17}/pristane, C_{17}/norpristane, n-C_{18}/norpristane, and n-C_{18}/phytane.

Gas chromatography analyses were performed on different instruments and by different laboratories. The number of microorganisms was calculated using the plate count method (modified ISO 6222; 1988 [E] standard). Oil-degrading microorganisms were counted using the method of Song and Bartha (1990). The concentration of total recoverable phosphorus was measured in accordance with ASTM D 4183-82 or NEN 6662 (Dutch guideline), and Kjeldahl total-nitrogen was measured in accordance with Nordforsk, 1975:6 (Nordic guideline), or NEN 6481 (Dutch guideline).

Results and Discussion

Compositional Differences Between Fresh and Degraded Diesel Oil

Diesel oil is a complex mixture of hydrocarbons produced by the distillation of crude oil. The dominant

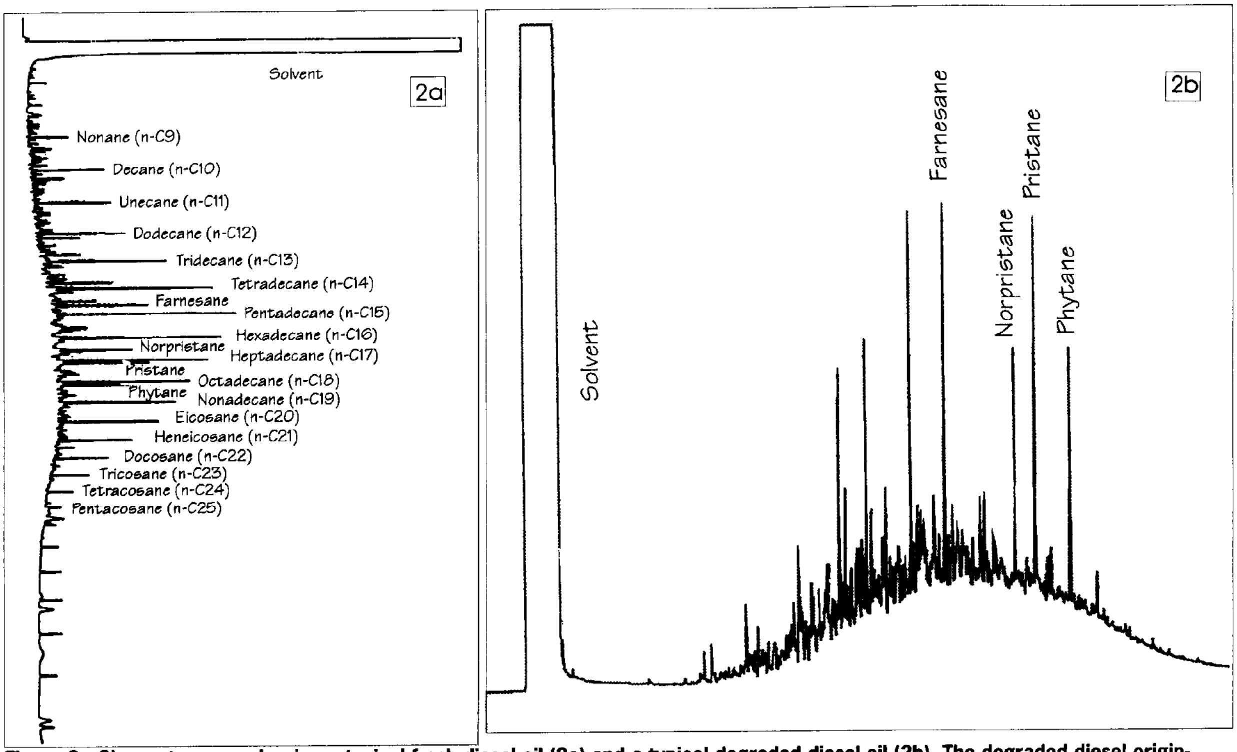

Figure 2. Chromatograms showing a typical fresh diesel oil (2a) and a typical degraded diesel oil (2b). The degraded diesel originates from a soil sample from a 22-year-old spill.

hydrocarbons in diesel oil are n-alkanes (straight-chained alkanes) in the range of C_9 to C_{20}, representing a boiling range of approximately 160 to 360 C. In addition to n-alkanes, diesel oil contains branched-chained alkanes (e.g., isoprenoids), cyclo-alkanes, and aromatics (Christensen et al. 1987). On a chromatogram, fresh diesel oil produces a typical picture, with the n-alkanes appearing as dominant peaks that form a regular pattern covering the entire length of the chromatogram.

The range of n-alkanes reflects the manufacturing distillation and varies slightly among different fresh diesels. Figure 2a shows an example of a chromatogram of a fresh diesel oil. In this particular diesel oil, the n-alkanes exist in the range of C_9 to C_{25}, with C_{15} as the most abundant component, and with the typical isoprenoids of farnesane, norpristane, pristane, and phytane present at concentrations well below the concentration of the corresponding n-alkanes (n-alkanes with the nearest boiling point). A large number of unidentified components are generally present at very low concentrations in the interval between the n-alkanes and the isoprenoids.

A highly degraded diesel oil, like the sample from the 22-year-old spill presented in Figure 2b, has a completely different composition. The degraded diesel oil is dominated by the isoprenoids, while the n-alkanes are mostly absent. This difference in composition forms the basis for determining the degree of degradation expressed as a ratio between n-alkanes and isoprenoids.

The composition of fresh diesel from the last 20 years was determined by comparing analyses of diesel produced in 1992 with two diesel products from 1974. The diesel produced in 1974 has been stored in stockpiles since 1974 by the Association of Danish Oil Reserves Stocks to guard against supply problems. It can be assumed that diesel oil stored in such large amounts and under conditions with virtually no evaporation or contact with water will have practically the same composition now as when it was stored. The comparison demonstrated that the chromatogram of diesel manufactured in 1974 resembles chromatograms of diesel produced in 1992 with dominating n-alkanes and low concentrations of isoprenoids in clear contrast to chromatograms of degraded diesel.

The variations in the composition of fresh diesel were investigated by analyzing 11 different diesel oils from five different oil companies. All the oils had the same general appearance on the chromatograms. The typical appearance is an array of n-alkanes in the C_9 to C_{20} range, and isoprenoids (farnesane, norpristane, pristane, and phytane) in concentrations lower than the corresponding n-alkanes with the same carbon number. Despite the overall similarities, some of the five degradation ratios examined differed considerably in fresh diesels, while others were relatively constant. Table 2 illustrates that the ratios had a standard variation of 20 to 40 percent, depending on the ratio. All ratios were investigated throughout the study.

Although the general composition and some of the ratios remained relatively constant, other components varied. The reasons for these variations, both among different fresh diesels and among oil products produced over the last 20 years, are the following: (1) the addition of cracked oil fractions; (2) the addition of different additives; and (3) the different crude oil sources (Wrang et al. 1990). The addition of cracked oil or additives has

Table 2

Average Ratios and Standard Deviation Between Different Compounds in Fresh Diesel Oil Originating from Different Oil Companies

	# of Samples	Average	Standard Deviation
C_{17}/Farnesane	11	0.66	0.26
C_{17}/Pristane	11	1.98	0.83
C_{17}/Norpristane	11	2.53	0.80
C_{18}/Phytane	11	1.85	0.45
C_{18}/Norpristane	11	1.99	0.55

no influence on the degradation ratios. The dominant components in cracked oil are aromatic compounds; n-alkanes and isoprenoids are not present. The additives include many different components, many of which are non-hydrocarbon components containing oxygen or nitrogen (IARC 1989). The ratios are unaffected because neither n-alkanes nor isoprenoids are added.

The different crude oil sources are the factors most likely to affect the variation among different diesel products. The manufacturing process often involves blending different distillates and oil fractions, and therefore specific oil products are expected to vary less than undistilled crude oil, which explains the low variability in the ratios C_{17}/pristane found in this study. Another argument is that most of the crude oil consumed in northern Europe originates from relatively few sources, primarily from the Middle East and the North Sea, thus minimizing the variability.

Effect of Vaporization, Leaching, and Microbial Action of Diesel Oil in the Subsurface Environment

The quantity of a certain component evaporating from the diesel oil depends on the vapor pressure and the relative content of that component; the vapor pressure is related closely to the boiling point (Lymann et al. 1990). The boiling points of diesel components correspond approximately to the retention time, and the effects of the evaporation process can be seen on the chromatogram as a systematic removal, starting with the elimination of all components with short retention times, including both n-alkanes and isoprenoids. Although extensive evaporation can also affect components with higher boiling points, the ratio between n-alkanes and isoprenoids as a whole will not change (Wrang et al. 1990).

As seen in Figures 2a and 2b, the diesel oil from the 22-year-old spill differed substantially from fresh oil. The old diesel was completely dominated by isoprenoids, as were the other degraded diesel samples in this study. Evaporation alone cannot explain these changes in the proportions of n-alkanes and isoprenoids, which indicates that other processes may be more important. The limited effect of evaporation on diesel oil in the subsoil has been found in other investigations that determined only 0.1 to 0.6 percent of diesel oil evaporated from the soil (Bossert and Bartha 1984; Lindhardt et al. 1991).

The effect of leaching on diesel oil is more difficult to estimate from the chromatograms. The components in diesel generally have a very low solubility, and the components with relatively high solubility, e.g., the monoaromatics, are present in very low concentrations. In addition, the components in each of the ratios have nearly the same solubility. For this reason, it was expected that leaching would have a limited effect on the composition of the diesel (Larsen et al. 1992). In addition, leaching was expected to be limited because the oil-affected soils examined were all situated below paved areas, restricting the percolation of rain water.

In contrast to evaporation and leaching, microbial action generally will affect the components according to their configuration and not their vapor pressure. While the components in the ratios have nearly the same solubility and volatility, they differ with respect to degradability. Both microbial action and evaporation remove the n-alkanes. Evaporation removes the n-alkanes and isoprenoids at the same rate, depending only on the vapor pressure, whereas microbial action removes n-alkanes much faster than isoprenoids. For this reason the isoprenoids will gradually become more dominant compared with the n-alkanes. The composition of the diesel taken from a 22-year-old spill was dominated completely by the relatively bioresistant isoprenoids (Figure 2b). This demonstrates that in samples from the center of the oil-affected soil body microbial action was by far the most important process affecting the composition of diesel oil in the subsurface environment. Other processes, including evaporation and leaching, played only insubstantial roles.

Microbial action within the oil-affected soil was inhibited by a combination of the relative lack of nutrients and oxygen and the inaccessibility of hydrocarbons. These conditions clearly slowed the rate of alteration of the diesel oil within the subsurface environment.

To study the relationships among the most important factors influencing microbial degradation, a detailed study was undertaken at the Provestenen site. The correlations among the factors were subjected to a principal component analysis (STSC Inc. 1991). Figure 3 contains the results of this analysis; it shows a positive correlation among those factors located close to each other and a negative correlation where the factors were located on a straight line through both the factors and origin (0, 0).

As Figure 3 illustrates, there was a close positive correlation among the different degradation ratios, except in the case of the n-C_{17}/farnesane ratio, and a positive correlation between concentration and depth. Negative correlations existed between the depth in meters below ground/concentration in mg/kg and n-C_{17}/farnesane ratios. The close correlation among the degradation ratios was expected because they all express the biological degradation. The C_{17}/farnesane ratio, however, was unrelated to any of the other degradation ratios, indicating that this ratio is unsuitable for estimating the degree of degradation. The positive correlation between depth and concentration was probably a consequence of the shape of the oil-affected soil body, because the concentration of oil in general will increase toward the ground water table. The negative correlation with the C_{17}/farnesane ratio appeared to be a coincidence.

Other than the above, there were no intercorrelations among the factors. Neither the current microbial count, the total number of microorganisms, nor the number of oil-degrading microorganisms appeared to be related to any degradation factor or ratio or to the total concentration of diesel oil. A significant microbial growth on oil would be expected to respond to some kind of correlation between the biomass and the concentrations or the degradation ratios. The lack of any such correlation is an indication of inhibited microbial action and of the fact that degradation took place slowly under the study condition. Current estimates of biomass may not correlate with the extent of long-term degradation.

The analyses showed both microbially degraded diesel oil and the presence of microorganisms. They also revealed high concentrations of diesel oil even after exposure in the soil for 22 years, but showed no correlation between oil concentration and the size of the microbial biomass. The Provestenen investigation provided no explanation for such a slow and limited microbial degradation. Accordingly, the dominating factor that influenced the rate of alteration of the diesel oil composition in these natural environments, as expressed by the ratio of n-alkanes to isoprenoids, was age, i.e., length of time that the diesel had been present in the subsurface environment.

It is hypothesized that the degradation may be explained in the following ways:

- Degradation by an active microbial population acclimated to the unfavorable conditions in the soil affected by oil
- Degradation by an active microbial population located in microenvironments within the soil affected by oil which provided more favorable conditions for microbial activity
- Degradation by enzymes released into the soil environment by decaying microorganisms
- Degradation by exogenic oil-degrading enzymes from non-adapted microorganisms.

The first two explanations involve the use of diesel oil as a growth substrate for the microorganisms, which again involves an adaptation of the enzyme system to degrade the oil components. An adaptation will not take place unless the microorganisms gain more energy from the metabolism of the oil components than is used to synthesize oil-degrading enzymes (Grady 1985). For the microbial populations as a whole, conditions in strongly oil-affected soils are believed to inhibit the production of enzymes because of limited oxygen and nutrients, high concentrations of compounds adversely affecting microbes, low biological availability, or any combination of these factors. Small parts of the total microbial population, however, may have been able to grow on the oil under these unfavorable conditions or in more favorable microenvironments. Although this small population may have been related to the concentration of the oil, it was impossible to measure such a limited population using the methods involved in this study.

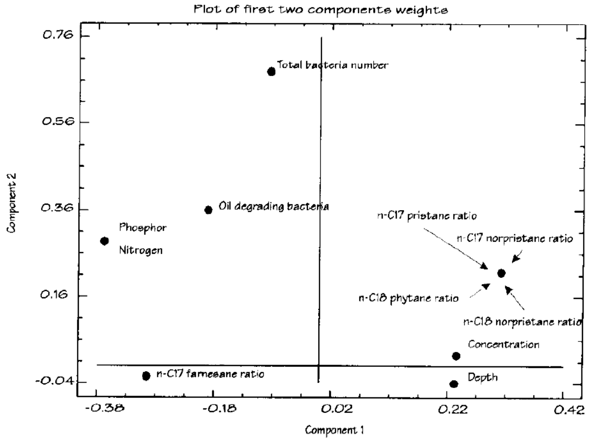

Figure 3. Principal component analysis of 12 different factors/parameters from the 22-year-old spill.

Even if the microorganisms have not adapated or are actively altering the oil, the mere presence of microorganisms could result in a low rate of alteration of the diesel component. Oil-degrading enzymes are probably present at low concentrations even in microorganisms not adapted to oil degradation; these enzymes may be released in the soil environment as the cells decay. Enzymes in the soil environment may also arise from exogenic enzymes, which are enzymes transported out of cells.

In the Specific Soil Environment Under Service Stations the Age of Oil Spills Can Be Determined from the Degree of Degradation

The correlation analysis on data from the 12 locations with a known date of sudden release into the environment demonstrated a clear relationship between the age of the oil and the degradation ratios from the oil-affected soil bodies (see Table 3). The correlations varied from 0.52 to 0.89, depending on the actual ratio and whether the correlation was calculated from the average ratio from each site or from all data collected.

The C_{17}/pristane ratio had the highest correlation with the age of the diesel, with a correlation coefficient of 0.89 based on the average degradation ratio and a correlation coefficient of 0.66 based on all data. The high correlation between C_{17}/pristane and the age reflects to some extent the original low variation in the ratio in fresh diesel (see Table 2).

Table 3

Correlation of Age and Different Component Ratios*

	R^2 All Data (−)	R^2 Average of Stations (−)	σ Standard Error on Estimate (years)
C_{17}/Pristane	0.66	0.89	2.1
C_{17}/Norpristane	0.61	0.73	3.3
C_{18}/Phytane	0.52	0.73	3.2
C_{18}/Norpristane	0.55	0.69	3.5

*Values of R^2 and standard error on estimates on the average of all stations

The correlation based on the average degradation ratios took into account variation in the ratio within the soil of each location, which may indicate variation in the environment or the presence of microenvironments.

It has been suggested that the proportion between the surface and the volume governs the diffusion of oxygen and nutrients into the oil-affected soil body. Thus it is likely that for oil-affected bodies with the same volume, a body with a large surface will be degraded faster than a body with a limited surface, simply because of differences in the supply of oxygen and nutrients. The shape of the oil-affected body is a function of soil type, porosity, amount of spilled oil, and other factors. Since these factors varied among the 12 locations, the shape of the bodies would appear random. If the degradation ratio were a function of the shape, the ratios from the 12 locations would vary randomly because the shapes of the bodies vary randomly. However, this was not the case; thus it is concluded that the shape of the body did not determine the degree of degradation inside the body.

Figure 4 shows the correlation between the C_{17}/pristane ratio and the age of the diesel spill. The dotted line represents a linear approach to the relationship. The two innermost dashed lines represent the 95 percent confidence interval of the average degradation ratios from each location. As discussed previously, it is impossible to explain fully the nature of the relationship, but the data suggest a linear relationship indicating a 0th order kinetic of the degradation of the n-alkanes.

The high correlation between the C_{17}/pristane ratio and age can be used to estimate the age of oil within a subsurface environment. By evaluating the C_{17}/pristane ratios and comparing the values with the ages as plotted in Figure 4, it is possible to determine the age of the diesel spill at the 95 percent confidence level to within two years for diesel that is between five and 20 years old, with some slightly greater variability at the extremes (less than five years and more than 20 years old). At certain points along the curve, e.g., for diesel approximately 12 years old, it appears possible to determine the age of the oil with even greater accuracy at the 95 percent confidence level.

When using the curve to determine the age of a diesel spill it is important to remember that the degradation ratio indicates the age of a sudden spill. Often, property damage results from a continuous spill or the mixing of several different spills. In those cases, the degradation ratio will underestimate the age of the initial spill or the first date of the property damage. A mixture of degraded and fresh diesel generally will be dominated by the fresh diesel because the degraded diesel is present in lower concentrations. This implies that the presence of fresh diesel oil does not necessarily indicate only a recent oil spill, although the presence of degraded diesel oil is a strong indication of an old spill.

Conclusions

The study demonstrates that the degree and rate of alteration of diesel oil can be related to the time the oil has been in the ground. The analysis of 15 different diesel oils reveals a relatively low variation in the C_{17}/pristane and C_{17}/norpristane ratios. The analysis of diesel oil stored in stockpiles since 1974 shows that its composition is basically the same as diesel oil produced in 1992. In contrast, the composition of degraded diesel differs significantly from the composition of a fresh diesel oil; the fresh diesel is dominated by n-alkanes, while the degraded diesel is dominated by isoprenoids, which are more bioresistant.

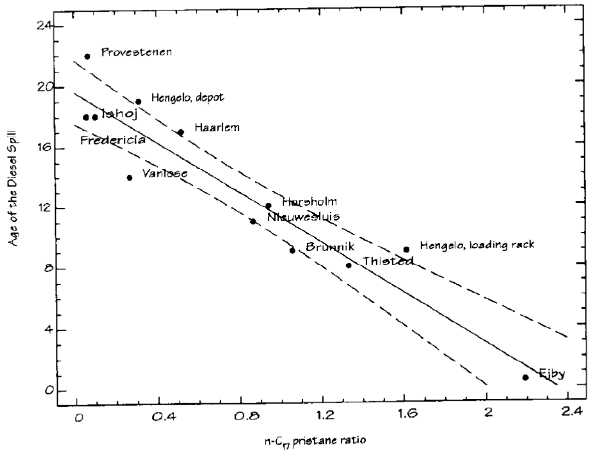

Figure 4. Relationship between the age of the oil spill and the C_{17}/pristane ratio over a 22-year period.

Based on the ability to distinguish between fresh diesel oil produced within the last 20 years and degraded diesel oil, the degree of degradation of the samples is compared to the time the oil has been in the ground. Statistical analysis shows a correlation factor of 0.89 for the C_{17}/pristane ratio based on the average degradation ratio for each oil-affected soil body. This is a high correlation factor and allows the C_{17}/pristane ratio to determine the age of a diesel oil spill within a range of ± 2 years at a 95 percent confidence level.

Acknowledgments

The authors wish to thank the firms De Ruiter Milieutechnologie bv, Tauw Infra Consult bv, and Geofox bv for letting us use reports. The work has not been subjected to these firms' peer review and, therefore, does not necessarily reflect the views of the firms.

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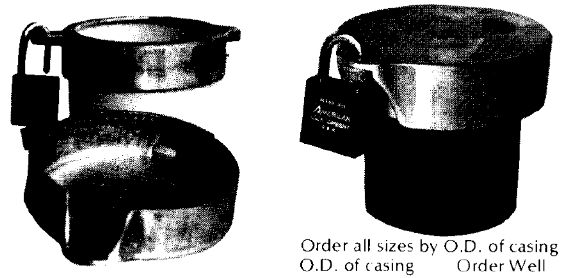


Patterns of Chemical Changes During Environmental Alteration of Hydrocarbon Fuels

by Isaac R. Kaplan, Yakov Galperin, Hossein Alimi, Ru-Po Lee, and Shan-Tan Lu

Abstract

This paper discusses major environmental alteration processes and describes a set of chemical tests that have been developed to monitor compositional changes in hydrocarbon fuels released into the environment. The methods examine various homologous series of hydrocarbons including straight chain (paraffins or n-alkanes), branched chain (isoparaffins or isoprenoids), alicyclic (naphthenes or alkylated cyclohexanes), polycyclic (steranes and terpanes), and aromatic structures (benzene, toluene, ethylbenzene, xylenes, alkylated benzenes, polycyclic aromatic hydrocarbons, and aromatic steranes). Each one of these groups of hydrocarbons has a different tolerance to environmental alteration by evaporation, dissolution (water washing), and biodegradation. When used as an analytical system on environmental samples, the data obtained provide information on fuel type recognition patterns and on degradation levels of the various fuels, allowing for an estimate of residence time.

Pages 113–124

Introduction

Major Alteration Processes in the Environment

It has been well established, with a large literature citation extending back more than 40 years, that crude oil in the environment is altered by a series of processes leading to tar balls and asphaltenic residues (Zobell 1946; McKenna and Kallio 1965; Winters and Williams 1969). These processes involve evaporation, water solution or water washing, and biodegradation of various components. As a general rule, the low molecular weight hydrocarbons with the highest vapor pressure will escape from the crude oil rapidly. Next, in the presence of either standing water or rain, the soluble components begin to be removed. Benzene is the most water soluble hydrocarbon (1750 ppm), followed by toluene (550 ppm) and other monoaromatic hydrocarbons with solubilities ranging from 100 to 200 ppm. The olefins and light hydrocarbon gases such as methane and ethane are also among the most soluble hydrocarbons (Galland and Yaws 1992). By contrast, paraffins from C_6 to C_{30} have relatively low solubilities ranging from 12 ppm to less than 1 ppb.

Following the selective removal of the most volatile and most soluble components of crude oil (or fuels), the residual components can remain in a sterile environment for an indeterminate period of time. For example, crude oil has been produced from early Paleozoic reservoirs more than 500 million years old and Precambrian source rocks approaching one billion years in age (Halbouty et al. 1970; Tong and Huang 1991; Walter 1982), such as the Weiyuan in the Sichuan Basin in China and sediments in McArthur River Area, Northern Territory, Australia (Wang et al. 1989; Womer 1986). The three controlling parameters that regulate the microbiological decomposition rate of the hydrocarbons in refined fuels and crude oil are (1) temperature, (2) the presence of nutrients and oxygen, and (3) the presence of free or adsorbed water. Depending on the indigenous bacterial species, typically the rate of biodegradation doubles for every 10°C increase in temperature. The requirement of oxygen for biodegradation of hydrocarbons has been known for several decades. It is assumed that in environments where it is absent, hydrocarbons will either not decompose or decompose slowly. The question of aerobic vs. anaerobic breakdown of hydrocarbons has been investigated since the early work of Zobell (1946). Recent publication suggests that there is evidence for selective anaerobic decomposition (Rueter et al. 1994). Nutrients are usually sufficiently present in shallow soil or ground water to support a microbial biota. Most of the weathering studies on crude oils (Kolpack and Meyer 1970; Magoon and Isaac 1983; Douglas et al. 1993; Blanc and Connan 1992) that aimed at determining detailed changes in the chemical constituents have directed their attention to the high-molecular-weight low-solubility fractions, including the so-called biomarkers shown in Figure 1.

This paper addresses the chemical changes that occur when three representative refined fuels (i.e., gasoline, diesel fuel #2, and fuel oil #6, or Bunker C fuel) are released on land rather than in a marine environment. Although a large literature is growing on the bulk changes that occur during environmental alteration and remediation of escaped fossil fuels, previous work has concentrated largely on volatile aromatic hydrocarbons (BTEX), on the polynuclear aromatic hydrocarbons (PAH) (because of their potential toxicity), and on the paraffinic (n-alkane) fraction of hydrocarbons, because the latter are the most rapidly degraded.

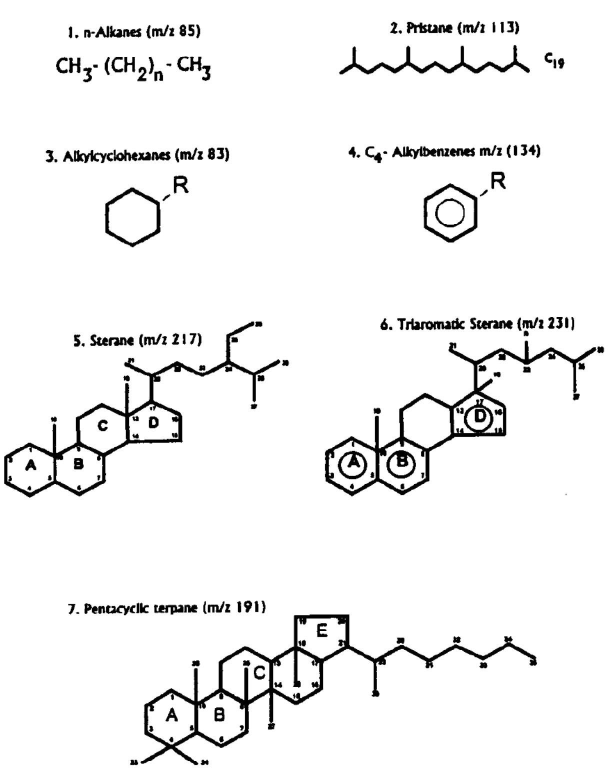


Figure 1. Chemical structures of representative hydrocarbons.

Table 1
Gross Composition of Typical Hydrocarbon Fuels (Percent)

Composition	Gasoline	Diesel #2	Bunker C
Paraffins	45	55	14
Cycloparaffins	5	12	7
Olefins	7	5	—
Aromatics	43	24	34
Polar + residuals	—	4	45

Monitoring Environmental Alteration in Chemical Composition

Most fuels have chemical compositions with no sharp cut-offs for the concentration of constituent hydrocarbons (Table 1). Minor amounts of hydrocarbons are present out of the commonly recognized range, at both the low and high boiling ends, and are frequently not identified unless special precautions are taken. For example, the common range for gasoline is from propane (C_3) to dodecane (C_{12}); however, C_{13} and C_{14} n-alkanes are detected often when gasoline is highly altered by evaporation. Because these hydrocarbons are also present in mineral spirits, jet fuels, kerosene, and diesel fuels, care needs to be taken to prevent misidentification of the escaped fuel. Likewise, certain important indicators for both diesel and Bunker C fuel (some PAH compounds and biomarkers) are present in low relative concentration and can only be detected if the corresponding fraction is concentrated after its separation on a silica gel column. Errors in identification can also be made when soil or water extracts are evaporated too extensively during sample preparation for analysis. In this case, the volatile hydrocarbon components in the C_3 to C_{10} range can be selectively lost, leading to misidentification of the fuel type present. Additionally, errors in identification of a fuel type arise when hydrocarbon compounds that are vulnerable to environmental alteration (such as n-alkanes) are used as the only criterion for identification. For these reasons, it is advisable to measure numerous hydrocarbon species, especially those displaying a homologous series, for the following three purposes: (1) to identify a particular fuel type; (2) to determine mixing ratios of different fuels; and (3) to estimate the relative state of degradation. The data derived may also permit the estimation of the approximate length of time that any one of the fuels identified has been in the environment.

Criteria for Investigation of Fuel Hydrocarbon Parameters

Automotive Gasoline Fuel

Automotive gasoline is a generic term used to describe volatile, inflammable petroleum fuels used primarily in internal combustion engines. It is a complex mixture of hydrocarbon compounds predominantly in the C_3 to C_{12} range, with a nominal boiling-point range of 40 to 230°C (100 to 450°F). Gasolines are blended from several refinery process streams, including various naphtha streams from direct distillation of crude oil at atmospheric pressure (light straight-run naphtha), catalytic and thermal cracking processes, catalytic reforming processes, and from alkylation and isomerization of the light distillate streams. There are more than 300 individual compounds recognized to date in gasoline (Whittemore 1979). For practical purposes, it is sufficient to identify about 90 major hydrocarbons in the C_3 to C_{10} range by high-resolution gas chromatography with a flame ionization detector (GC/FID).

For the purpose of analyzing the environmental history of fugitive gasoline, we developed a set of parameters, some of which were previously discussed by Kaplan (1992) and Kaplan et al. (1992), to differentiate the chemical composition and to characterize aging processes of different fuels. The following 10 parameters are routinely measured: (1) BTEX (EPA method 8020); (2) C_3 to C_{10} volatile hydrocarbons by GC/FID; (3) C_8 to C_{30} n-alkanes by GC/FID and by gas chromatography-mass spectrometry (GC/MS); (4) alkylbenzenes and alkylnaphthalenes by GC/MS; (5) alkylcyclohexanes by GC/MS; (6) lead alkyl additives and lead scavengers by gas chromatography with an electron capture detector (GC/ECD); (7) oxygenated additives (alcohols and ethers) by two-dimensional GC/FID (ASTM method D4815); (8) simulated distillation by GC/FID (ASTM method D2887); (9) pigment (dye) additive distribution; and (10) $^{13}C/^{12}C$ and D/H stable isotope ratios. In this paper, we will only address items 1 through 5.

Volatile Gasoline Range Hydrocarbons

The EPA method 8020 (especially with dual column confirmation measurement) yields reliable results for BTEX hydrocarbon concentrations (Table 2) and their relative distribution (Table 3). Because the volatility and aqueous solubility between benzene and xylenes varies by a factor of 10, BTEX results offer an excellent set of parameters for measuring water washing and evaporative alteration. A large literature addresses these issues (Bruce et al. 1991; Potter 1989; Odermatt 1994). Changes in the BTEX composition after gasoline enters the environment are shown in Table 4 for gasoline residues in free product, ground water, and soil.

The immediate observable environmental change shown in Table 4 relative to the BTEX contents in dispensed gasolines (Table 2) is the reduction of about 40

Table 2

Average and Range of BTEX Hydrocarbon Content (mg/mL) in Different Grades of Dispensed Gasolines

	Benzene		Toluene		Ethylbenzene		Xylenes	
Gasoline Grade*	Range	Average	Range	Average	Range	Average	Range	Average
Regular leaded (5)	6.6-14.8	9.2	18.6-64.4	32.6	6.2-14.0	9.1	32.1-77.4	47.2
Regular unleaded (12)	5.0-19.4	10.2	17.9-56.6	28.7	5.8-15.4	8.0	27.1-76.6	39.6
Unleaded plus (8)	7.1-18.2	11.9	21.6-62.8	36.7	6.0-15.1	9.3	28.6-81.5	45.7
Super unleaded (12)	6.6-18.9	11.5	22.4-72.2	40.9	6.6-19.1	10.1	33.4-90.8	50.6

*Number in parentheses denotes number of sample analyses averaged.

Table 3

Ratios Calculated from the BTEX Data of Different Grades of Dispensed Gasolines

Gasoline Grade*		Benzene/ Toluene	Benzene/ Ethylbenzene	Benzene/ Xylenes	Toluene/ Ethylbenzene	Toluene/ Xylenes	Ethylbenzene/ Xylenes	B + T/ E + X
Regular leaded (5)	Average	0.28	1.0	0.20	3.6	0.70	0.19	0.74
	Range	0.23-0.36	0.92-1.10	0.19-0.20	3.0-4.6	0.59-0.83	0.18-0.19	0.67-0.98
Regular unleaded (12)	Average	0.36	1.28	0.26	3.6	0.72	0.20	0.82
	Range	0.28-0.41	0.86-1.7	0.18-0.32	2.9-4.2	0.57-0.83	0.19-0.22	0.64-0.95
Unleaded plus (8)	Average	0.32	1.28	0.26	3.9	0.80	0.20	0.88
	Range	0.28-0.37	0.85-1.6	0.19-0.32	3.0-5.0	0.63-0.94	0.19-0.23	0.70-1.05
Super unleaded (12)	Average	0.28	1.14	0.23	4.0	0.81	0.20	0.86
	Range	0.24-0.33	0.77-1.6	0.16-0.30	3.1-5.6	0.61-1.02	0.18-0.21	0.67-1.13

*Number in parentheses denotes number of sample analyses averaged.

Table 4
Average and Range of BTEX Hydrocarbon Content in Altered Gasolines Collected in Different Matricies and Various Climatic Environments

	Benzene		Toluene		Ethylbenzene		Xylenes	
Sample Type*	Range	Average	Range	Average	Range	Average	Range	Average
Free product (mg/mL) (25)	3.6-12.6	6.3	13.4-55.3	23.7	3.2-16.0	6.5	19.1-78.1	39.5
Water (μg/mL) (366)	0.3-20.8	3.2	0.03-21.4	3.5	0.1-7.6	1.2	0.2-17.0	5.7
Soil (μg/g) (21)	0.01-10.0	1.2	0.01-77.4	4.6	0.01-50.9	5.3	0.01-220	21.7

*Number in parentheses denotes number of sample analyses averaged.

Table 5
Ratios Calculated from BTEX Data of Altered Gasolines

Sample Type*		Benzene/ Toluene	Benzene/ Ethylbenzene	Benzene/ Xylenes	Toluene/ Ethylbenzene	Toluene/ Xylenes	Ethylbenzene/ Xylenes	B + T/ E + X
Free product (25)	Average	0.26	0.97	0.16	3.60	0.60	0.16	0.65
	Range	0.18-0.34	0.40-1.6	0.05-0.30	1.8-6.3	0.29-1.0	0.12-0.23	0.30-1.1
Water (366)	Average	2.90	2.70	0.56	2.90	0.61	0.21	0.97
	Range	0.09-21.6	0.13-10.9	0.01-3.5	0.1-9.6	0.04-4.2	0.08-0.55	0.11-3.4
Soil (21)	Average	0.26	0.23	0.06	0.87	0.21	0.24	0.48
	Range	0.03-100	0.02-2.9	<0.01-25	0.03-2.5	0.02-0.59	0.18-9.5	0.07-2.6

*Number in parentheses denotes number of sample analyses averaged.

percent in benzene concentration in free-floating product. Toluene, ethylbenzene, and especially xylenes demonstrate less noticeable reduction. The reason for this is that, due to its highest solubility among BTEX hydrocarbons, benzene will preferentially diffuse out of the product and partition in the ground water phase. This is also evident from the average concentrations of BTEX hydrocarbons in water samples, where benzene displays an enrichment relative to toluene, ethylbenzene, and xylenes. By contrast, the reverse occurs in the soil where toluene and especially ethylbenzene and xylenes are preferentially retained. Therefore, when the concentration ratios of benzene/toluene, benzene/ethylbenzene, benzene/xylenes, toluene/ethylbenzene, and toluene/xylenes are compared in free product, water, and soil samples (Table 5), the changes discussed previously are seen easily.

In the course of numerous gasoline-contaminated site studies, it has been found that a useful parametric ratio to evaluate the gasoline partitioning is benzene+toluene/ethylbenzene+xylenes (B+T/E+X). For the examples shown in Table 3 for dispensed gasoline, the average ratio has a narrow range of 0.74 to 0.88, whereas the average ratios for product, water, and soil (Table 5) are 0.65, 0.97, and 0.48, respectively.

The advantage of using the B+T/E+X parameter over ratios of individual BTEX hydrocarbons is that one can smooth out variations in the composition of manufactured gasoline and accommodate processes that preferentially remove benzene from the ground water. During the past 20 years, there have been attempts made to limit the content of benzene in gasoline because of its recognized hazard to human health. The reduction in benzene content was often compensated by toluene, and to a lesser extent, ethylbenzene and xylenes. The content of benzene, therefore, has fluctuated more than other BTEX hydrocarbons. By coupling benzene with toluene, the fluctuations are minimized. Benzene concentration can also be diminished dramatically during remediation of a site, especially if vapor extraction has been used to remove gasoline contamination.

Laboratory BTEX solubility studies conducted by the authors demonstrated that the B+T/E+X ratio of newly introduced gasoline in water ranges from about 1.0 to 5.0, depending on the amount of gasoline in contact with water. When the ratio near the source of the gasoline release falls in this range, it indicates that a recent release into the water has occurred. The ratio in the vicinity of the source of release drops as a function of time and environmental controls, and values below 0.5 are usually indicative of residence ages longer than 10 years. Ratios greater than 5 are typically encountered at a distance from the source and signify preferential removal and transport of benzene and toluene by water away from the source of release.

The C_3 to C_{10} composition of the gasoline range hydrocarbons provides an essential set of chemical characteristics that are important in (a) determining source relationships; (b) identifying fuel grade (low or high octane); (c) differentiating automobile gasoline from white gas, aviation fuel, and mineral spirits; and (d) establishing degree of degradation. Free products are normally analyzed by direct injection, whereas ground water and soil samples are analyzed by purge-

Table 6
Average and Range of Bulk PIANO Composition of Dispensed Gasolines

Grade of Gasoline*		Paraffins	Isoparaffins	Aromatics	Naphthenes	Olefins
		Relative Percent				
Regular leaded (5)	Average	10.7	32.0	45.0	7.8	4.6
	Range	10.4 - 11.0	31.7 - 32.5	44.1 - 45.3	7.5 - 8.0	4.3 - 5.0
Regular unleaded (12)	Average	10.2	37.6	38.7	6.0	7.1
	Range	8.4 - 11.3	32.5 - 40.3	32.9 - 43.7	3.2 - 9.7	1.5 - 13.7
Unleaded plus (8)	Average	10.8	37.0	41.5	5.6	5.1
	Range	8.7 - 13.3	34.5 - 40.0	40.0 - 42.9	3.6 - 6.6	2.9 - 9.6
Premium unleaded (12)	Average	9.4	34.9	48.4	2.9	3.9
	Range	7.1 - 13.6	26.2 - 39.7	43.4 - 59.8	1.2 - 5.3	1.0 - 7.3
Overall average		10.3	35.4	43.4	5.6	5.2

*Number in parentheses denotes number of sample analyses averaged.

Table 7
Average and Range of Bulk PIANO Composition for Altered Gasolines

Sample Type*		Paraffins	Isoparaffins	Aromatics	Naphthenes	Olefins
		Relative Percent				
Free product (25)	Average	10.2	31.8	49.0	4.5	4.0
	Range	4.3 - 18.3	20.9 - 40.2	27.1 - 70.1	1.2 - 9.0	1.9 - 5.7
Soil (10)	Average	2.8	15.1	79.4	1.2	1.5
	Range	0 - 5.3	0 - 31.6	60.4 - 98.7	0 - 2.6	0.8 - 2.1
Water (15)	Average	4.7	22.2	63.1	7.1	5.3
	Range	0.8 - 10.9	2.2 - 56.9	26.8 - 94.3	1.1 - 16.6	0.2 - 19.6

* Number in parentheses denotes number of sample analyses averaged.

and-trap preconcentration followed by injection into a 100-m capillary chromatographic column.

Compositional characteristics of leaded and unleaded gasolines are conventionally described in terms of bulk relative contents of paraffins, isoparaffins, aromatics, naphthenes, and olefins (PIANO) and are shown in Table 6. Examples of changes that occur in the bulk PIANO composition of gasoline when it enters soil and ground water and when it accumulates as free product are shown in Table 7. Based on the average gasoline composition, a set of ratios can be established that allows estimation of degree of alteration by evaporation, water washing, and biodegradation. Examples for two newly dispensed gasolines, dissolved gasoline in a ground water sample, and gasoline in a soil sample are shown in Table 8. The evaporation ratios compare the distribution of different members of the same hydrocarbon type (i.e., paraffins and isoparaffins) with different Henry's law constants. Water washing ratios compare benzene and toluene with nonaromatic hydrocarbons of about the same molecular size and volatility. Total aromatics content is compared also with total paraffins and naphthenes. The biodegradation parameters compare olefins (hydrocarbons highly susceptible to biodegradation) with paraffins, as well as isoparaffins plus naphthenes with paraffins. The ratio comparisons demonstrate that aromatic compounds are strongly concentrated in the ground water and soil relative to the naphthenes, paraffins, and isoparaffins. In accordance with known aqueous solubility, n- and isoparaffins are preferentially concentrated relative to olefins in soil, while the reverse tendency is observed in ground water.

Semi-Volatile Gasoline Range Hydrocarbons

It has been found that in addition to alkanes, the three homologous series represented by alkylbenzenes, alkylnaphthalenes, and alkylcyclohexanes are among the most useful for hydrocarbon fuel fingerprinting. Alkylbenzenes and alkylnaphthalenes are more resistant to biodegradation than most of the other gasoline hydrocarbons (Eganhouse et al. 1993). The longer the alkyl chain attached to the aromatic ring, the more resistant the hydrocarbon is to biodegradation (Volkman 1984). The alkylnaphthalenes appear to be more resistant to degradation than the alkylbenzenes. Alkylcyclohexanes are less soluble than the alkylbenzenes and more resistant to biodegradation compared to paraffins. They should persist, therefore, for a significantly longer time in the environment than the alkylbenzenes and paraffins (Kaplan and Galperin 1996).

Determination of the distribution of hydrocarbon series is accomplished by analyzing a sample using GC/

Table 8

Examples of Degradation Ratios and Bulk Composition Calculated from the Gasoline Range (C_3 to C_{10}) Analysis of Two Newly Dispensed Gasolines, a Ground Water Sample, and a Soil Sample

Parameter	87 Octane Gasoline	92 Octane Gasoline	Water	Soil
Evaporation				
n-pentane/n-heptane	2.1	1.4	0.8	0.5
2-methylpentane/2-methylheptane	7.2	4.6	2.0	0.8
Water Washing				
benzene/cyclohexane	4.3	9.6	19.3	3.2
toluene/methylcyclohexane	10.8	20.5	13.0	3.9
aromatics/total paraffins	0.8	0.9	4.6	4.2
aromatics/naphthenes	6.3	13.2	16.0	35.0
Biodegradation				
(C_4-C_8 paraffins + isoparaffins)/C_4-C_8 olefins	6.7	8.1	5.2	13.9
3-methylhexane/n-heptane	1.6	1.5	1.1	1.2
methylcyclohexane/n-heptane	0.6	0.5	1.6	1.2
isoparaffins + naphthenes/paraffins	4.6	5.7	4.1	4.9
Octane Rating				
2,2,4-trimethylpentane/methylcyclohexane	2.2	5.1	0.4	2.3
Relative Percentages				
Paraffinic	9.6	7.5	4.1	3.5
Isoparaffinic	38.3	39.7	12.1	15.0
Aromatic	38.6	43.4	75.1	76.9
Naphthenic	6.1	3.3	4.7	2.2
Olefinic	7.4	6.2	4.0	2.4

MS in full scan mode and selecting a series of characteristic ion fragments for each hydrocarbon homologous series (i.e., m/z 85 for iso- and n-alkanes; m/z 83 for alkylcyclohexanes; and m/z 134 for C_4-alkylbenzenes) (Figure 1). For polynuclear aromatics, the m/z values are identified in Table 9.

To demonstrate the distribution of the different hydrocarbon species, we show a set of mass chromatograms and bar diagrams for a newly dispensed gasoline (Figure 2), a lightly altered gasoline in ground water (Figure 3), and a severely altered gasoline in ground water (Figure 4), all collected from the same site. The comparison of these figures demonstrates that as alteration progresses, the higher volatility (lower molecular weight) hydrocarbons are most rapidly removed and the alkanes and isoalkanes (m/z 85) are largely eliminated. The alkylcyclohexanes display a significant reduction in CH-1 (see appendix for key), which is the dominant hydrocarbon in freshly dispensed gasoline, and a systematic increase in the CH-2/CH-1 ratio. For the C_4-alkylbenzenes (see appendix for key), 1,3-diethylbenzene (peak #20 in the m/z 134 mass chromatogram) is rapidly diminished and the group of peaks from 21 to 27 decrease in relative content. The four hydrocarbons that persist are represented by peaks 28, 31a, 31, and 32. There is also a noticeable reduction in the peak height of 1,2,3,5-tetramethylbenzene (peak #31) relative to 1,2,4,5-tetramethylbenzene (peak #31a).

The three branched-chain isomers of octane labeled in Figures 2 through 4 as i-8 (2,5(2,4)-dimethylhexane), i-8′(2,3,4-trimethylpentane), and i-8″(2,3-dimethylhexane) are always present in gasoline that has been manufactured with the alkylation process (to boost the octane number). The dominant C_8-isoparaffin formed during the alkylation process is isooctane (2,2,4-trimethylpentane),which may reach concentrations as high as 5 percent of the gasoline hydrocarbon content in high-octane fuels. This compound, however, is readily identified by C_3 to C_{10} range GC/FID or by GC/MS at m/z 57. In gasoline where alkylation has been part of the manufacture process, 2,3,4-trimethylpentane (i-8′) gives the dominant isoparaffinic peak in the m/z 85 mass chromatogram. Where alkylation has not occurred in the manufacture, only the dimethylhexanes are present with 2,3-dimethylhexane (i-8″) displaying the dominating peak. This is also the case for JP-4 military jet fuel.

The observable changes in aromatic hydrocarbons (see bar diagrams in Figures 2 through 4) are in the reduction of alkylbenzenes and the relative increase in naphthalene and the alkylnaphthalenes. Among the suite of alkylbenzenes measured, the C_3-alkylbenzenes diminish more rapidly than the other three alkylbenzenes shown in the figures.

Table 9

Relative Concentrations of Aromatic and Polynuclear Aromatic Hydrocarbon Compounds in Gasoline, Diesel, and Bunker C Reference Fuels

			Gasoline	Diesel Fuel	Bunker C Oil
No.	m/z	Compound	Relative Percent		
1	120	C_3-alkylbenzenes	57.6	1.2	0.3
2	134	C_4-alkylbenzenes	20.4	2.1	0.8
3	148	C_5-alkylbenzenes	4.3	1.6	0.9
4	162	C_6-alkylbenzenes	0.6	1.0	0.3
5	128	C_0-naphthalene	11.2	0.7	1.6
6	142	C_1-naphthalenes	5.5	5.6	5.8
7	156	C_2-naphthalenes	0.2	24.6	13.6
8	170	C_3-naphthalenes	0.1	26.1	9.4
9	184	C_4-naphthalenes	—	11.8	3.0
10	166	C_0-fluorene	—	0.8	0.5
11	180	C_1-fluorenes	—	2.1	1.2
12	194	C_2-fluorenes	—	3.0	1.8
13	208	C_3-fluorenes	—	0.4	1.4
14	222	C_4-fluorenes	—	—	0.7
15	154	C_0-biphenyl	—	0.1	0.2
16	168	C_1-biphenyls + dibenzofuran	—	2.1	0.6
17	182	C_2-biphenyls + C_1-dibenzofuran	—	3.8	2.8
18	178	C_0-phenanthrene	—	1.8	2.8
19	192	C_1-phenanthrenes	—	3.2	6.2
20	206	C_2-phenanthrenes	—	1.3	8.3
21	220	C_3-phenanthrenes	—	0.7	5.2
22	234	C_4-phenanthrenes	—	—	2.0
23	202	C_0-pyrene/fluoranthene	—	—	2.6
24	216	C_1-pyrenes/fluoranthenes	—	—	2.2
25	230	C_2-pyrenes/fluoranthenes	—	—	3.4
26	244	C_3-pyrenes/fluoranthenes	—	—	1.9
27	258	C_4-pyrenes/fluoranthenes	—	—	0.7
28	228	C_0-chrysene	—	—	1.1
29	242	C_1-chrysenes	—	—	2.3
30	256	C_2-chrysenes	—	—	1.2
31	270	C_3-chrysenes	—	—	1.0
32	284	C_4-chrysenes	—	—	0.3
33	148	C_1-benzothiophenes	—	—	0.4
34	162	C_2-benzothiophenes	—	0.8	0.8
35	176	C_3-benzothiophenes	—	1.4	0.7
36	190	C_4-benzothiophenes	—	1.0	0.3
37	204	C_5-benzothiophenes	—	—	0.1
38	184	C_0-dibenzothiophene	—	0.6	0.5
39	198	C_1-dibenzothiophenes	—	1.5	1.4
40	212	C_2-dibenzothiophenes	—	0.7	3.0
41	226	C_3-dibenzothiophenes	—	—	2.1
42	240	C_4-dibenzothiophenes	—	—	0.8
43	234	C_0-naphthobenzothiophene	—	—	0.3
44	248	C_1-naphthobenzothiophenes	—	—	0.9
45	262	C_2-naphthobenzothiophenes	—	—	0.6
46	276	C_3-naphthobenzothiophenes	—	—	0.4
47	290	C_4-naphthobenzothiophenes	—	—	0.1
48	252	Benzo (B+K) Fluoranthene	—	—	0.08
49	252	Benzo (E) pyrene	—	—	0.10
50	252	Benzo (A) pyrene	—	—	0.10
51	252	Perylene	—	—	0.03
52	231	Triaromatic steranes	—	—	1.2
53	245	Triaromatic steranes	—	—	0.6

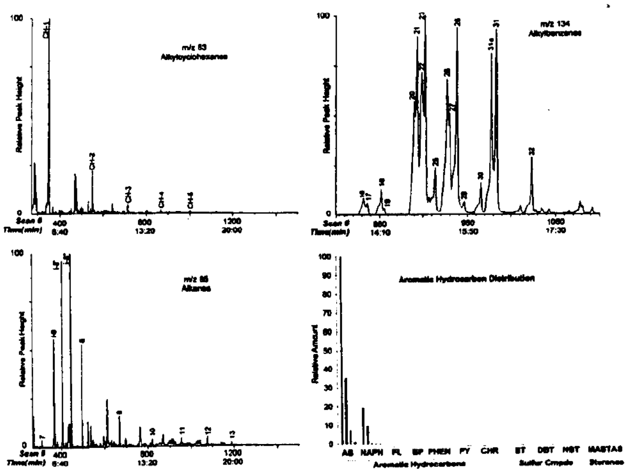


Figure 2. Mass chromatograms and bar diagram of a newly dispensed gasoline.

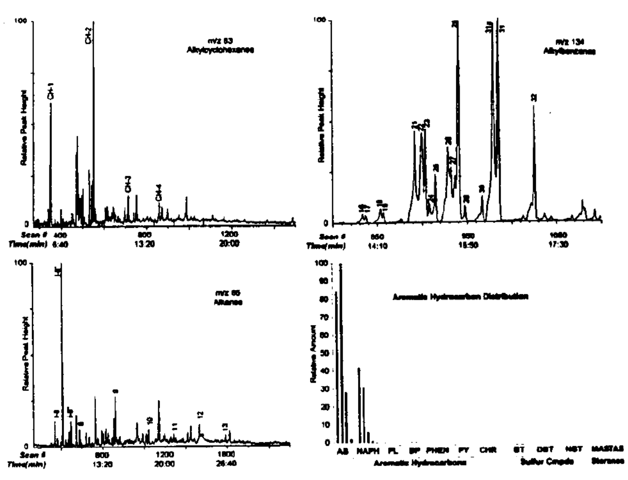


Figure 3. Mass chromatograms and bar diagram of gasoline in ground water.

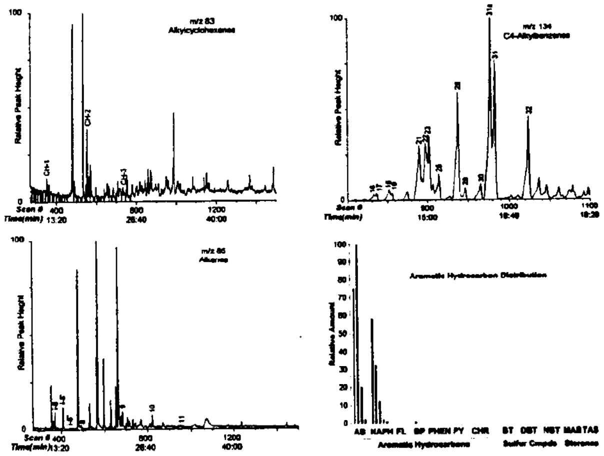


Figure 4. Mass chromatograms and bar diagram of severely altered gasoline in ground water.

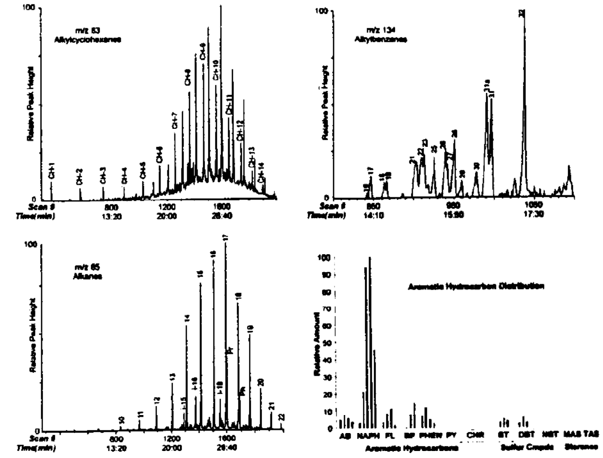


Figure 5. Mass chromatograms and bar diagram of unaltered diesel fuel.

Diesel Fuel #2

Diesel fuel is characterized by a smooth n-alkane distribution pattern (Figure 5), maximizing at about C_{14} to C_{17} and diminishing down to about C_{23}. It also has an isoparaffin (or isoprenoid) distribution extending from i-C_{10} to i-C_{20} (phytane), with i-C_{19} (pristane) dominating. The bulk composition of diesel fuel #2 consists of hydrocarbons with carbon numbers predominantly in the range of C_9 to C_{24} and boiling in the range of approximately 163 to 382°C (300 to 730°F). Diesel fuel is a blend of straight-run and catalytically cracked streams, including straight-run kerosene, straight-run middle distillate, hydrodesulfurized middle distillate, and light catalytically and thermally cracked distillates. Its bulk composition is shown in Table 1. It is noteworthy that this fuel has a wide range of PAH hydrocarbons (bar diagram in Figure 5), extending from naphthalenes (dominant) to phenanthrenes, as well as the sulfur-containing aromatics, such as benzothiophene and dibenzothiophene.

To determine the characteristics of diesel fuel #2, the following seven tests are routinely conducted: (1) C_8 to C_{34} n-alkanes and isoparaffins by high-resolution GC/FID and GC/MS; (2) alkylcyclohexanes from CH-1 to CH-14 by GC/MS; (3) alkylbenzenes by GC/MS; (4) PAH compounds by GC/MS; (5) tricyclic terpanes (if present) by GC/MS; (6) simulated distillation by GC/FID (ASTM method D2887); and (7) $^{13}C/^{12}C$ and D/H stable isotope ratios.

In this paper, we describe methods 1 through 4 and show three examples of environmental change occurring in diesel in a free product and in soil (Figures 6 through 8). Chemical changes due to biodegradation can most easily be observed from the n-alkane patterns. Figure 5 displays the chromatographic pattern for a newly dispensed diesel, whereas Figure 6 shows the absence of n-alkanes in a biodegraded product with only isoprenoids remaining. A mildly altered diesel fuel in soil (Figure 7) displays a suite of n-alkanes (m/z 85) with associated isoprenoids (identified in m/z 113 mass chromatogram). It is evident from a comparison of the mass chromatograms in Figures 5 and 7 that the relative abundance of isoprenoids has increased over their content in the dispensed diesel. In a moderately

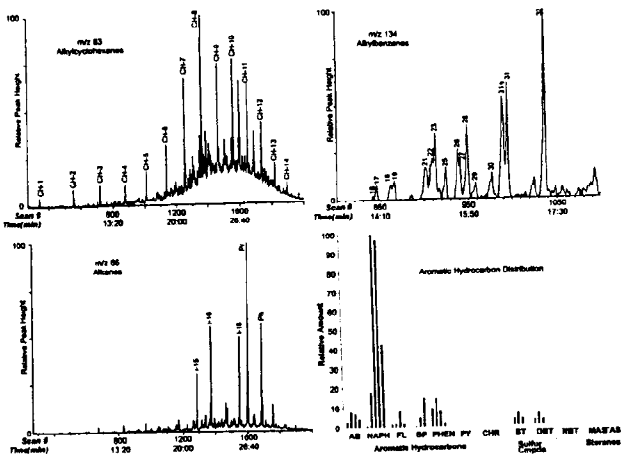


Figure 6. Mass chromatograms and bar diagram of altered diesel in floating product.

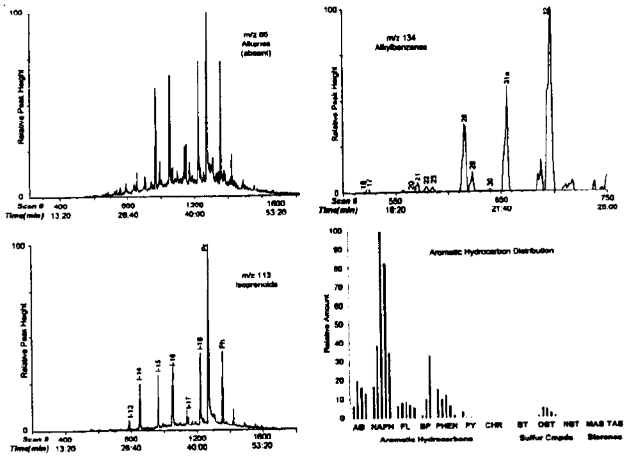


Figure 8. Mass chromatograms and bar diagram of severely altered diesel in soil extract.

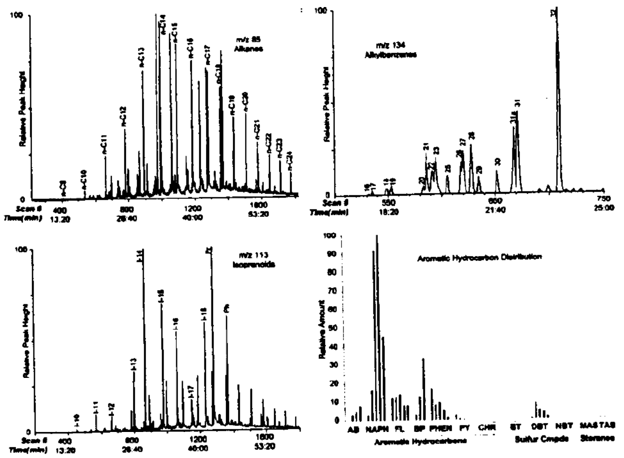


Figure 7. Mass chromatograms and bar diagram of altered diesel in soil extract.

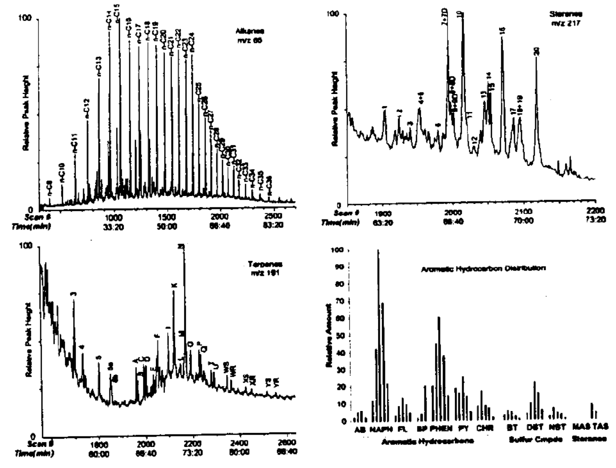


Figure 9. Mass chromatograms and bar diagram of unaltered Bunker C fuel.

degraded diesel present in soil (Figure 8), no n-alkanes are detectable at m/z 85, but all the isoprenoids remain (m/z 113). The presence of the isoparaffins (characterized by specific ion-fragments at m/z 85 and m/z 113) is particularly important in estimating degree of biodegradation. The most stable of the isoprenoid compounds is i-C_{19} (pristane). During severe biodegradation, the lower molecular weight isoprenoids from i-C_{10} to i-C_{18} and phytane are preferentially removed after n-alkane depletion. Pristane then remains as the dominant paraffinic constituent in degraded diesel. This can be seen from the m/z 85 mass chromatogram in Figure 6 and m/z 113 mass chromatogram in Figures 7 and 8. The alkylcyclohexanes distribution in the free product (Figure 6) as well as in moderately altered soil samples shows little change (possibly an increase in CH-8 relative to CH-9 in the original diesel). However, in severely altered diesel in soil samples, the alkylcyclohexanes have been reduced to below detection.

Alkylbenzenes in the free product display little alteration (Figure 6) over that in the starting diesel (Figure 5). For example, hydrocarbon #31 shows a slight increase over #31a; however, it is not apparent if this small change is significant. In the severely altered diesel fuel (Figure 8), the three dominant C_4-alkylbenzenes appear as peaks 28, 31a, and 32, whereas hydrocarbon peak 31 has been completely removed.

Following the examination of several sites in Denmark containing diesel fuel #2 in soil, Christensen and Larsen (1993) concluded that it was possible to estimate the length of time the diesel fuel had been in the environment by using the numerical values of the n-C_{17}/Pr ratios derived from the newly dispensed diesel and from environmental samples. They obtained a linear relationship extending over a range of about 20 years. Using their plot, we derived an equation to estimate age (T) as follows:

$$T(\text{years}) = -8.4\,\frac{n\text{-}C_{17}}{Pr} + 19.8$$

When n-C_{17} = 0, T≥19.8 years.

Examples of measured values for n-C_{17}/Pr and n-C_{18}/Ph ratios in new diesel fuel and degraded diesel in free product and soil are shown in Table 10.

Table 10

Biodegradation Ratios for Diesel Fuel #2 in Free-floating Product and in Soil Extracts

Sample	n-C_{17}/P_r	n-C_{18}/Ph	C_4-AB/C_2-Phen	C_1-Naph/C_2-Phen
Free-floating Product				
New diesel fuel	2.4	3.9	1.6	4.3
Degraded diesel fuel	1.2	1.4	1.2	3.4
Severely degraded diesel fuel	0	0	1.0	2.2
Soil Extract				
Degraded diesel fuel	1.1	0.8	1.7	3.2
Severely degraded diesel fuel	0	0	0.3	1.7

Among the least affected by alteration hydrocarbon components appear to be some of the monoaromatic and PAH members. In this group of compounds, the alkylbenzenes are first to be altered by biodegradation, followed by naphthalene and methylnaphthalenes. Some of the alkylphenanthrenes and alkyldibenzothiophenes are altered in a manner that may be used for determining relative rates of change. Table 9 gives a list of the alkylbenzenes and PAH present in gasoline, diesel fuel, and Bunker C fuel, and Table 10 shows two important PAH parameters (i.e., C_4-alkylbenzenes/C_2-phenanthrenes and C_1-naphthalenes/C_2-phenanthrenes), which may be useful in determining alteration changes of diesel in free-floating product and in soil extracts. The ratios demonstrate that for both pairs, the C_2-phenanthrenes are more stable than the alkylbenzenes and the alkylnaphthalenes.

Bunker C Fuel

This fuel is also known as heating oil #6. It is a viscous fluid with a hydrocarbon range from C_9 to approximately C_{36} and a boiling range of 171 to 566°C (340 to 1050°F). It is mainly used as a boiler fuel in ships, commercial, and industrial heating. The main feature that differentiates Bunker C fuel from crude oil is the lack of the volatile condensate fraction and the presence of PAH compounds benzo(B+K)fluoranthene, and benzo(E+A)pyrene in Bunker C fuel (Table 9). These hydrocarbons are formed during high-temperature distillation involved in the processing of crude oils. Seven methods used to characterize the Bunker C fuel are as follows: (1) C_8 to C_{40} n-alkanes and isoalkanes by high resolution GC/FID and GC/MS; (2) pentacyclic, tetracyclic, and tricyclic terpanes; (3) regular steranes and diasteranes; (4) aromatic steranes; (5) PAH; (6) simulated distillation by GC/FID (ASTM method D2887); and (7) $^{13}C/^{12}C$ and D/H stable isotope ratios. For this paper, we are only describing methods 1 through 5. Methods 2 through 5 all require GC/MS identification.

The terpanes (characteristic ion at m/z 191) and steranes (characteristic ion at m/z 217) are high-molecular-weight hydrocarbons (Figure 1) commonly referred to as biomarkers (Peters and Moldowan 1993). They originate from the polycyclic lipids found in bacteria and plants. Because of their particular structure, with numerous chiral centers and side chains, the biomarkers represent a large number of different chemical compounds as well as a set of isomers (or enantiomers) of the same compound. These can then be used for stability considerations and comparison of fuel patterns. Among the terpanes, the C_{30}-pentacyclic terpane (hopane) and certain tricyclic terpanes are the most stable (Butler et al. 1991). Compared to the regular tetracyclic steranes, the diasteranes are the most resistant to biodegradation.

Another indicator group of compounds in Bunker C oil consists of aromatic hydrocarbons extending from monoaromatic members to PAH. This group also includes sulfur-containing benzo-, dibenzo-, and naphthobenzothiophenes (Table 9). Concentration ratios of some of these compounds appears to be useful in determining extent of biodegradation.

An example of change occurring in a severely altered Bunker C fuel in soil can be seen from the comparison of Figures 9 and 10. The paraffinic fraction (m/z 85) has been depleted to below detection (Figure 10). The terpane pattern (m/z 191) shows that two peaks dominate the residual hydrocarbons; they are K (C_{29},17α, 21β-30-norhopane) and N (C_{30}, 17α, 21β-hopane). Sterane changes were not large, although an increase in C_{28}, 24-methyl-13α, 17β-dicholestane (20S) is evident (Figure 10). For the PAH fraction, the naphthalenes, fluorenes, and phenanthrenes were significantly reduced and the benzo-, dibenzo-, and napthobenzothiophenes were reduced to values barely above detection limits.

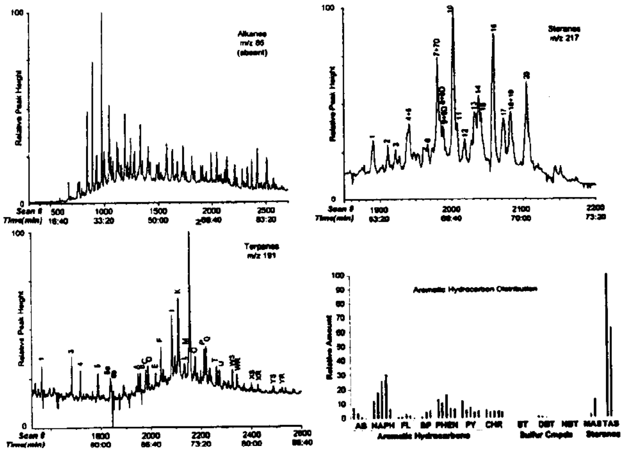


Figure 10. Mass chromatograms and bar diagram of severely altered Bunker C fuel in soil extract.

Table 11
Biodegradation Ratios for Bunker C Fuel in Soil Extracts

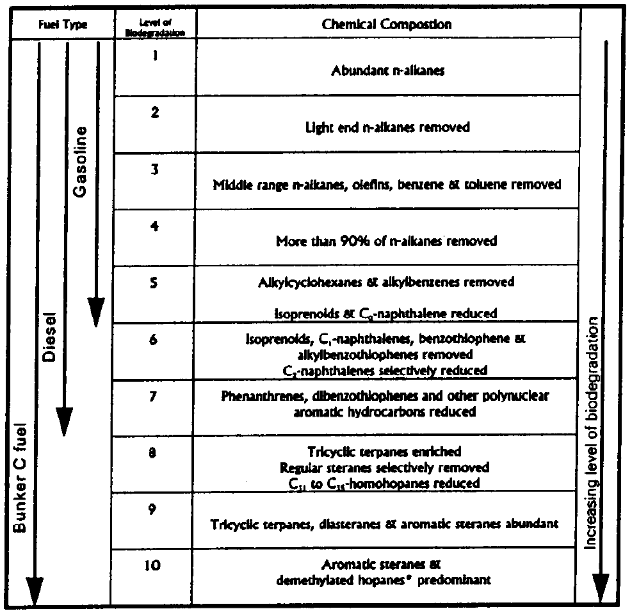
Sample	n-C_{17}/P_r	n-C_{18}/Ph	C_2-Phen/C_2-DBT	Phen/Chr	Phen: $\frac{3+1}{9+1}$
New Bunker C fuel	2.2	2.6	2.5	5.0	2.0
Degraded Bunker C fuel	1.6	2.0	0.77	3.3	0.91
Severely degraded Bunker C fuel	0	0	0.53	2.0	0.4

The hydrocarbons that increased significantly in relative concentration are the mono- and triaromatic steranes. Most crude oils and Bunker C fuels contain highly resistant modified steranes in which either one ring (the C ring) or all three six-membered rings become aromatized (due to heat exposure) and the steranes are converted to monoaromatic or to triaromatic steranes (see Figure 10). In the example shown in Figure 10, the triaromatic steranes became the dominant PAH in the soil.

Changes in various hydrocarbon parameters in Bunker C fuel during biodegradation are shown in Table 11. All of these parameters may become useful in estimating the degree of alteration of Bunker C in the environment. The ratios in Table 11 are based on the relative stability of different hydrocarbons to biodegradation. The n-C_{17}/Pr ratio has already been discussed. The n-C_{18}/Ph ratio is about as good a biodegradation indicator as the prior ratio, since n-C_{18} has similar properties with n-C_{17} and phytane has the same stability properties as pristane. The decrease in the C_2-phenanthrene/C_2-dibenzothiophene and phenanthrene/chrysene ratios (Table 11) is a function of the greater relative stability of dibenzothiophene and chrysene over phenanthrene. The last ratio shown in Table 11, phenanthrene 3+2/9+1, relates to the position of the methyl group in the phenanthrene molecule. It indicates that 1-methyl- and 9-methylphenanthrene are more stable to biodegradation than 3-methyl- and 2-methylphenanthrene.

Conclusions

Based on the analyses of various homologous series of hydrocarbons in gasoline, diesel #2 fuel, and Bunker C fuel, a pattern has emerged for estimating types and relative rates of degradation in free product, ground water, and soil samples. This report provides examples of compositional changes based on BTEX, C_3 to C_{10} gasoline range hydrocarbons, and C_8 to C_{40} mid-range hydrocarbons obtained by gas chromatography. Specific hydrocarbon groups such as the alkylcyclohexanes, the alkylbenzenes, PAH, and steranes and terpanes were measured using GC-mass spectrometers. Based on the comparison of newly dispensed fuels with those in the environment, a scheme has been prepared (Figure 11) to illustrate the relative degradation level of different hydrocarbon types in fuels with a volatility range from gasoline to Bunker C fuel.



* = Present under certain conditions only

Figure 11. Change in gasoline, diesel fuel, and Bunker C composition during biodegradation.

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Environmental Forensics (2001) **2**, 347–358
doi:10.1006/enfo.2001.0069, available online at http://www.idealibrary.com on IDEAL®

Age-dating Diesel Fuel Spills: Using the European Empirical Time-based Model in the U.S.A.

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(*Received 1 August 2001, Revised manuscript accepted 5 October 2001*)

In 1993, a paper was published by Christensen and Larsen that offered a method for determining the age of diesel oil spills in soil (Christensen and Larsen, 1993 *Ground Water Mount. R.* **Fall**, 142–149). It presented an empirical time-based model of the degradation of diesel fuel in soils using chemical data gathered at petroleum release sites in Denmark and the Netherlands. Now, evaluation of the validity of the application of this work to subsurface petroleum releases in other countries remains.

In the U.S.A., investigations assessing date(s) of release of diesel fuel in soils, e.g. age dating of subsurface petroleum contamination, have considerable interest. Litigation-driven scientific investigations with accompanying expert testimony in a court of law are underway. The number of instances where application of the Christensen and Larsen empirical time-based model to petroleum-contaminated properties is growing in the U.S.A.

This paper presents two case studies which evaluate the applicability of the Christensen and Larsen empirical time-based model to petroleum-contaminated properties in general. It illustrates the approach using gas chromatographic data from two recently-completed projects evaluating the applicability of the Christensen and Larsen model to a No. 2 fuel oil/diesel fuel surface spill in the U.S.A. Results showed that the application of the model to petroleum-contaminated soils was scientifically valid, provided its applicability was evaluated using hypothesis testing for specific changes in the characteristics of the petroleum hydrocarbon distribution in a number of soil samples collected over time at one site. The paper offers observations on the application of the Christensen and Larsen model to petroleum found in the light non-aqueous phase liquid (LNAPL) phase and groundwater.

Keywords: petroleum product; release date; No. 2 fuel oil/diesel fuel; hydrocarbon degradation; age-dating; petroleum contamination.

Introduction

In the U.S.A. today, legally-based proceedings surrounding instances of environmental contamination are commonplace. Such proceedings include but are not limited to regulatory compliance negotiations with state and Federal Government regulatory agencies, negotiations among principal responsible parties to a contaminated property case, and litigation among parties involved in environmental contamination cases. When considering petroleum contamination cases, being able to determine when, i.e. during what time period, a petroleum release began may constitute the key piece of technical evidence in a legal proceeding. Litigation involving major crude oil spills provides the fodder for legendary technical stories. Litigation involving petroleum product releases are much more common in the United States.

Various petroleum products are involved in such cases, and include light distillate fuels like automobile gasoline, aviation gasoline, and petroleum-based mixed solvents such as mineral spirits, Stoddard's solvent or naphtha; mid-range distillate fuels such as jet fuels/kerosenes, No. 2 fuel oil/diesel fuels, No. 4 fuel oils and heavier diesel fuels; and residual petroleum products. As a result of man's search for petroleum resources, our understanding of the petroleum geochemistry is well represented in the refereed technical literature (Philp, 1986). Further, our scientific understanding of the degradation processes associated with petroleum contamination in the environment is long standing and well represented in the refereed technical literature (Singer and Finnerty, 1984; Senn and Johnson, 1987; Best and Dawson, 1993; Kaplan *et al.*, 1996, 1997).

Currently in the United States, scientific investigations assessing date(s) of release of diesel fuel in soils, e.g. age dating of subsurface petroleum contamination, have considerable interest. One particular paper in the refereed technical literature addresses the subject of assessing date(s) of release of diesel fuel in soils (Christensen and Larsen, 1993). The Christensen and Larsen paper presented an empirical time-based model on the subject of diesel fuel-contaminated soils and a method for determining the age of diesel oil spills in the soil (Figure 1). Technical discussion of this paper has appeared in the chemical literature (Kaplan *et al.*, 1996, 1997; Bruya, 2001; Murphy and Morrison, 2001) as an approach to the age-dating of diesel fuel spills.

Litigation-driven scientific investigations, with accompanying expert testimony in a court of law, are underway. The number of instances where application of the Christensen and Larsen empirical time-based model to petroleum-contaminated properties is growing in the United States, and an examination is needed

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Presented first at: First International Congress on Petroleum Contaminated Soils, Sediments, and Water. London, England. 14–17 August 2001.

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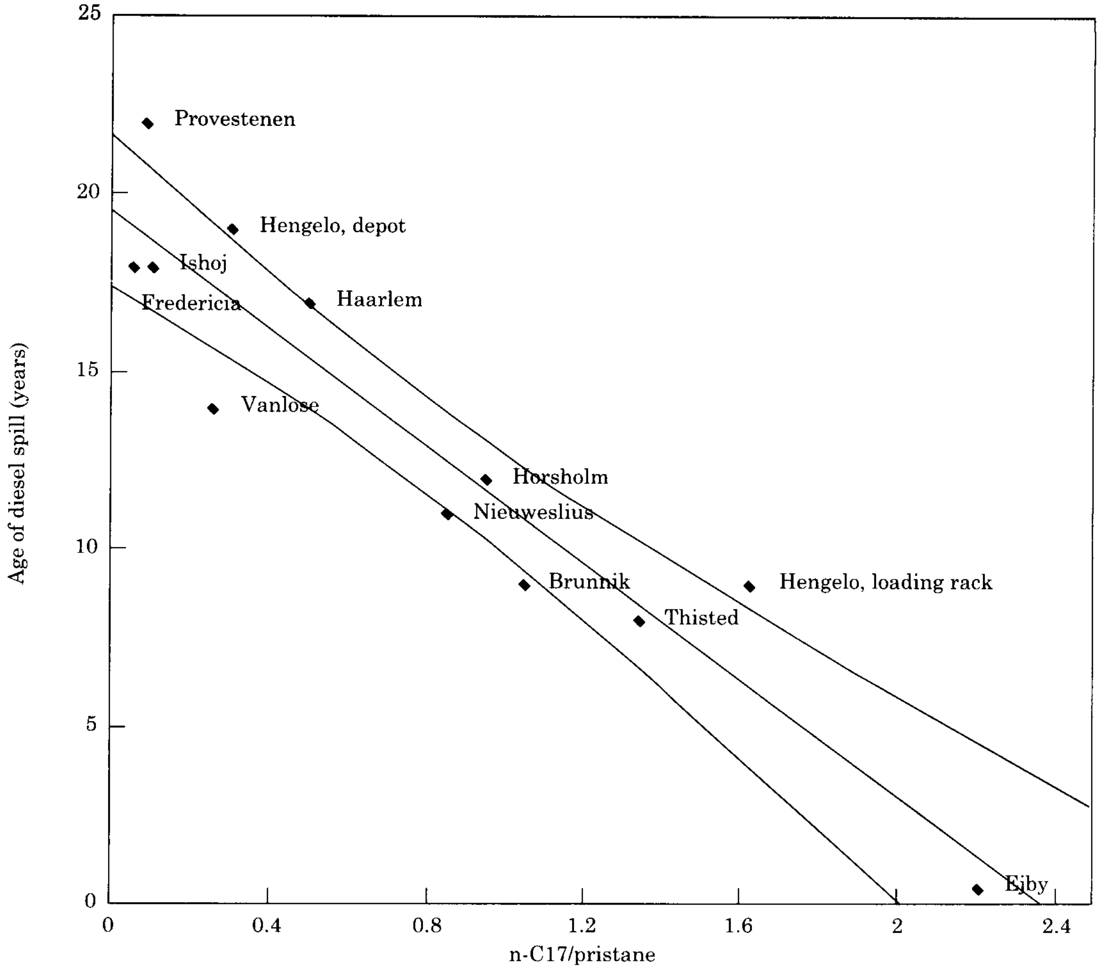


Figure 1. Reconstruction of the published relationship between the age of the diesel spill and the n-C_{17}/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993).

to assess the applicability of the Christensen and Larsen age-dating model to specific locations in the United States.

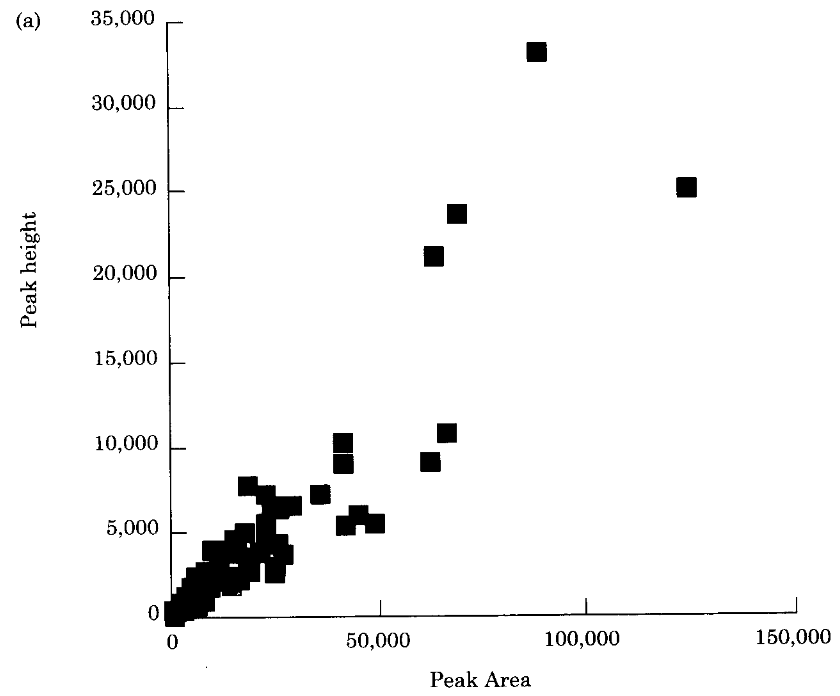
This paper evaluates the Christensen and Larsen empirical model, offering one method of examining the applicability of this age-dating model by use of two case studies completed in the past few years in the United States. Emphasis is placed on study design as illustrated by the two case studies. Property locations and detailed analytical results are provided; however, due to legal concerns, the identification of the responsible parties is withheld.

Study Methods

Both case studies dealt with subsurface contamination from mid-range distillate fuels (No. 2 fuel oils/diesel fuels), both were completed after the publication of the Christensen and Larsen (1993) paper and both relied on the publication to different degrees. In both cases the contaminated properties being studied were located in the general area of what is known as the New England states in U.S.A., an area comprising the states of Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, and Connecticut.

All analytical data were obtained from project-specific reports or were generated directly during the investigation. All available data were evaluated for conformance with the Christensen and Larsen model. While certain sample selection criteria were cited in Christensen and Larsen (1993), no analytical data were rejected from the two case studies based solely on agreement or non-agreement with these criteria. In the first case study, Case Study A, analytical data on the concentrations of petroleum in soils were obtained over a 2-year time period using both previously existing analytical data and newly-generated data. In the second case study, Case Study B, all analytical data were obtained over a multi-year period from previously-completed technical reports.

Analytical data from gas chromatographic analyses for petroleum hydrocarbons were used in both cases. Gas chromatographic data regarding concentrations of resolvable petroleum hydrocarbons were obtained from data files maintained by the analytical laboratories that had completed the original work. Copies of all analytical data reports were obtained and analysed in detail to identify the prominent hydrocarbon peaks in each chromatogram, including the major normal alkane and isoprenoid hydrocarbons, as well as the general boiling point distribution of the resolved petroleum contamination. Normal alkanes and isoprenoid hydrocarbons were identified by comparison of the relative retention time (RRT) of the unknown with



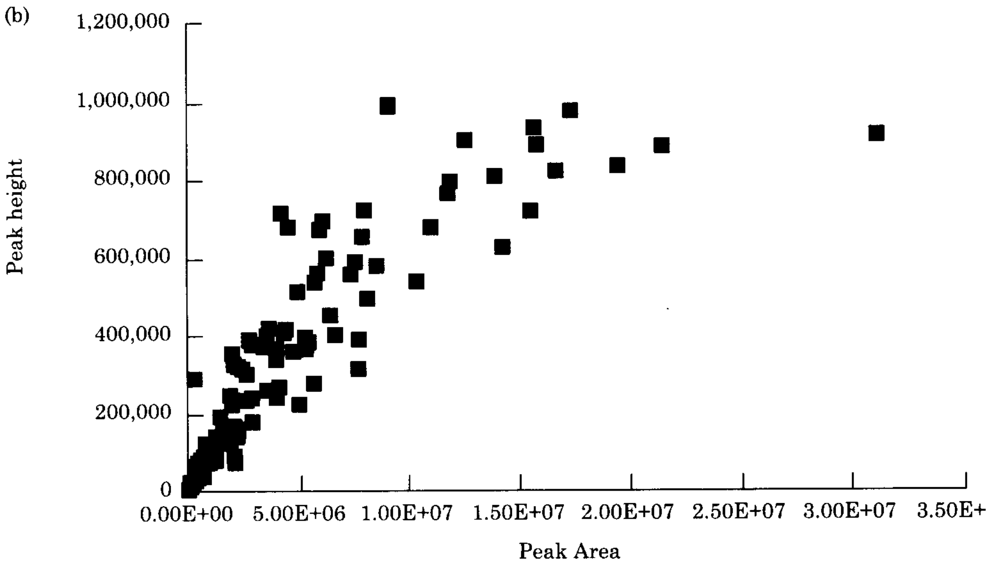


Figure 2. Example chromatographic data showing (a) acceptable relationship between peak area and peak height, and (b) an unacceptable degree of variability in the relationship between peak area and peak height.

the RRT of the peak of interest in an analytical standard, either a mixture of normal alkanes from n-C_{10} through n-C_{24} for example, or from a petroleum standard such as a No. 2 fuel oil/diesel fuel that was routinely used in the analytical laboratory that completed the original work (ASTM E 355-77; Journal of Chromatography Library Volume 22A). The identification of individual hydrocarbon peaks was performed by the analysis of a laboratory standard analysed in parallel with a particular batch of field samples, using the same laboratory instrument. The isoprenoid hydrocarbon phytane was used as the reference peak for calculation of all RRTs. All resolvable hydrocarbon peaks were assigned an RRT and peak identifications were made when the RRT for an individual peak was within ±0.002 retention units. If a specific peak fell out of the standard range, it was not further identified. Further, normal alkanes were not identified unless a homologous series of n-alkanes could be confirmed to be present in the samples. Documentation of a homologous distribution of normal alkanes was important to establish consistent identification of petroleum contamination in all samples. Identification of the isoprenoid hydrocarbons from C_{13} through C_{20}

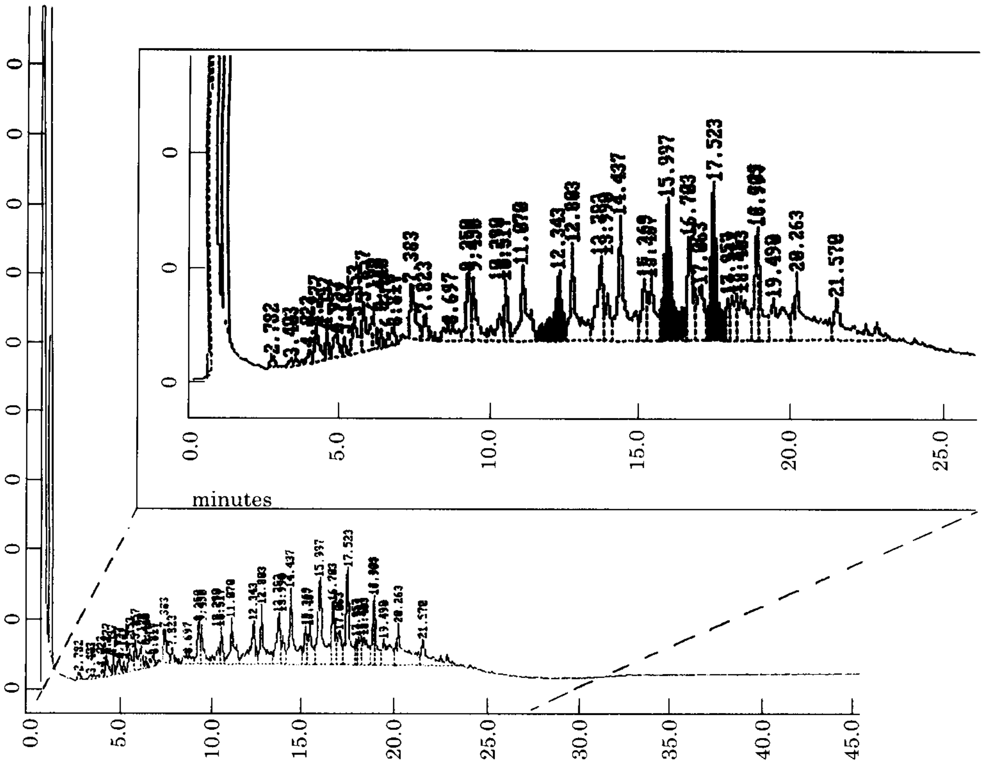


Figure 3. Gas chromatogram and sectional blowup of diesel oil standard showing results of the computerized area integration that included too much area for selected individual peaks.

(IP13, IP14, IP15, IP16, IP18, IP19 and IP20) was not difficult as these particular hydrocarbons were usually the most prominent peaks found in the chromatograms.

Once all hydrocarbons were identified, the relationship between peak area and peak height was analysed to assess the quality of the chromatographic data. To accept the raw data files, a linear relationship between peak area and peak height was required (Figure 2(a)). A linear relationship is theoretically expected in such a relationship; when least squares linear analysis techniques resulted in a statistically significant relationship whose level of significance depended upon the number of samples, the correlation coefficients usually were greater than 0.95. Samples where a curvilinear relationship between peak area and peak height was documented (Figure 2(b)), either from non-linear detector behavior or inappropriate integration software (Figure 3), were rejected. If a statistically-significant linear relationship between peak area and peak height was documented, peak height data were chosen for further analysis. The peak height data were used to calculate the n-C_{17}/IP19 ratio for each sample.

All n-C_{17}/IP19 ratio data were used to determine the applicability of the Christensen and Larsen weathering model to the site-specific data by hypothesis testing. Using hypothesis testing procedures, it was possible to examine the n-C_{17}/IP19 data against two different scenarios: Case Study A involved the determination of what land area had been contaminated by mid-range distillate fuel from a leaking underground storage tank prior to 1985, and Case Study B involved a determination of what portion of a contiguous property had been contaminated by a large spill of mid-range distillate fuel that occurred during tank filling operations on 25 December 1974. The null hypothesis for each case stipulated that the date of release of the distillate fuel under question was reflected in the n-C_{17}/IP19 data, i.e. that the Christensen and Larsen model was applicable to the data on the degradation of hydrocarbon in the petroleum product found on the property in question. Therefore, agreement between the Christensen and Larsen model and the site-specific n-C_{17}/IP19 data was considered confirmation of the date of the property contamination for all samples being tested. Rejection of the null hypothesis because the testing results showed that site-specific n-C_{17}/IP19 data did not fit the Christensen and Larsen model and that the environmental contamination found in selected samples did not result from the release scenario being examined.

Case Study A

Case Study A determined the onset of subsurface petroleum contamination at property owned by a heavy industrial company in New England. Reports covering a 3-year period established subsurface contamination at the property. Detailed hydrocarbon source identification analyses indicated that there was a mid-range distillate petroleum product in the subsurface environment that appeared to originate at a contiguous property in the immediate vicinity of excavations where two leaking underground petroleum storage tanks had been removed in 1985. However, the owner of the underground storage tanks had changed and it was not clear which owner was responsible for the release of the distillate fuel to the environment. Thus, the issue was whether the petroleum contamination in the environment occurred on or before 1985 when the property transfer took place.

Table 1. Sample location/identification numbers, dates the soil samples were collected and the n-C_{17}/IP19 ratios for each sample for Case Study A

Sample location/ identification no.	Date soil sample collected	n-C_{17}/IP19
MW1-S2	11/1993	1.06
MW2-S4	11/1993	1.04
MW3-S3	11/1993	1.02
CT-WE1-SS-001	12/1993	1.09
CT-WE3-SS-003	12/1993	1.04
CG-WE6-SS-003	12/1993	0.96
CG-SB5-SS-002	12/1993	0.96
CG-SB9-SS-006	12/1993	0.98
CG-WE7-SS-004	12/1993	1.00

Mean value n-C_{17}/IP19 1.02.
Standard deviation = 0.05.

In 1995, soil samples were collected during the tank excavation in the vicinity of the excavation and on the subject industrial property. In addition, one sample of the contents of the underground storage tank was collected and analysed with the soil samples. All quantitative data files from the laboratory analyses were examined in detail to identify prominent normal saturated and branched chain hydrocarbons. A detailed comparison of the resultant peak identifications among all soil samples was completed before any quantitative data were used. The n-C_{17}/IP19 ratio was calculated for all samples, and the data were used in the examination of the applicability of the Christensen and Larsen weathering model. Results are presented in Table 1.

Hypothesis testing was used to evaluate the difference in the n-C_{17}/IP19 ratios in the soil samples compared with the tank contents sample over a time period covering the transfer of property ownership. Using the tank contents data, the hypothesis was structured according to the tenet that the soils data fit the Christensen and Larsen model, with the latest release date to be the date of transfer of property ownership in 1985. Figure 4 presents the results of this hypothesis testing. The fact that all nine soil samples fell into the 95% confidence interval of the model sustained the hypothesis that the use of the Christensen and Larsen model was valid for this site.

Further, differences in the n-C_{17}/IP19 ratio were assessed to evaluate the spatial variability of the date of release of the mid-range distillate product at the contiguous property. The overall variability of the n-C_{17}/IP19 ratio was surprisingly low. Results of the summary statistical analysis of the entire nine-sample data set are presented in Table 1. The relative standard deviation of the mean value of the data set was determined to be very low, 4.5%. As the n-C_{17}/IP19 data show, there appears to be relatively uniform

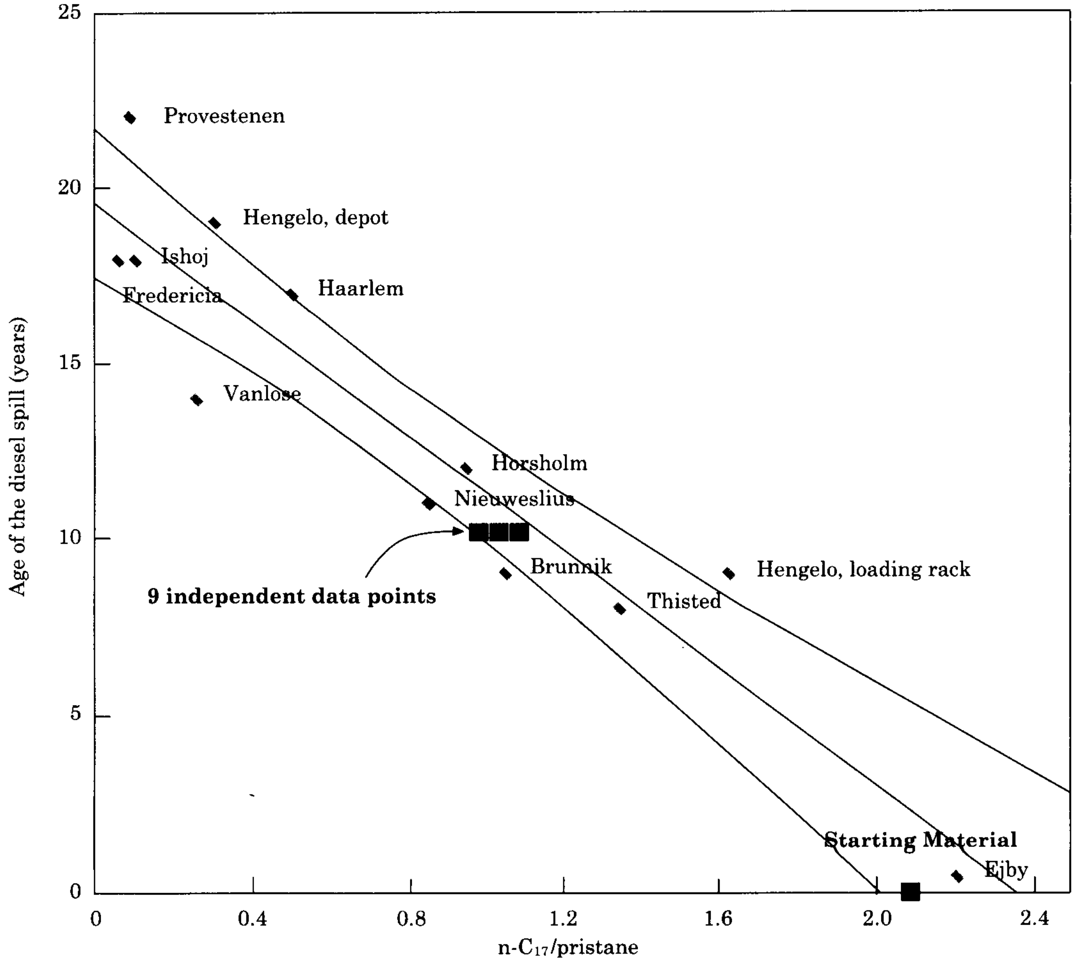


Figure 4. Case Study A data plotted over the published relationship between the age of the diesel spill and the n-C_{17}/IP19 ratio of various mid-

Table 2. Sample location/identification numbers, dates the soil sample data files were initially created and the n-C_{17}/IP19 ratios for each sample for Case Study B

Sample location/ identification no.	Date sample collected by matrix	n-C_{17}/IP19
Matrix - Soil		
GZ-09, S-2	2/4/92	0.25
GZ-11, S-2	2/4/92	0.22
GZ-32, S-2	12/4/92	0.19
SS-02-1	6/6/95	0
SS-02-4	6/6/95	0
S-4	6/11/95	0.24
Area 2 S-7	6/6/95	0.25
S-6	6/11/95	0
S-10	6/11/95	0
S-11	6/11/95	0
SS-02-14	6/10/95	0
SS-02-15	6/10/95	0
SS-02-15, #2	8/2/95	0
SS-02-16	6/23/95	0.26
SS-02-22	8/4/95	0
SS-02-28	6/23/95	0
SS-02-33	8/3/95	0
SS-02-34	6/27/95	0
SS-02-34, #2	8/3/95	0
TP2-2, S-3	5/12/95	0
TP2-4, S-4	5/12/95	0
TP-2-5, S-3	5/12/95	0
GZ-33-103	4/16/95	0
95140 S-1	6/19/95	0
95140B G14	6/19/95	0
95140B P1	6/19/95	0
AES-2	6/10/95	0
AES-3	6/10/95	0
AES-4	6/10/95	0
Soil Sample S-1	6/28/95	0
Matrix - NAPL		
GZ-31	12/1/92	0.31
GZ-33	12/1/92	0.30
Matrix - Groundwater		
GZ-5	10/31/91	0.21
GZ-09	1/29/92	0.19
GZ-11	1/24/92	0.20
GZ-22	1/19/92	0.17
GZ-35	12/1/92	0.51
GZ-35, #2	12/2/92	0.34

Groundwater mean value n-C_{17}/IP19 = 0.27

Groundwater standard deviation = 0.13

weathering of the mid-range distillate that had been released to the garage property site. Given the low variability of the n-C_{17}/IP19 ratio, the release of the mid-range distillate at the contiguous property site does not appear to be a slow or chronic release. It appears that the release occurred over such a time frame that there is only a small relative standard deviation among all nine soil samples and very little differences in the age of the release mid-range distillate determined. It was observed that the highest ratios were found in the immediate vicinity of the former underground storage tank. The lowest ratios were found at soil boring locations furthest away from the suspected area of release.

The fact that the soil hydrocarbon data were consistent with application of the Christensen and Larsen model, the highest ratios found in the immediate vicinity of the underground storage tank, and the lowest ratios found at locations furthest away from the was released prior to 1985 and subsequent environmental contamination rested with one property owner. Subsequent negotiations among responsible parties resolved the issue of liability in manner consistent with the scientific findings of the case.

Case Study B

Case Study B involved the question of responsibility for subsurface contamination of a property immediately contiguous to a service station that was the site of a well documented release of No. 2 fuel oil/diesel fuel. On 24 December 1974, during subsurface filling operations being conducted in cold weather, the tank truck driver fell asleep in the truck cab and when the hose connection fell off, spilled up to several thousand gallons of middle distillate fuel onto the service station property. The spilled oil was collected by a concrete pipe drainage system and spread into the subsurface of the adjacent property. Surface oil contamination was removed shortly after the initial spill, but no oil was recovered from the adjacent property subsurface environment. In December 1991, distillate fuel contamination was discovered in a widely dispersed area of the adjacent property and property damage liability had to be determined.

The property developer conducted environmental investigations for some period of time. Existing technical reports were reviewed and the results of hydrocarbon analyses using glass capillary column gas chromatography were obtained. No analysis of the spilled fuel was available. Chemical data covering the time period of 1991/1992 and 1995 were available, providing data coverage for two distinct time periods at one site. All quantitative data files from the laboratory analyses were examined in detail to identify prominent normal saturated and branched chain hydrocarbons. The n-C_{17}/IP19 ratios were calculated for all samples and the data were applied to statistical testing of the applicability of the Christensen and Larsen weathering model. The n-C_{17}/IP19 ratio data are presented in Table 2.

Hypothesis testing was used to evaluate the difference in the n-C_{17}/IP19 ratios in the soil samples over two different time periods. However, there were additional factors that came into play in Case Study B. In 1974 no gas chromatographic analyses of the spilled oil had been completed; consequently, there were no chemical data on the starting n-C_{17}/IP19 ratio of the spilled oil. Further, the state of the art of chemical analysis in 1974 was evolving and glass capillary gas chromatography was only beginning to make its way into the United States chemical laboratories. One of the earliest published analysis of distillate fuel (e.g. diesel fuel) using glass capillary gas chromatography can be found in Grob and Grob (1974), where the n-C_{17}/IP19 ratio can be determined to be greater than 2.0 as the n-C_{17} peak in the chromatogram probably is slightly off scale.

The area of New England is unique in that there are no petroleum refineries in the six states comprising the area since the later part of the 1960s. Consequently since then, all petroleum products have been manufactured outside the region and are imported by pipeline, rail or marine transportation. Documentation

Table 3. Calculated n-C_{17}/IP19 ratios from various samples of No. 2 fuel oil/diesel fuel from technical works published during the late 1960s and early 1970s in the northeast states, U.S.A.

Sample	n-C_{17}/IP19	Year(s)	Reference
Spilled No. 2 fuel oil, barge Florida, Buzzards Bay, MA.	2.6	1969	Blumer *et al.* (1970*a*)
Spilled No. 2 fuel oil, barge Florida, Buzzards Bay, MA.	2.3	1969	Blumer and Sass (1972)
Laboratory Standard No. 2 fuel oil	1.7	1969/1970	Burns and Teal (1971)
Fuel oil No. 2	2.0	1970	Blumer *et al.* (1970*b*)
Fuel oil, R/V Knorr	2.2	1972	Farrington and Tripp (1977)
No. 2 fuel oil	1.6	1972	Zafiriou *et al.* (1972)
No. 2 fuel oil	1.7	1972	Zafiriou *et al.* (1972)
No. 2 fuel oil	1.6	1972	Zafiriou *et al.* (1972)
No. 2 fuel oil	1.7	1972	Zafiriou *et al.* (1972)
No. 2 fuel oil/diesel fuel	2.0	1972	Zafiriou *et al.* (1972)
Mean value n-C_{17}/IP19 = 1.9 Standard deviation = 0.34			

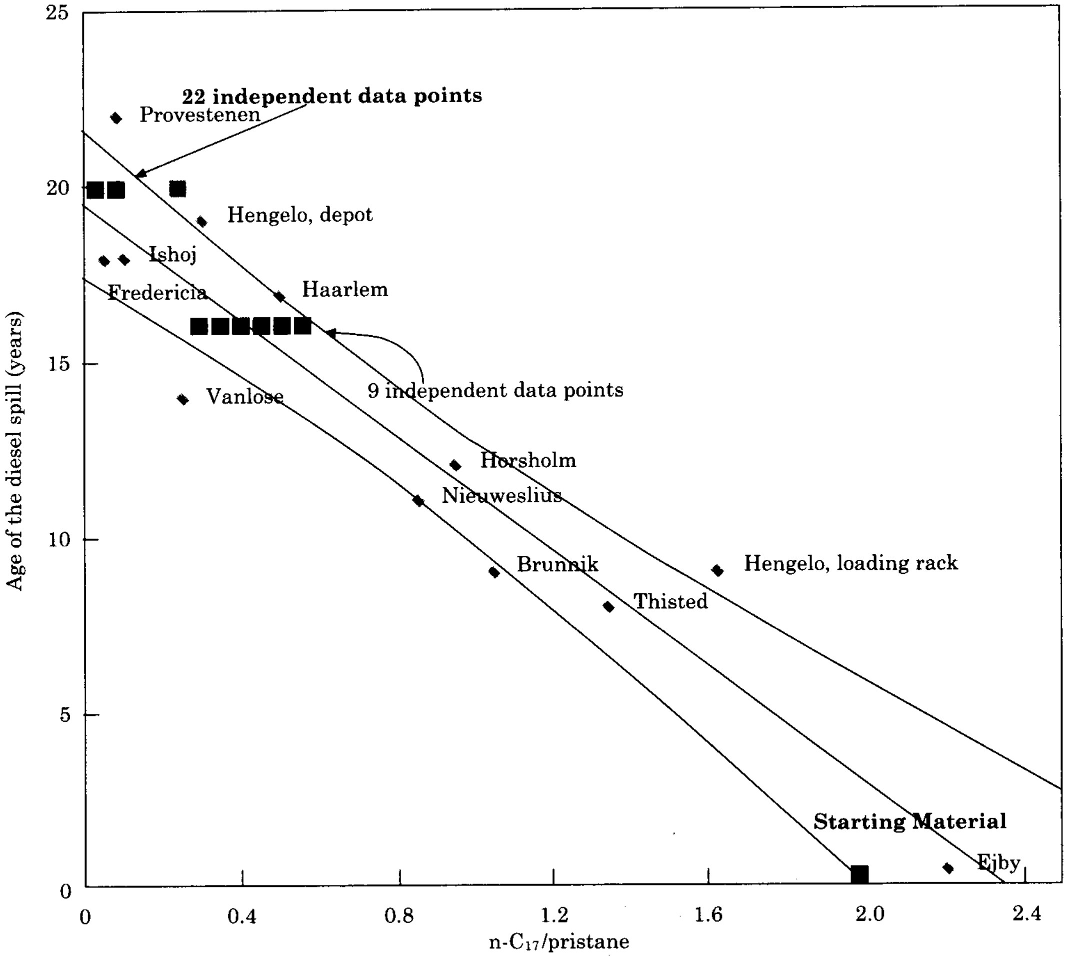


Figure 5. Case Study B data plotted over the published relationship between the age of the diesel spill and the n-C_{17}/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993).

oil/diesel fuel being imported into the New England region of the United States in the 1970s was available in the scientific literature due to concerns about the environmental impact of oil spills. Table 3 summarizes the years, sources and n-C_{17}/IP19 ratios that were calculated from the available gas chromatograms published in the oil spill literature of the 1970s. The mean value calculated from these data were used together with the soils data from the study site in the hypothesis testing for Case Study B.

Table 4. Annual temperature ranges (°F) and average annual precipitation (inches per year) at major cities of Netherlands and Denmark compared to selected cities in U.S.A. (World Almanac 1996). The average daily temperature data include a period of 30 years from 1961 to 1990

City Country	January Max	 Min	July Max	 Min	 Annual
	precipitation				
Amsterdam	40	32	69	59	
Netherlands	26				
Copenhagen Denmark	36	29	72	55	23
Albany, NY	30	11	84	60	
U.S.A.	39				
Anchorage, AK U.S.A.	21	8	65	52	16
Atlantic City, NJ U.S.A.	40	21	85	65	40
Boston, MA	36	22	82	65	
U.S.A.	42				
Chicago, IL	29	13	84	63	
U.S.A.	36				
Denver, CO U.S.A.	43	16	88	59	15
Houston, TX U.S.A.	61	40	93	72	46
Miami, FL U.S.A.	75	59	89	76	56
San Francisco, CA U.S.A.	56	42	72	54	20
Seattle, WA U.S.A.	45	35	75	55	37

Results of the hypothesis testing for Case Study B are presented in Figure 5. The fact that all soil data from the two sampling intervals fell into the 95% confidence interval of the model in two separate and distinct time frames sustained the hypothesis that the use of the Christensen and Larsen model was valid for this site. Therefore, combined with the existing site-specific knowledge of the December 1974 oil spill and details of the site-specific conditions of the adjacent property, it was concluded that the contamination represented in the soils data originated from the December 1974 oil spill.

An interesting aspect of the n-C_{17}/IP19 data in Case Study B is that gas chromatograms of groundwater and non-aqueous phase liquid (NAPL) samples also were available, being analysed together with soils samples. The n-C_{17}/IP19 data for the groundwater and NAPL samples were statistically identical to those of the soil samples, although the groundwater data exhibited somewhat more scatter. Such comparability of n-C_{17}/IP19 data calls into question the discussion by Kaplan *et al.* (1996, 1997) on the separation of age-dating NAPL samples, and, by inference from the Case Study B data, groundwater samples. Also, the limitation of the Christensen and Larsen model involving the need to use contaminated soils saturated by distillate fuel (i.e. diesel fuel) also may be in need of closer examination. The data in Case Study B by no means indicate that in all cases the n-C_{17}/IP19 ratios for groundwater and NAPL samples will be identical to those found in soil samples. Case Study B NAPL and groundwater data indicate that all matrices should be open to complete evaluation in order to perform a scientifically rigorous site investigation, and a prudent scientist will review all available chemical and site-specific data to determine what the data show for a given site investigation.

Discussion

For both case studies, the application of the Christensen and Larsen model could not be rejected, providing a means of age dating different petroleum releases at these two sites which represent two different oil spill scenarios. The fact that age-dating of petroleum releases could be completed in a scientifically rigorous manner using existing technical literature on the subject must not be ignored. Consequently, the use of an age-dating approach for distillate fuel oil spills must factor into any environmental investigation as an useful tool to be considered by an investigator. Further, the scientific literature on the subject of age-dating of No. 2 fuel oil/diesel fuel cannot be ignored nor dismissed a priori and should be part of a comprehensive site assessment. There are, however, other considerations that should be taken into account also to ensure that the use of the Christensen and Larsen model is appropriate for the particular property in question.

One of the more important of the environmental factors which an investigator must consider in applying the Christensen and Larsen model is the specific area of the United States where the oil release occurred. Temperature regimes in New England are comparable to the temperature regimes in Denmark and the Netherlands (Table 4). In other areas of the United States, such as the West Coast, Pacific Northwest and northern tier of states in the Midwest, temperature regimes are comparable as well, but a prudent investigator will document such site-specific conditions. In the southern United States, where the soil temperatures commonly are above 10°C or 48°F (Table 4), selecting an adequate study design will facilitate an evaluation of the applicability of the Christensen and Larsen model in warmer sites. Confirmation of the application of the Christensen and Larsen model to warmer sites in the United States has not been reported in the literature.

Demonstrating changes in the hydrocarbon distribution of normal alkanes versus isoprenoid hydrocarbons is critical to establishing that degradation of hydrocarbons occurs at the site being investigated. Gas chromatography is the technique of choice for this purpose. Knowing the starting composition of the released oil is one way of documenting change in the hydrocarbon composition of spilled oil contaminated soils at the study site. Unfortunately, documentation of the chemical composition of the released oil is not always possible, either because such data were never collected in the first place, or the data are no longer available when analysing 10–15-year-old petroleum release. Therefore, published data on the chemical composition of distillate fuels being used in the region of the country where the study is being conducted should be consulted. Review of the chemical literature for New England in the 1970s (Table 3) and in the

Table 5. Calculated n-C_{17}/IP19 ratios from various samples of No. 2 fuel oil/diesel fuel from technical works published during the late 1970s, 1980s and early 1990s in the northeast states, U.S.A

Sample	n-C_{17}/IP19	Year(s)	Reference
API Reference			
No. 2 fuel oil	2.75	1977	Gordon *et al.* (1978)
'Local' No. 2 fuel oil	2.0	1979	Gearing *et al.* (1979)
API Reference			
No. 2 fuel oil	1.6	1979	Gearing *et al.* (1979)
No. 2 fuel oil	1.76	1978–1979	Gearing *et al.* (1980)
No. 2 fuel oil	2.75	1980	Hyland (1981)
No. 2 fuel oil	1.81	1981	Gearing *et al.* (1980)
No. 2 fuel oil	2.3	1982	Gearing and Gearing (1982)
No. 2 fuel oil	1.92	1983	Gearing and Gearing (1983)
No. 2 fuel oil	2.0	1982	Oviatt *et al.* (1982)
First Source - Spilled Arthur No. 2 fuel oil	3.1	1990	Wade (unpublished data)
Second Source - Spilled Arthur Kill No. 2 fuel oil	2.2	1990	Wade (unpublished data)
Spilled No. 2 fuel oil North Cape Oil Spill	2.81	1996	NOAA (1996)
Mean Value n-C_{17}/IP19 = 2.25 Standard Deviation = 0.49			

1980s and the 1990s (Table 5) shows that while there may be differences in the chemical composition of No. 2 fuel oil/diesel fuel from company to company and spill to spill, the mean and standard deviation of the accumulated data fall within the 95% confidence interval of the Christensen and Larsen model and hence application of the age-dating model is appropriate for mid-range distillate fuels in the New England region of the United States. In fact, it is interesting to note that the mean and standard deviation data for the n-C_{17}/IP19 ratio data in Tables 3 and 5 are not statistically different from one another, nor are they different from the mean and standard deviation data for petroleum products in Europe as cited in Christensen and Larsen (1993). These mean and standard deviation data are virtually identical to the results of a survey of fuel oil composition published in 1999 (Morrison, 1999). It is interesting to speculate that the same manufacturers probably are using the same basic starting crude oils, the same manufacturing specifications, and the same chemical refining processes in the United States and in Europe, and that such agreement on the n-C_{17}/IP19 ratio over a 95% confidence interval from different data sets should not come as too much of a surprise.

In Case Study B, an additional advantage existed over the Case Study A design. In Case Study A only one interval of hydrocarbon degradation could be tested against the Christensen and Larsen age-dating model. In Case Study B there were two different and distinct time periods that could be tested against the model. Case Study B illustrates an important point of providing multiple sampling and analysis intervals for the age-dating model. Obviously, the more points used in the model, the stronger the model results become. However, increasing the number of sampling events extends the length of the project and directly increases project costs. Eventually a point of diminishing returns is reached, making further project work unproductive.

However, there was a further strength in the Case Study B data; comparison of the 1991/1992 soils chromatographic data with the 1995 soils chromatographic data showed change in the presence of normal saturated hydrocarbons in the n-C_{10} to n-C_{22} range. As all samples had been analysed by the same analytical laboratory using the same sample processing protocols, the same analytical instruments and even the same analysts completing the work, comparison between the two groups of analytical data was technically defensible. Detailed review of the 1991/1992 samples showed that it was possible to identify the normal alkanes and the isoprenoid hydrocarbons in the analytical data for all samples. It was not possible to identify normal alkanes in the 1995 data, only isoprenoid hydrocarbons could be identified in the vast majority of the samples. The fact that normal alkanes were found in the 1991/1992 data and absent in the 1995 data was consistent with the Christensen and Larsen model in a manner that validated the use of this model at this particular site within the time frame consistent with the existing site-specific information regarding the 1974 oil spill.

Moreover, review of the 1995 soil chromatographic data revealed prominence of the early isoprenoid hydrocarbons (IP13, IP14, IP15, and IP16), indicating little, if any, isoprenoid hydrocarbon degradation at that time. Given the documented loss of normal alkanes combined with the prominence of early isoprenoid hydrocarbons, the condition of the chromatograms indicated that the majority (or perhaps even all) of hydrocarbon degradation had been confined to the normal alkanes, a accepted sign of the first stages of petroleum product degradation in the environment. Had hydrocarbon degradation been more extensive in the soil samples, the early isoprenoid hydrocarbons would have been severely reduced in prominence or may have been absent altogether, perhaps leaving only the later isoprenoid hydrocarbons (IP18, IP19, and IP20) and a prominent unresolved complex mixture (UCM) in the chromatograms.

By following the results of the analyses of these two case studies, application of the Christensen and Larsen

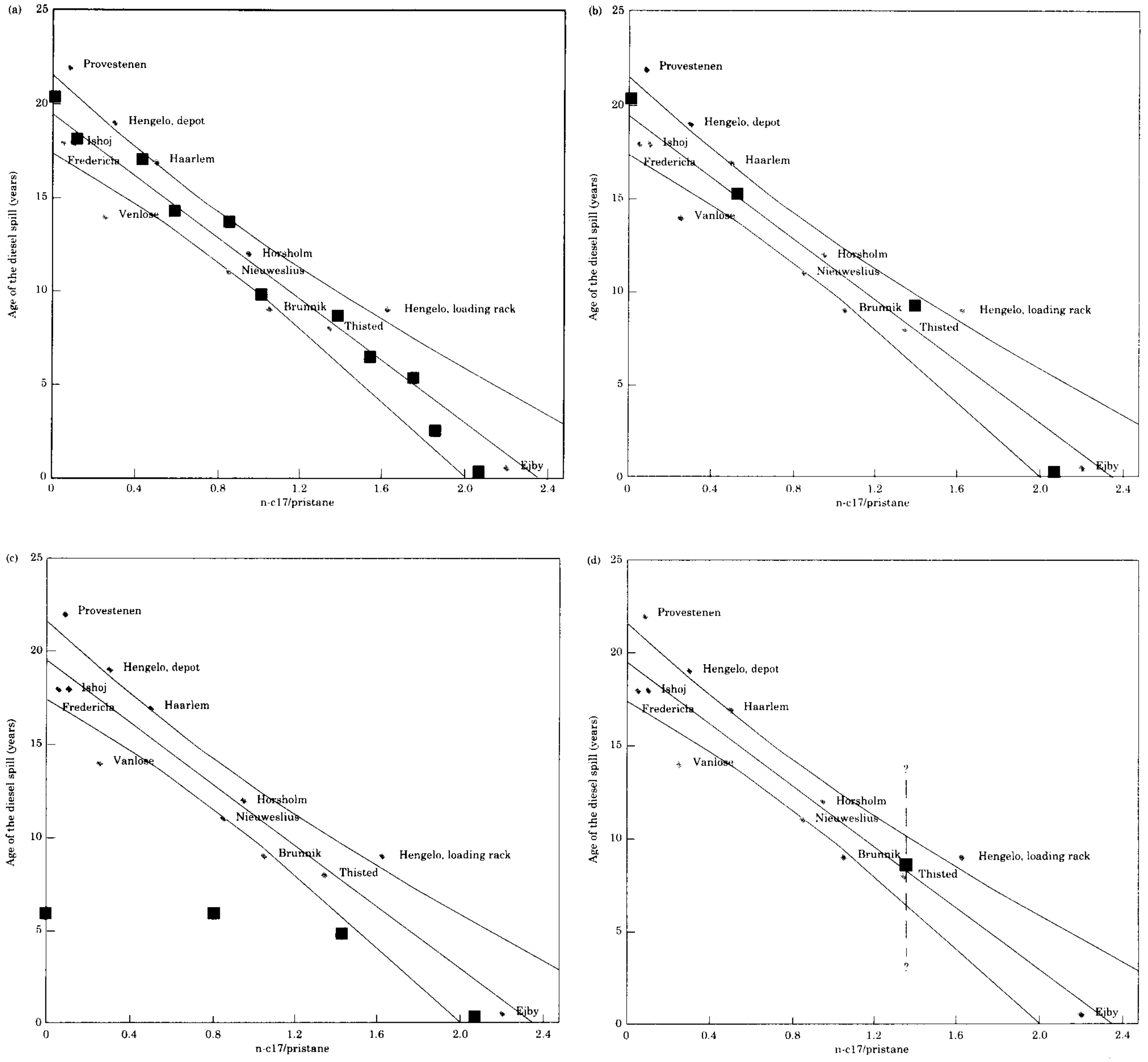


Figure 6. (a) Complete data coverage of petroleum hydrocarbon degradation sequence superimposed over the published relationship between the age of the diesel spill and the n-C$_{17}$/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993). Such an approach probably is not the best use of time and project resources. (b) Partial data coverage of petroleum hydrocarbon degradation sequence superimposed over the published relationship between the age of the diesel spill and the n-C$_{17}$/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993). Such coverage provides better use of project resources while testing the Christensen and Larsen model. (c) Partial data coverage of petroleum hydrocarbon degradation sequence superimposed over the published relationship between the age of the diesel spill and the n-C$_{17}$/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993). Such coverage demonstrates non-compliance with the Christensen and Larsen model, but does describe the change of n-C$_{17}$/IP19 with time at the site. (d) Single coverage of petroleum hydrocarbon degradation data superimposed over the published relationship between the age of the diesel spill and the n-C$_{17}$/IP19 ratio of various mid-range distillate fuels as cited in Christensen and Larsen (1993). Not knowing anything about the origins of the sample forces the investigator to assume that Christensen and Larsen applies in order to age-date the contamination, which can prove to be an unwarranted assumption.

model to the study of hydrocarbon degradation at sites in the United States becomes an issue of study design. Documentation of the degradation of hydrocarbons in samples collected over time at a site is the main point. Gas chromatography is the tool of choice. Time is the independent variable, and the rate of degradation then can be determined. Evaluation of the effectiveness of site-specific factors such as availability of electron acceptors, moisture, soil type, soil temperature, etc., is incorporated into the data on the degradation of petroleum hydrocarbons when these data are collected over time at the site in question. If documented changes in the average hydrocarbon distribution at a site are found to be consistent with known petroleum hydrocarbon degradation processes, the investigator can have confidence that degradation has occurred at the site. While this conclusion may seem trivial, documentation of the effects of hydrocarbon degradation is exactly what application of the Christensen and Larsen model to sites in the United States requires.

Determining the study design becomes a consideration of time and project resources available to complete the work. On one hand, complete duplication of the Christensen and Larsen model over a 20 year time frame may not an efficient use of resources (Figure 6(a)) for a single project. On the other hand, selective sampling and analysis at the site will result in the n-C_{17}/IP19 data necessary to statistically examine the use of the Christensen and Larsen model (Figure 6(b)). The more data the better, but only to a limiting point. The number of, and time interval between, sampling/analysis activities at a site most likely will be determined by economic and legal considerations together with scientific issues. Therefore, a prudent and thorough investigator will use a combination of existing literature support and site specific physical and chemical data to complete the investigation. If the n-C_{17}/IP19 data support application of the Christensen and Larsen model to a specific site, the data points will fall within the 95% confidence interval of the model (Figure 6(b)). If the n-C_{17}/IP19 data do not support application of the Christensen and Larsen model, over time the data points will not fall within the 95% confidence interval of the model; Figure 6(c) is an example of the latter instance. In gathering data as shown in Figure 6(c)), an investigator has documented first that the Christensen and Larsen model does not apply at this site, and second that hydrocarbon degradation occurs at a more rapid rate compared with the Christensen and Larsen model. Such information is valuable in a comprehensive site assessment of petroleum contamination and results such as presented in Figure 6(c) are not wasted time and effort. Moreover, reliance upon a single determination of the n-C_{17}/IP19 ratio at a site with no other site-specific data, might lead an investigator to assume that the Christensen and Larsen model is applicable to the site. Such an assumption that may or may not be warranted (Figure 6(d)).

Conclusions

Results from two case studies demonstrated that application of the Christensen and Larsen model for petroleum-contaminated soils in some areas of the U.S.A. can be considered scientifically valid. However, when considering an area with a larger land mass compared with that studied by Christensen and Larsen, applicability of the age-dating model must be ensured by taking additional steps, such as those demonstrated in the two case studies:

(1) Consideration of the area of the United States in which the study is being completed may be important to ensuring comparability of the temperature regimes of the study area and the Christensen and Larsen model;
(2) Review of existing chemical data must be done with considerable care, evaluating the quality of the chromatographic data and the method of integration used by the originating analytical laboratory;
(3) While data on the chemical composition of the spilled oil may not always be available, historical evidence is available for the chemical composition of mid-range distillate fuel that was used in the region of the United States where the site is located;
(4) Avoid age-dating of single, stand alone, samples;
(5) Placing a minimum of two points on the graph of the age-dating model assists in establishing comparability of the model to the specific situation with which the investigator is dealing, but the more data points that can be placed on the model the better the result;
(6) Demonstrating that hydrocarbon degradation of normal alkanes is proceeding in the soils at the site can be accomplished by establishing a time series of field sample collections, with proper consideration of statistical representation of random sampling of the site in question;
(7) Hypothesis testing of the applicability of the Christensen and Larsen age-dating model to the site in question using the assembled chemical and physical data ensures impartial adherence to the Scientific Method, an important but sometimes overlooked principle in legal proceedings.

A prudent investigator will examine all site-specific information available, all chemical data available in all matrices sampled, to determine what the universe of data are in a given investigation. It is possible that in some circumstances, the application of the Christensen and Larsen model to petroleum found in the groundwater and/or NAPL phases as well as to petroleum in soil in the United States may be appropriate.

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Use of Ternary Analysis Techniques in Forensic Geochemical Assessment of Subsurface Gasoline Contamination

By Michael J. Wade

This article reports the results of an assessment of groundwater contamination at a study site in the New England area of the U.S. Historical monitoring efforts found contaminated groundwater from gasoline range hydrocarbons at monitoring wells at the study site as well as in groundwater monitoring wells hydraulically down gradient from the study site. Available chemical data consisted only of groundwater concentrations of BTEX compounds (benzene, toluene, ethylbenzene and the xylene isomers) and the oxygenate additive methyl *t*-butylether (MTBE). No other chemical data were available and no possibility of collecting additional samples for chemical analysis existed. Laboratory data were collected by different contractors over an eight year time period from 1988 to 1996 using different standard analytical techniques.

Background Information on the Chemical Fate of Gasoline-Range Hydrocarbons in Groundwater

Detailed chemical analyses of component changes can be used to determine different source(s) for petroleum hydrocarbons and also help to estimate the time of onset of all identified sources. In most subsurface investigations in the United States, reporting of the groundwater concentrations of selected monoaromatic hydrocarbons benzene, toluene, ethylbenzene and the three isomers of Σxylene (o-xylene, m-xylene, and p-xylene) collectively referred to as the BTEX compounds, using standard analytical methods is required by regulatory agencies. Much of the time, BTEX data are all the chemical data that are available for assessment without going to the expense of additional analytical monies, which can be considerable depending on the analytical testing selected. When BTEX component data are all that are available, relatively simple data analysis techniques can be useful in the determination of separate sources and different times of release of each identified source. Such data can guide selection of types and locations for any further sampling and detailed high-precision chemical analyses of gasoline that can be used to confirm initial findings from the BTEX data. More often than not, however, additional analytical testing does not contribute significantly to an advancement of knowledge over and above what can be gained using the BTEX data alone.

Table 1. Concentrations of Selected BTEX Components over Time for Subsurface Releases of Three Separate Gasoline Formulations Showing the Degradation of Various BTEX Components (Hubbard *et al.*, 1994).

BTEX Component	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
10 % MTBE Case						
Benzene	21.6	22.9	15.9	9.9	6.4	5.5
Toluene	13.9	17.1	8.1	1.4	0.8	0.2
Ethylbenzene	2.5	2.5	1.8	0.7	0.3	0.08
p-Xylene	2.5	2.9	1.9	0.8	0.3	0.2
m-Xylene	6.7	6.7	2.9	0.3	0.2	0
o-Xylene	3.6	4.2	2.9	1	0.6	0.3
100% PS-6 Gasoline Case						
Benzene	17.8	19.8	14.5	5.5	5.2	2.9
Toluene	12.7	11.2	9.4	1.4	0.1	0.02
Ethylbenzene	2.6	2.2	1.8	0.9	0.1	0.06
p-Xylene	2.5	2.2	1.9	0.8	0.1	0.1
m-Xylene	6.5	6	3.4	0.4	0.1	0
o-Xylene	3.8	3.6	2.9	1.4	0.3	0.3
85% Methanol Case						
Benzene	16.1	19.1	17.5	12	9.8	10.2
Toluene	11	13.9	10.2	2.2	0.6	0.2
Ethylbenzene	2	2.2	1.4	1	0.7	0.6
p-Xylene	1.9	2.4	1.4	0.8	0.7	0.5
m-Xylene	5	6.1	3.3	0.6	0.1	0
o-Xylene	2.8	3.6	2.4	1.4	1.1	0.5

Gasoline hydrocarbons released to the subsurface environment undergo numerous physical and chemical interactions over time. Published research on the behavior of petroleum components in the environment has identified the principal governing factors that influence changes in petroleum composition (TRC Environmental Consultants, Inc. 1985; Thomas et al. 1998; Miralles-Wilhelm et al. 1993.; Hubbard et al. 1994; Mormile et al. 1994). Component changes in petroleum products are made from vaporization, photolysis, hydrolysis, solubilization, adsorption/desorption and microbial degradation. Once petroleum is released into the environment, these processes begin to alter the composition of the petroleum and over time their effects can be observed. This process is collectively referred to as petroleum product weathering.

In the subsurface environment, the effects of photolysis and vaporization are minimal. Hydrolysis of individual petroleum components is dependent upon the chemical structure of individual components. Solubilization of petroleum products is dependent upon the partitioning of individual petroleum components between soil, water and petroleum matrices. Distribution and redistribution of petroleum products and major components within each petroleum product is most heavily influenced by adsorption/desorption reactions between soil, groundwater and petroleum products themselves. The most important process governing the composition of petroleum products in the subsurface is microbial activity.

The type of microbial degradation of petroleum hydrocarbons in the subsurface is governed by the availability of oxygen. Oxygen-governed microbial degradation is referred to as aerobic degradation. Having ample supplies of dissolved oxygen in the subsurface will speed degradation of petroleum components. In the absence of appreciable concentrations of oxygen, other species such as nitrate, sulfate, and metals such as iron will be used as a source of oxygen (or electrons) for oxidation/reduction reactions. Such degradation of petroleum hydrocarbons in the subsurface in the absence of oxygen is termed anaerobic degradation. Anaerobic hydrocarbon degradation is generally regarded as a slower process compared to aerobic hydrocarbon degradation.

Scientific studies of gasoline degradation in the subsurface have focused on the effects of changes on major components such as the BTEX compounds over time under controlled circumstances. Review of such studies following concentrations of BTEX components over distance and time provides an understanding of the basic changes that occur among the BTEX compounds as gasoline weathers. A controlled subsurface contamination experiment was completed in an aerobic unconfined shallow sand aquifer in Ontario, Canada (Hubbard et al., 1994). The final report provided chemical data on the transport and fate of BTEX compounds. Table 1 presents the data from the aerobic degradation experiment which includes estimates of total mass for BTEX compounds at

Figure 1A. Ternary Plot of Toluene, Ethylbenzene and Total Xylenes (Σ Xylenes) of Groundwater Mass Estimates for 10% MtBE Gasoline Over a Time Period of 462 Days Exposure in an Aerobic Subsurface Environment

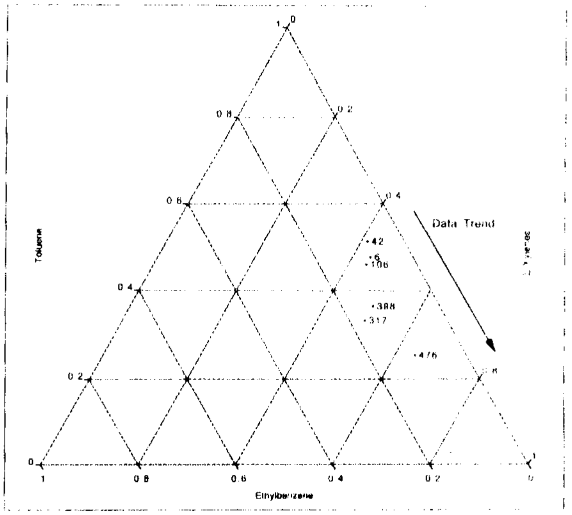

Figure 1B. Ternary Plot of Toluene, Ethylbenzene and Total Xylenes (Σ Xylenes) of Groundwater Mass Estimates for 100% PS-6 Gasoline Over a Time Period of 462 Days Exposure in an Aerobic Subsurface Environment.

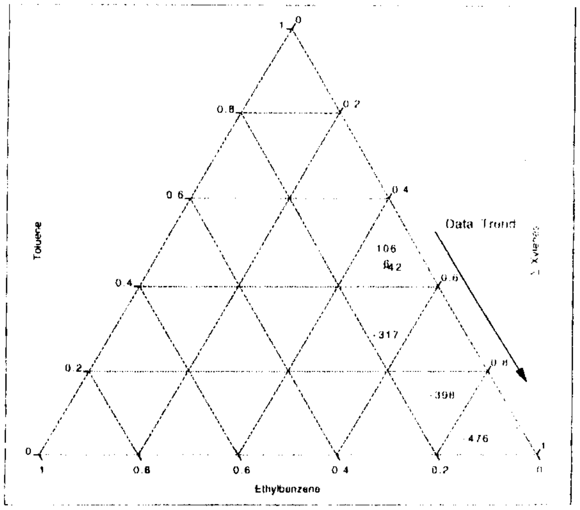

Figure 1C. Ternary Plot of Toluene, Ethylbenzene and Total Xylenes (Σ Xylenes) of Groundwater Mass Estimates for 85% Methanol Gasoline Over a Time Period of 462 Days Exposure in an Aerobic Subsurface Environment.

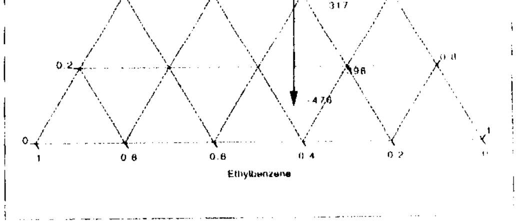

Table 2. Existing Analytical Information, Listing Well Number, Date Sampled (or Analyzed), Laboratory Reporting Results, Analytical Method Used, and Concentrations (ug/L) of Common Gasoline Components in Groundwater.

Well	Date	Laboratory	Method	Benzene	Toluene	Ethylbenzene	Σ Xylenes	MtBE
KOW-1	6/30/88	Lab A	EPA 624	12000	56000	Trace	29000	44000
KOW-3	6/30/88	Lab A	EPA 624	12000	41000	3700	21000	15000
KOW-5	6/30/88	Lab A	EPA 602	4300	16000	3100	13800	N/A
KOW-6	6/30/88	Lab A	EPA 602	14	0	36	5	N/A
KOW-7	6/30/88	Lab A	EPA 602	27	3	9	8	N/A
KOW-1	3/17/89	Lab B	SW-846 8020	10820	40600	4770	29970	20700
KOO-3	3/17/89	Lab B	SW-846 8020	10610	19324	2890	21245	37240
MW-5	3/17/89	Lab B	SW-846 8020	3986	15524	2948	13645	0
MW-3	4/15/94	Lab C	EPA 624	2500	27000	3900	32400	0
MW-5	4/16/94	Lab C	EPA 624	900	29000	5700	40000	0
MW-5D	4/16/94	Lab C	EPA 624	900	27000	4700	33000	0
MW-6	4/17/94	Lab C	EPA 624	500	11000	2600	20600	0
KOW-2	4/18/95	Lab D	SW-846 8015	600	7300	980	29800	0
KOW-3	4/18/95	Lab D	SW-846 8015	0	7600	2600	23700	0
MW-5	4/18/95	Lab D	SW-846 8015	120	29	74	477	0

N/A = Not analyzed.
Trace = Second analysis not completed on undiluted sample.

each sample time for three different gasolines, a 10% MtBE gasoline, a 100% PS-6 gasoline, and an 85% methanol gasoline. As can be seen from these data, BTEX compounds toluene, ethylbenzene and the three xylene isomers were all shown to degrade in relation to benzene.

Analysis of petroleum components using ternary analysis has been reported (Luhrs and Pyott 1992). In fact, use of ternary analysis has been underway to show differences in soil and/or rock types for decades (e.g., USGS Professional Papers 317-319, 1959; Hunt 1979). In this article, ternary analysis has been expanded, providing details on hydrocarbon interaction over time and space. Figure 1 presents ternary plots of the changes in relative concentrations of three BTEX compounds toluene, ethylbenzene and the arithmetic total of all three xylene isomers (Σxylene) over a total time period of 476 days for the three different gasoline experiments conducted in Ontario, Canada. Figure 1A presents a ternary plot of the changes in relative concentrations of selected BTEX compounds toluene, ethylbenzene and Σxylene over the time period of 476 days for the 10% MTBE gasoline experiment. Figure 1B presents a ternary plot of the changes in relative concentrations of selected BTEX compounds toluene, ethylbenzene and Σxylene over the time period of 476 days for the PS-6 gasoline experiment. Figure 1C presents a ternary plot of the changes in relative concentrations of selected BTEX compounds toluene, ethylbenzene and Σxylene over the time period of 476 days for the 85% methanol experiment.

While a similar general behavior was shown for all three different types of gasoline, there were important differences in the degradation of BTEX compounds in the 85% methanol gasoline compared to the other two types of gasoline. A continuation of individual data trends shown in Figure 1 would eventually result in the complete loss of toluene and ethylbenzene with the enrichment of the ΣXylenes number to the vicinity of 1.0 for MTBE and PS-6 gasoline, while for 85% methanol gasoline the proportions could be expected to be somewhat different. Based on these data, older gasoline could be expected to have elevated relative contributions of ΣXylenes and proportions of individual BTEX components would be skewed towards the bottom right side of the ternary data plot. Such effects have been reported previously (Wade, 1997; Siegel 1999).

Over the 476 days of the experiment, the relative proportions of ethylbenzene and total sum of all xylene isomers ΣXylenes) were observed to decrease relative to the proportion of toluene, which was shown to remain relatively constant at 0.9 relative to the other two components of this type of data treatment. In terms of concentration (mass), all three of these BTEX components were observed to decrease over time; it is only with a ternary data display treatment shown in Figure 1 that the relative behaviors of individual BTEX components become apparent.

Ternary Analysis of BTEX Components at the Study Site

The BTEX groundwater data from samples taken at a study site in the New England area using a historical data set covering a span of eight years. Due to site access and budget considerations, no additional data collection efforts were possible. Accordingly, all existing data were examined to assess the relative contributions of individual BTEX compounds at all sampling points from the first sample collection and laboratory analysis event in 1988, to the newest set of groundwater analyses in April 1996 (Table 2). Data were obtained on concentrations of groundwater BTEX compounds and MTBE using historical data compiled by others starting in 1988 and ending in 1996. Confirming data from the analysis of groundwater from monitoring well KOW-1 made in 1996 were also reviewed.

Figure 2A. Results - Groundwater Data from 1988 through 1995

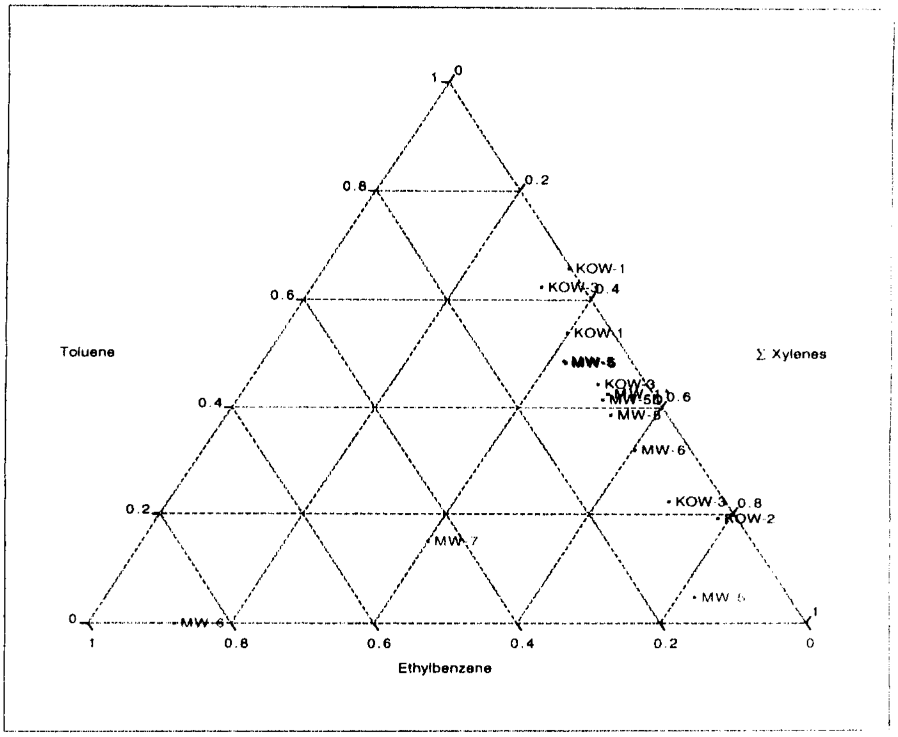

Figure 2B. Results - Groundwater Data from 1988 through 1995, plus confirming data in 1996.

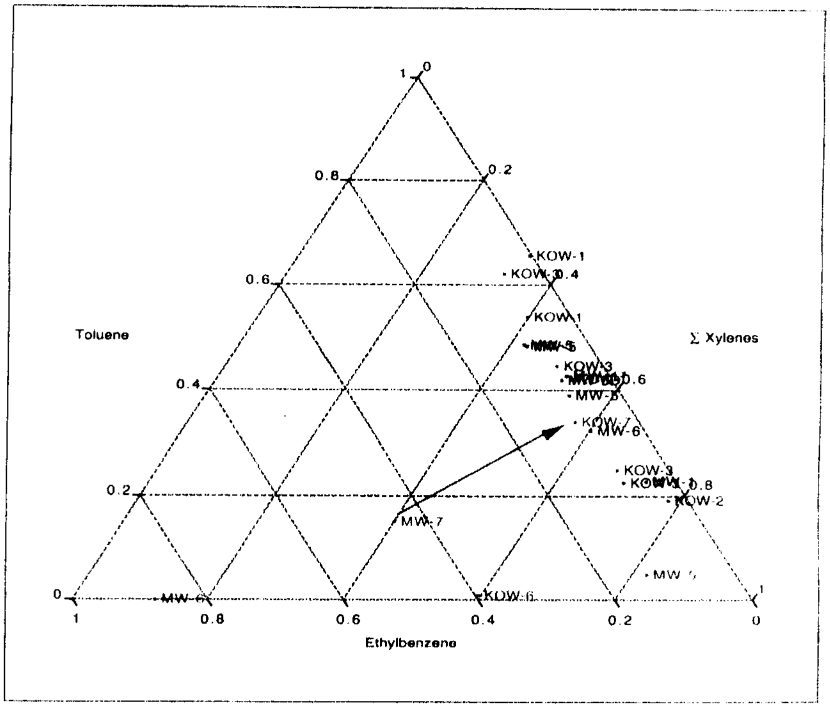

Figure 2 presents a ternary data analysis for all historical BTEX groundwater data for toluene, ethylbenzene and the arithmetic sum of all three xylene isomers (ΣXylenes) from the Site. Selected sample points were labeled in Figure 2 to illustrate salient points in the data analysis. Data trends for the selected BTEX compounds from the study site conform to data trends shown in the Hubbard et al. (1994) study of the behavior of subsurface gasoline BTEX components.

As can be seen from Figure 2A, BTEX data from all sampling points KOW-1 and KOW-3 from 1994, 1995, and 1996 samplings all appear in the same relative position in the ternary data plot. It is important to note that there are no data outliers for KOW-1 and KOW-3 --- all BTEX data for KOW-1 and KOW-3 are found in the same isolated position. The KOW-1 and KOW-3 data aggregation was separate from that of the KOW-6 and KOW-7 BTEX data, indicating that there is not only a compositional difference in the BTEX data, but also that there is a difference in the degradation state of the gasoline at KOW-1 and KOW-3 compared to that of KOW-6 and KOW-7.

Analysis of the entire data set, running from 1988 through 1996 showed a dramatic shift in the positioning on the ternary plot of monitoring well KOW-7 (Figure 2B). The shift in the position of the 1996 KOW-7 data identifies the time horizon when the second gasoline arrived at monitoring well KOW-7, that is sometime between sampling in 1995 and again in 1996.

Direct comparison of specific hydrocarbon degradation rates between the study site data and the Hubbard et al. (1994) data would not be appropriate because not only do individual degradation rates differ at different sites, but degradation rates within one site can differ from location to location as well. However, a comparison of the relative degradation state of BTEX hydrocarbons within the study site is relevant. From the historical data, it is reasonable to expect that the times of release of the gasoline found at KOW-1 and KOW-3 in 1988 and 1989 were similar to each other, with the gasoline hydrocarbons at KOW-1 and KOW-3 in 1994, 1995 and 1996 were indicative of the same gasoline only older and in a more degraded state.

It was interesting to note that the gasoline found in monitoring wells KOW-1 and KOW-3 in 1996 showed relative BTEX distribution of degraded gasoline while at the same time having the significant concentrations of the oxygenate additive MTBE. The persistence of the oxygenate additive MTBE to subsurface microbial degradation has been reported (Barker et al., 1991; Mormile et al., 1994). Consequently, data from monitoring wells KOW-1 and KOW-3 over the time period of 1988 to 1996 clearly document the release of MtBE-treated gasoline.

From the analysis of historical groundwater BTEX data, it was concluded that the gasoline hydrocarbon distribution in the vicinity of KOW-1 and KOW-3 was newer than the gasoline represented by the hydrocarbon distribution in the vicinity of KOW-6 and KOW-7. The microbial degradation state of gasoline hydrocarbons at these KOW-1 and KOW-3 at the Site are different, with more advanced degradation at KOW-6 and KOW-7.

Presence of the Oxygenate Additive Methyl t-butylether (MTBE)

The conclusions from the ternary analysis of historical BTEX data were substantiated from an analysis based on finding the oxygenate additive methyl t-butylether (MTBE) at various monitoring wells. During the 1970s and 1980s, automobile gasoline formulation in the U.S. was undergoing a period of important changes. The use of octane enhancing chemicals such as alkylated lead and manganese-based compounds was being curtailed, while the development of oxygenate additive compounds such as methyl t-butylether (MTBE) and others was being expanded. The timing of the use of MTBE in gasoline markets around the U.S. provides an age-dating approach for subsurface gasoline contamination, provided such data are used together with data on the site-specific degradation of gasoline hydrocarbons.

Starting in the 1970s, the U.S. Environmental Protection Agency began an orderly phase down on the use of lead antiknock additives in U.S. gasoline from 1.2 grams per gallon (gpg) to a maximum of 0.5 gpg. There were some interruptions in the leaded gasoline phase down and it was not a smooth reduction. For example, as a consequence of the Arab Oil Embargo, a one-year delay in the phase down was approved by President Carter in 1979-1980 to allow major domestic producers to market leaded gasoline containing 0.8 grams per gallon until October 1, 1980 (Ethyl Corporation Annual Report, 1978). Also as a consequence of reduced gasoline supplies in the U.S. during the late 1970s, a manganese-based antiknock compound MMT was used in unleaded gasoline grades for the peak gasoline driving time in 1979. Otherwise MMT was approved for use only in leaded gasolines. Subsequently in the USA, use of MMT was banned altogether later in the 1980s.

Use of MTBE in the U.S. automobile gasoline supply for unleaded gasoline was approved by the U.S. Environmental Protection Agency in March 1979 (Federal Register, Vol 44, No. 45, Tuesday, March 4, 1979). As millions of barrels of gasoline were consumed daily in the U.S. during the 1970s and 1980s (Petroleum Supply Annual, 1992 and 1993), MTBE-treated gasoline was not immediately available at all areas of the country simply because of the approval by the EPA. In the U.S. during the decade of the 1980s, various gasoline manufacturers introduced MTBE-treated gasolines at different times. In fact, it is important to know which gasoline supplier serviced which areas of the U.S. in the decade of the 1908s when using MTBE data to determine timing of subsurface gasoline releases.

Using such data, gasoline hydrocarbons containing MTBE found in the groundwater at monitoring wells KOW-1 and KOW-3 in 1988 and 1989 had to have been released to the subsurface environment in the time frame no earlier than in the early 1980s. And MTBE-formulated gasolines could have been released later than this time frame if the gasoline were a formulation of another gasoline retailer. In such cases, knowledge of the gasoline supplier to any particular study site becomes important. In this case, site-specific knowledge of gasoline supplier ruled out one supplier of MTBE-treated gasoline in favor of another supplier. Such information was consistent with the finding of two different gasolines in the ternary analyses.

Conclusions

A chemical data set from groundwater samples collected at a coastal property in Massachusetts, including the BTEX compounds and the oxygenate additive MTBE (covering a span of eight years from 1988 to 1996) was examined. The historical data were used to determine the type(s) of subsurface contamination present, estimate the age of onset of any identified subsurface petroleum contamination, and evaluate data on an independent groundwater sample collected and submitted to an independent analytical laboratory to confirm or refute findings from the historical data.

Two different gasoline formulations were apparent from the ternary analysis of BTEX compounds. Analysis results showed the effect of hydrocarbon weathering resulting in the conclusion that there are separate types of gasolines represented in the historical data. Specifically, two different gasolines were identified as having been released at the Site: an older more degraded gasoline that did not contain MTBE and a newer less degraded gasoline that contained higher concentrations of MtBE.

Based on the composition of gasoline-range hydrocarbons and their degradative states, it was estimated that the gasoline at monitoring wells KOW-1 and KOW-3 was probably released in the mid-to later-1980s after higher amounts of MTBE had begun to be used in gasoline formulations. Based on the extent of hydrocarbon degradation and the presence of MTBE at monitoring wells KOW-1, KOW-3, and MW-1, it was concluded that in subsequent years, this older gasoline had undergone weathering reactions and had moved away from its apparent source.

Compared to BTEX concentrations at KOW-1 and KOW-3, much lower hydrocarbon concentrations were found at monitoring wells KOW-6 and KOW-7 throughout most of the data set with a dramatic shift in the ternary position of KOW-7 in 1996 data. The hydrocarbon distributions at these two off site wells exhibited advanced hydrocarbon degradation patterns and contained no MTBE. This type of contamination was indicative of older gasoline, formulated before the early to mid-1980s, with arrival of a second gasoline at KOW-7 sometime between 1995 and 1996.

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APPENDIX F
ROTUNDO COALESCING-PLATE OIL-WATER SEPARATOR

Oldcastle Precast Group

ROTONDO PRECAST®

Northeast Region
Avon, CT

Rotondo Precast > Environmental > Pollution Control Structures > **Oil/Water Separators**

Modular M-Pak® Coalescing Plate Stacks

- the state-of-the-art in coalescing plate design
- provide more horizontal separation area in a smaller volume than any other media available
- specially formed for continuous self-cleaning of oil and solids to make maintenance easier; easily upgraded

Large double doors

- in cast aluminum or galvanized steel; capable of supporting H20 vehicular loading
- allow easy daylight inspection and regular cleaning without entry
- enables convenient servicing using wet vacuum equipment
- allow transfer of large components and equipment

Optimum configuration of baffles and openings

- developed after extensive trials and test-runs and in-house hydraulic analysis
- promote evenly distributed laminar flow conditions throughout separation chamber for optimum performance

In-flow Control Chamber

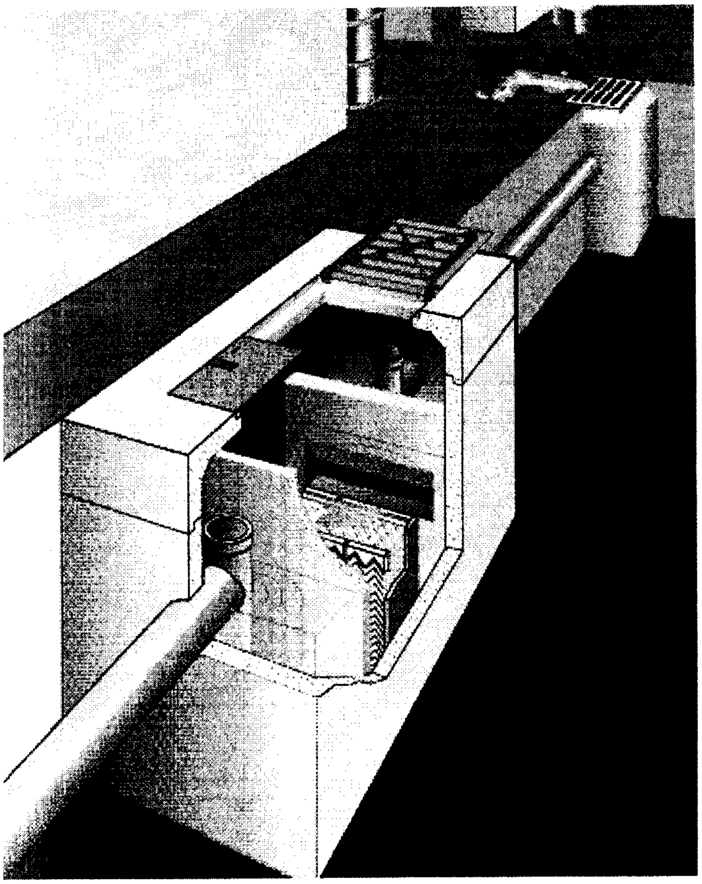
- Dissipates turbulence
- Collects heavy grit and floatable debris.

Tee-sections at both inlet and outlet

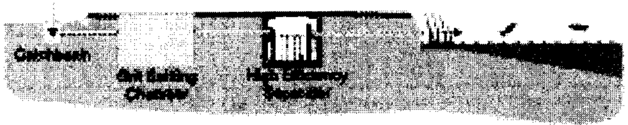
- provide convenient sampling points, secondary oil containment and full venting of incoming water

The Coalescing-Plate Oil-water separator

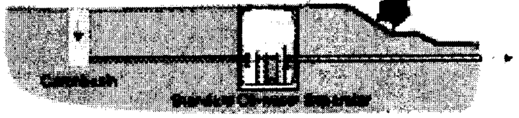
for Durability, Performance and Servicability



- **Precision-formed, high quality reinforced concrete retention structure**
  —Nothing compares to an Oldcastle precast vault that is specially designed for the strength, water-tightness and the durability needed for water-treatment structures
- **Modular M-Pak™ Coalescing Plate Stacks**
  —the state-of-the-art in coalescing plate design
  —provide more horizontal separation area in a smaller volume than any other available media
  —specially formed for continuous self-clearing of oil and solids to make maintenance easier; easily upgraded
- **Large double doors**
  —in cast aluminum or galvanised steel; capable of supporting the H20 vehicular loading
  —allow easy daylight inspection and regular cleaning without entry
  —enable convenient servicing using wet vacuum equipment
  —allow transfer of large components and equipment
- **Optimum configuration of baffles and openings**
  —developed after extensive trials and test-runs and in-house hydraulic analysis
  —promote evenly distributed laminar flow conditions throughout separation chamber for optimum performance
- **In-flow Control Chamber**
  —Dissipates turbulence
  —Collects heavy grits and floatable debris.
- **Tee-sections at both inlet and outlet**
  —provide convenient sampling points, secondary oil containment and full venting of incoming water.



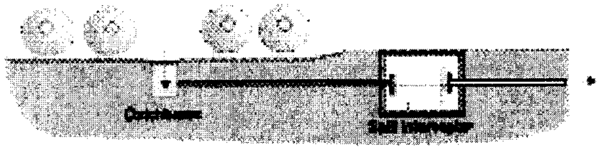
High Efficiency / High Performance Unit
installed with grit chamber upstream



Standard Treatment Unit -restricted flows
(Deep Installation with risers)

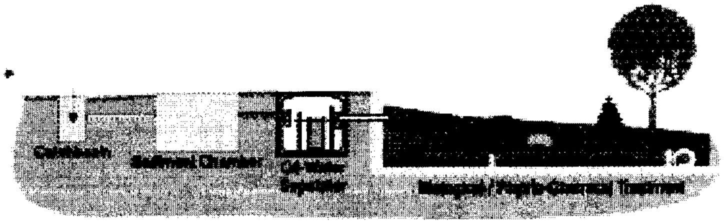
Oldcastle's oil-water separators meet the needs of a wide range of run-off applications:

- High performance removal of fugitive oil from storm and washdown water,
- Interception capacity for accidental surface releases
- Enhanced pretreatment for biological and physio-chemical purification systems



Spill interceptor installation
- upgradable to higher-performance water treatment

Stormwater Treatment with
upstream diversion of large flows



Upstream protection of biofiltration treatment systems

When you put all of the pieces of the puzzle together, the advantage of Oldcastle's separator becomes clear.

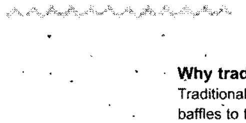
The Challenge of a Real Environmental Problem

Where most of the oil in water comes from:

It is a well known fact that chronic hydrocarbon contamination of surface water results more from small quantities of oil from regular *fugitive* sources than from large accidental spills. Fugitive sources include leaking containers, machinery, vehicles and similar releases that are difficult to avoid.

How much is too much?

Current environmental water quality standards for oil and grease are frequently set at levels as low as 5, 10 and 15 mg/liter†. This is about half a teaspoon of oil in a 55 gallon drum of water.



What oil in stormwater looks like:

Because much of the oil that gets into water is quickly broken up into tiny droplets, you often don't notice it at all. Only when you inspect a sample of water can you make out tiny spheres. In fact droplets of oil range in size from one or two to several hundred microns‡. In many cases this means that to meet effluent standards, separators have to at least be capable of removing all droplets of oil down to 50 or 60 microns and this is not easy.

Why traditional spill interceptors won't work:

Traditional spill interceptors —simple retention tanks with baffles to trap floating oil on the surface— play a useful *secondary containment* role in the event of a large accidental spill. However, unless they are extremely large they are unlikely to safeguard normal stormwater discharges from exceeding today's stringent standards for oil and grease. Small oil droplets separate very slowly from water and are more likely to pass right through one these vessels.

The Real *Science* of Oil-water Separation

What is gravity oil-water separation?

Oils are hydrophobic which means that they do not dissolve in water. Instead, when oil is well mixed with water, it exists as a near-suspension of tiny spherical droplets. Oil is lighter than water and for this reason, even though an oil droplet may be smaller than your eye can see, it rises up (slowly) in the water. Gravity separation is achieved, therefore, by creating the right conditions (*laminar flow*) in a flow-chamber where these droplets are given enough time to reach a horizontal surface where they will no longer be carried along by moving water.

Isaac Newton's laws of fluid and particle mechanics accurately describe the behaviour of these droplets (He didn't just discover gravity, you know). Because of his laws we know that these oil-droplets rise at constant speeds (or "terminal velocities"). They do not accelerate (for the same reason that parachutists do not continue to accelerate beyond a "terminal velocity" when they are falling to earth). Harvey Stokes is specifically responsible for deriving the accurate mathematical formula (known as "Stokes' Law") that we use for calculating the rising (or falling) velocity of tiny spherically shaped objects like oil-droplets.

How long does it take for oil to separate?

Stokes' law tells us how quickly (or slowly) small oil-droplets rise. A 60 micron droplet typically takes half an hour to rise a distance of just one foot in still water. So one of these is unlikely to get trapped on the surface of a simple retention vessel unless the vessel is extremely large (and provides plenty of retention time) or the water flow-rate is kept low.

Horizontal Separation Area

Besides Newton and Stokes, many engineers have made important contributions to the science of separation processes —none more so than Allen Hazen at the beginning of this century. He is attributed with the discovery of the principle of "surface loading": that the effectiveness of a simple gravity separation device is directly proportional to the area (on plan) of the separation (or sedimentation) chamber divided by the flow-rate. This is true for all liquid gravity separation processes. It is because of Hazen's principle that we know that a if a retention vessel is to continuously remove droplets as small as 50 and 60 microns from water, it will have to an area on plan of *at least* 4 square feet for every GPM* of flow through it.

Hazen, confirmed that the performance of a separator is *independent* of the depth of water in the separation tank. As early as 1904, he suggested the value of dividing a chamber vertically using a large number of horizontal plates to increase performance —increasing what we refer to as horizontal separation area.

Achieving High-Efficiency Gravity Oil-Water Separation

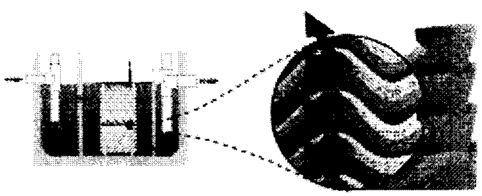
The Simple idea of Coalescing Plates

The first coalescing plates were just flat panes of glass stacked in a tank: dividing the water into many thin layers. Because glass is hydrophobic, oil tends to adhere to it whereas water does not. Modern coalescing plates are made with durable, tough plastics, like polypropylene, that have the same property. Though corrugated and inclined (to improve serviceability), the principle is exactly the same. When water flows through a separation chamber with coalescing plates spanning its cross-section, it gets divided into may thin layers. Each layer acts like an individual separation chamber with droplets only having to rise as far as the underside of one of the plates to be "caught".

Squeezing more horizontal area into a smaller separator.

Oldcastle provides more plates in a smaller separator volume than anyone else. Using Facet's M-Paks we can provide as much as 31 square feet of horizontal separation area in a single cubic foot.

Combine this with the hydraulic integrity of a well designed, space-efficient, rectangular concrete vault and you have the most efficient separator ever developed!



Making It Practical

If you can't maintain it, you don't want it

Although high performance is necessary for safeguarding today's effluent standards, it is not enough. Everyone knows that water treatment systems are only going to work as well as they are serviced and maintained. That is where Oldcastle's oil-water separator once again stands out. The key advantage of going with a vault design —long favoured by engineers in the field of water treatment— is that you can look inside and inpect the separator while it is operating. The film of oil that develops is easily skimmed off the surface of the water using standard wet/dry vac equipment. Sludge can be removed using regular septic tank pumping equipment.

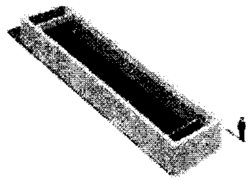
Gravity separation — not filtration!

Coalescing plate separators are gravity separation devices —not filters. Even though stacks of coalescing plates appear to occupy a large amount of space inside the separation chamber, they do not reduce the area of the flow cross-section significantly and do not result in a significant pressure-drop. In addition, to avoid plugging, the coalescing plates Oldcastle uses have been designed with inclinations and channels to enable solid particles that settle out in the plate-stacks to slide to the bottom of the chamber. The oil collects on the underside of the coalescing plates and gradually forms a film that flows upwards — eventually making its way undisturbed to the water surface in the separator chamber. In other words, gravity works with the plates to allow them to self-clear.

What it means to have a more efficient oil-water separator:

When you can get the same oil-removal performance with this —

...that you could previously only get with this —



...You have a number of extra advantages...

What are you going to do with all that extra space ?

---

† The concentration of pollutants, like oil, is nearly always measured in milligrams per liter (mg/l). The less precise term "parts per million" is used to mean the same thing. Environmental regulations invariably use mg/l to set water quality standards.

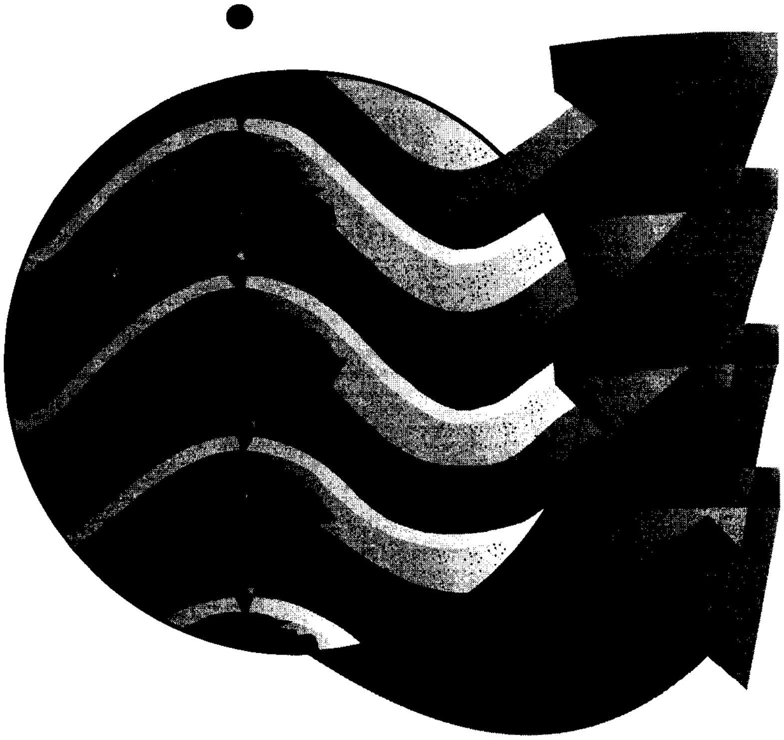
‡ What's a micron? A micron is a measure of length used to measure very small distances. One micron (or micrometer) is one thousandth of a millimeter or one inch divided by 25,400. 50 microns is the approximate limit of detection for the human eye — the thickness of a fine hair.

* Flow-rate is currently measured in GPM (Gallons per Minute) 1 GPM = 0.00223 CFS (Cubic feet per second) = 3.788 l/min. (liters per minute) = 63.1 x 10^{-6} m^3/s (meters cubed per second).

Oil-Water Separators

for surface runoff treatment

Guidelines
for
Design, Installation and
Operation



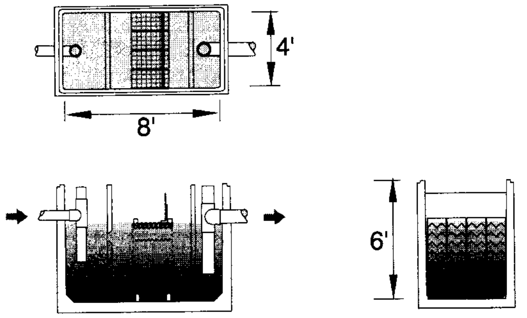
Oldcastle®

Flow-Ratings and Geometrical Data for Standard Configurations

The tables below may be used for guidance in choosing appropriate separator sizes. Models similar to those shown here, as well as custom models are available from all Oldcastle Precast manufacturing locations. Because of differing requirements of customers in different regions, some variations may exist between the standard features of models indicated here and those provided at each Oldcastle manufacturing location. Additional intermediate, larger and smaller sizes may also be available. Contact your local Oldcastle representative for guidance. Oldcastle Precast Inc. reserves the right to make modifications without notice in the course of technological progress and in response to customers' needs.

model: 48-OPS

Nominal Dimensions



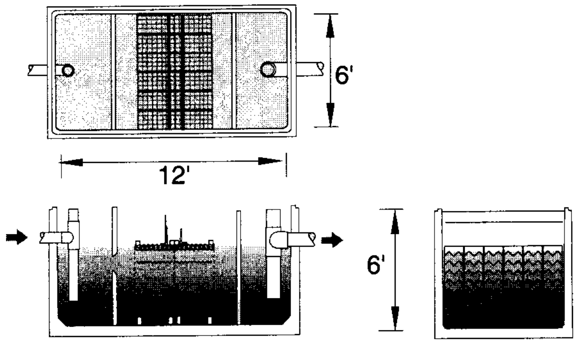
Nominal Capacity	1000 gallons
Standing Water Depth	4 feet
Vertical Plate Spacing	18.5 plates per foot
Horizontal Oil Separation Area	555 square feet

Standard Treatment	0.033	137 †

Pipe Diameters for Standard and High Performance Treatment Flow-rates ‡	Inlet Outlet	6" 8"

model: 612-OPS

Nominal dimensions



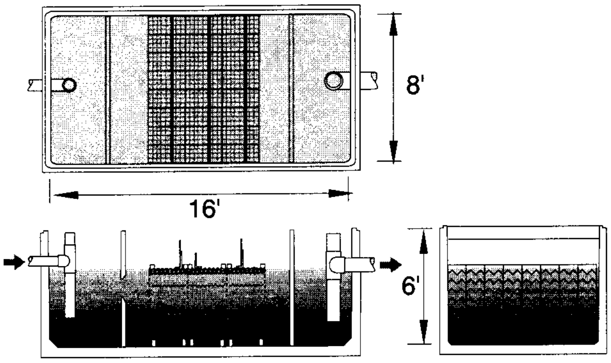
Nominal Capacity	2200 gallons
Standing Water Depth	4 feet
Vertical Plate Spacing	18.5 plates per foot
Horizontal Oil Separation Area	1665 square feet

Standard Treatment	0.033	411 †

Pipe Diameters for Standard and High Performance Treatment Flow-Rates ‡	Inlet Outlet	8" 10"

model: 816-OPS

Nominal Dimensions



Nominal Capacity	4000 gallons
Standing Water Depth	4 feet
Vertical Plate Spacing	18.5 plates per foot
Horizontal Oil Separation Area	2775 square feet

Standard Treatment	0.033	750 †

Pipe Diameters for Standard and High Performance Treatment Flow-rates ‡	Inlet Outlet	10" 12"

---

† Flow ratings are calculated on the basis of the provision of horizontal separation area according Hazen's surface-loading theory and are in accordance with the American Petroleum Institute's principles for separator sizing -API Publication 421, February 1990.

‡ Flow-rates in excess of the maximum surge value given above can result in stripping of captured oil from coalescing plates. The pipe sizes given above are suitable for flow-rates up to the Standard Treatment flow-rate for this model. Flow-rates in excess of this level may require larger pipes and hydraulic analysis of downstream conditions to ensure that the outlet pipe can carry water at the maximum flow-rate required without excessive head building up inside the separator chamber.

Understanding Separator Performance

How oil-removal effectiveness varies

Many factors affect separator performance. Large performance differences not only exist between different separator designs and models, but also between identical separators that are used in different environments and separators that are subjected to different incoming oil-water mixtures. The quantity of oil in the influent, its density (specific gravity) and water temperature all influence the performance of gravity separators. However, though significant, these factors are still not nearly as important as the physical nature of the oil-water mixture itself: the degree to which the oil is dispersed in the water: *the size of the oil-droplets*.

It is convenient to divide the different forms of oil-water mixtures into the following four main categories:

- The oil is a slick or film on the surface –In this case it has already separated from the water
- The oil is made up of relatively large drops –greater than 300 microns[†] in diameter (approximately) and globules dispersed throughout the water
- The oil exists as small droplets (greater than 10 microns in diameter, less than ~300 microns in diameter)
- The oil exists as extremely small particles (less than 10 microns) and emulsions

Most oil-water mixtures in runoff will tend to be a combination of these forms. The first two can be removed from water using the most rudimentary form of retention-vessel type oil-water separator (sometimes referred to as a "spill-trap"). Although the quantity of oil in this form can be substantial, its removal alone is seldom sufficient for safeguarding today's more stringent effluent water-quality standards for grease and oil.

The third form –droplets between 10 and 300 microns– can make up a significant quantity of the oil in runoff and is more difficult to remove. It is in their ability to remove this oil that individual separators differ most from each other. See next section below.

The fourth form of oil-water mixture usually occurs significantly after intense mechanical mixing or when surfactants, solvents or detergents are present. Significant quantities of this form of oil-water mixture can be avoided by preventing the use of detergents and by not using devices such as centrifugal pumps upstream of the separator. Otherwise more costly treatments may be necessary –such as biofiltration or physio-chemical methods.

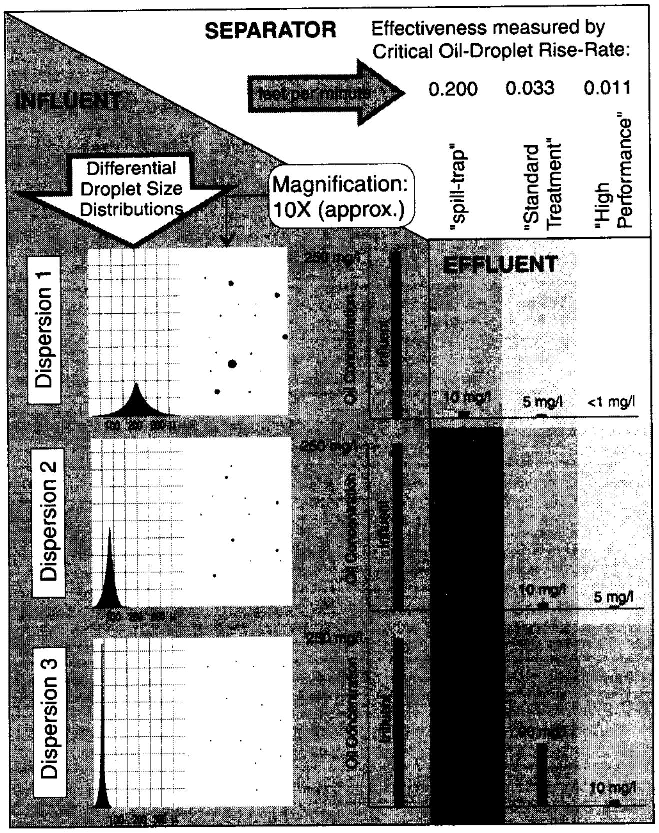


Figure 1: Comparison of oil-removal effectiveness of three separators for three different dispersions of oil. Note: the above data assumes influent oil with a specific gravity of 0.88 at a concentration of 250 mg/liter[‡] and water at a temperature of 50 °F.

Droplets in the 10 - 300 micron range

As mentioned above, it is in their ability to remove droplets within this range that oil-water separators differ most from each other. Figure 1 (above) shows the concentration of oil to be expected in the effluent from three different separators subjected to three different influent oil dispersions. As the same oil volume is dispersed as smaller and smaller droplets, the effectiveness of each separator decreases. The oil removal rates illustrated are typical of separators available today. Separator performance is characterized by its *critical oil-droplet rise-rate* (defined below). The 'High Performance' separator above clearly offers the best performance and would therefore provide the greatest safeguard for effluent water quality standards. However, when flow-rates are very large, this level of performance may not be the most economical solution. See choosing the section entitled, 'Choosing a suitable "critical rise-rate" value'.

[†] A micron (or 'micrometer') is a unit of length equal to one thousandth of a millimeter. (There are 25400 microns in one inch. 50 microns is the approximate limit of detection for the human eye.

[‡] Oil concentration in water is best measured and quoted in mg/liter (milligrams per liter). The less precise term, "parts per million", is frequently intended to mean the same thing. Environmental regulations use mg/liter.

Understanding Separator Performance (continued)

Basic measures of separator performance

All gravity separators rely on the tendency of droplets of oil to rise in water (because of their natural buoyancy). They are "caught" either when they make contact with and adhere to the surface of a solid object (such as a coalescing plate) or when they enter a layer of stationary water at the top of the separator chamber.

The Critical (Oil-Droplet) Rise-Rate

The rise-rate of an oil-droplet is the natural speed of ascent it has as it rises –the droplet's "terminal velocity". A separator, at a certain flow-rate, will capture all droplets that have rise-rates above a certain value. This value is the *critical rise-rate* of the separator at that flow-rate. The critical rise-rate is a convenient performance measure for any gravity separator - the way you describe the separator's effectiveness at removing oil. It is usually measured in feet per minute. The lower it is, the more effective the separator will be at removing oil and safeguarding a certain water quality standard.

Note: The term "surface loading" is sometimes used to mean the same thing as the term "critical rise-rate" (or "critical settling rate" in the case of sedimentation). However, the term "surface loading" is more usually a measure of the flow-rate through a gravity separation chamber divided by the chamber's area (on plan). Though sometimes the same, these values are not necessarily identical as will be seen in the section entitled "Hazen's Principle of Surface Loading".

The Design Flow-rate

The critical rise-rate changes as the flow-rate of water though a separator is increased or decreased. Therefore, to be meaningfully applied to a particular separator design, a critical rise-rate value must also be accompanied by a design flow-rate ("maximum operating flow-rate") value for which it applies. When the flow through the separator is increased, the critical rise-rate of the unit increases (i.e. the performance decreases). Conversely: when the flow-rate is reduced, the critical rise-rate is reduced (i.e. the performance increases).

The Effective Horizontal Separation Area

If you use a compatible set of units and divide the design flow-rate of a separator by its corresponding critical rise-rate you get an answer that has units of *area*. This number represents the effective horizontal separation area of the separator.

This number is convenient because it changes little with flow-rate. So it is essentially a single number that can be used to quantify the effectiveness of any separator. Separators that provide the greatest amount of effective horizontal separation area generally have the highest performance. Another advantage of the concept of effective horizontal separation area is that it may be estimated from the basic geometry of the oil-water separation chamber and its components.

–Horizontal separation area is covered later in more detail.

Effluent water quality standards

Effluent standards are quantitative limits placed on the amount of polluting substances allowed in water. Alone, they cannot be used to define separator performance. This is because the performance of all separators is dependent upon physical characteristics of the oil-water mixture going into a separator and not just their relative quantities.

Most separators *can* produce an effluent that meets a water quality standard –if the conditions are right. Unfortunately, it is also true that no separator can guarantee that the effluent will never exceed stringent standards –unless very strict control over what goes into it can also be guaranteed. This is because it is impossible to predict what the nature of the influent oil-water mixture characteristics will always be. What a good separator can do, however, is reduce the probability of the effluent being out of compliance significantly. In order to judge how well a separator is likely to do this, basic performance measures such as its *critical rise-rate* (as described above) must be determined. Only these types of performance measures are independent of the environmental conditions of any particular application.

Choosing a suitable "critical rise-rate" value

Critical rise-rates for separators can be chosen with values ranging from as little as 0.01 feet per minute to as much as half a foot per minute. The value you choose will depend on the intended function of the separator (as part of a site surface-water pollution prevention strategy), likely influent characteristics (oil quality and dispersion characteristics), effluent water quality standards and the sensitivity of the receiving environment.

Values at the lower end of the scale (0.01 feet per minute) are best chosen when design flow-rates can be kept reasonably low and where a very high performance is desirable. The upper end of the scale (0.5 feet per minute) would only be appropriate where the emphasis is on providing a low-cost unit for occasional spill interception where the spilled oil is unlikely to be dispersed significantly.

More frequently, however, the best approach has been to choose an intermediate value to balance costs and benefits. Large retention-tank separators in the past used to be designed with *critical rise-rates* of the order of 0.2 feet per minute. But the concentration of oil in the effluent from these devices has frequently been found not to meet today's more stringent standards. In applications that have to meet standards of the order of 10 mg/l, a value of 0.033 feet per minute (the rise-rate of a 60 Micron, 0.88 S.G., oil droplet in 50° F water) has been found to be a suitable choice[†]: removing a substantial portion of oil and safeguarding effluent quality to meet these standards in almost every case provided that proper control is exercised over the use of detergents and other problem substances.

[†] Washington State Department of Ecology recommends this value for coalescing-plate separators used in Storm water applications – *Stormwater Management Manual for the Puget Sound Basin*, February 1992. The American Petroleum Institute also suggests 60 Microns as a typical design oil-droplet size in the treatment of oil-refinery waste-waters – *Design and Operation of Oil-Water Separators*, API Publication 421, 1990.

Horizontal Separation Area

Hazen's Principle of Surface Loading

In 1904 Allen Hazen firmly established the principle of how the effectiveness of a sedimentation tank varies directly with the rate of flow through it, divided by its plan area[†]. This principle is not only valid for sedimentation processes, but applies to all liquid gravity-separation processes, including oil-water separation.

Uniformly distributed, laminar flow

When the flow is laminar and uniformly distributed throughout the separation chamber cross-section (See figure 2), the *critical rise-rate* is equal to the flow-rate divided by the area of the separation pool.

$$V_T = \frac{Q}{A_H}$$

–where A_H is the horizontal separation area (in square feet) as described above, Q is the flow-rate through the separator (in cubic feet per minute) and V_T is the *critical rise-rate* (in feet per minute).

Hence, the critical rise-rate (or settling-rate) for many separation devices is frequently taken as being equal to the *surface loading*. The "surface loading" on a gravity separation chamber is (by definition) equal to the flow-rate through the chamber divided by its area (on plan).

Other flow regimes

Flow is rarely perfectly uniform –although it is reasonable to assume it is in some instances. In other cases, however, eddies and turbulence are significant, especially at higher operating flow-rates. Such deviations from uniform, laminar flow serve to *reduce* the efficiency of gravity separation processes substantially. In order to account for this, a design factor, F, is incorporated into Hazen's equation:

$$A_H = F\frac{Q}{V_T}$$

–where A_H, Q and V_T are the same as in the equation used above and F is a dimensionless factor (always greater than or equal to 1) to account for inefficiencies due to non-uniform flow.

F cannot be less than 1 because the performance of a gravity separator cannot be greater than that predicted by Hazen's principle (which assumes ideal conditions). The American Petroleum Institute recommends different values between 1.2 and 1.75 for traditional retention-tank (baffle-type) separators[‡]. Many coalescing-plate separators and separators designed to ensure optimal flow distribution have near-ideal flow-conditions in the separator chamber: so that F is taken as being equal to 1 (or is omitted entirely). In the design of circular clarifiers (like those used in municipal water-treatment projects), F can also be taken as being equal to 1, because the flow-regime is essentially uniform-radial.

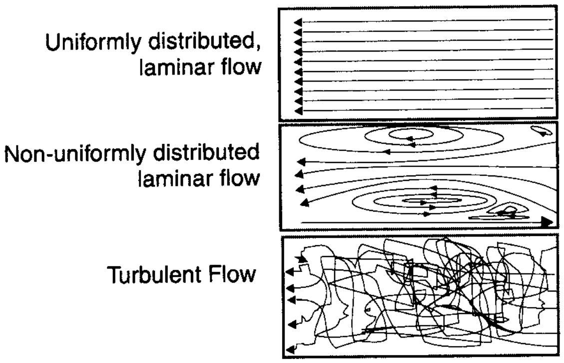


Figure 2: Illustrations of uniform-laminar, non-uniform laminar and turbulent flow.

Why "horizontal area" (and *not* depth)

Hazen's principle has been experimentally validated. It is also simple to derive analytically using basic hydraulic equations of continuity. The following is a derivation of Hazen's principle using a simple gravity separation flow-model.

Consider the illustration in Figure 3 of a simple rectangular oil-water separation chamber. The separation pool volume is composed of two zones or layers: a stationary liquid-layer and a moving liquid layer. Any water passing through the separator forms part of the moving liquid layer. The top layer is kept stationary by the presence of an oil-dam (or "scum board") before the outlet of the separator. The depth, d, is the maximum distance an oil-droplet will have to rise in order to reach the boundary between the stationary and the moving liquid layer. We will see, shortly, that it is not necessary to know exactly what "d" is.

Now, consider an oil-droplet moving through this separation chamber. This droplet has two velocity components as illustrated in Figure 3: a vertical componet and a horizontal component. The vertical velocity component is its natural rise-rate or "terminal velocity". An oil-droplet naturally rises in water because of its buoyancy. Equations, such as Stokes' law, can be used to calculate the rise-rate of any oil-droplet on the basis of its size and density, as well as other properties of the water. The symbol, V_T, is used here to represent this velocity component. The horizontal velocity component of this droplet (represented by the symbol V_H) is the same as the horizontal velocity of the surrounding water that carries it along.

If the oil-droplet can rise as far as the boundary between the moving liquid layer and the stationary layer, it will be captured, because its horizontal velocity will drop to zero to match the surrounding still water in this layer. But if the oil-droplet is not given enough time, it will pass out of the separation chamber before it has a chance to reach this boundary and will not be caught. Another way of stating this is: if the time required for separation is greater than the *residence time* of the water in the separator, the droplet will not be "caught".

[†] A common error in sizing gravity separation devices is to assume that performance is directly proportional to the vessel volume or the residence time of liquid in the chamber. While true for some reaction vessels, it is not in this case.

[‡] API Publication 421 – *Design and Operation of Oil-Water Separators*, 1990

Horizontal Separation Area (continued)

A separator must be designed so that even if the droplet comes into the chamber at the very worst location (i.e. at the bottom of the separator), there will still be enough *time* for it to rise up the full distance, d, to the boundary between the stationary and moving water layer. We will call this the required time to ensure separation or simply "the separation time" (represented by "t_s").
The amount of time available for the droplet to do this is called the *residence time* –the time the water spends in the separator chamber (represented by "t_r"). In other words, to ensure removal of this droplet, the separation time must be less than the residence time. We can therefore call the following expression our first basic condition for ensuring separation of this droplet:

$$\text{Condition to ensure separation: } t_s \leqslant t_r$$

We know the speeds in each direction and the maximum distances, d and L (See figure 3 below). We also know that, for motion in a straight line[†] at a constant speed, the time taken is simply the distance divided by the speed. So,

$$t_s = \frac{d}{V_T} \quad \text{and} \quad t_r = \frac{L}{V_H}$$

So now we can write:

$$\text{Condition to ensure separation: } \frac{d}{V_T} \leq \frac{L}{V_H}$$

We can then rearrange this expression and write

$$\text{Condition to ensure separation: } \frac{V_H \cdot d}{L} \leqslant V_T$$

Now, the basic principle of conservation of matter (known in fluid mechanics as "the continuity principle") tells us that the *superficial* horizontal velocity of the water (the actual horizontal velocity in uniformly distributed flow) is equal to the volumetric flow-rate (Q) divided by the area of the vertical flow cross-section:

$$V_H = \frac{Q}{A_V} = \frac{Q}{B \cdot d}$$

Now we can write:

$$\text{Condition to ensure separation: } \frac{Q \cdot d}{B \cdot d \cdot L} \leqslant V_T$$

Notice how the depth, 'd', now appears in both the numerator and the denominator of the left-hand-side expression. This means it cancels out of the expression – showing that *the depth of the separation chamber is <u>not</u> critical to separator performance*.
Now, it is easy to rearrange the expression that remains to get Hazen's principle. The horizontal area of the separation chamber is equal to its length multiplied by its width:

$$B \cdot L = A_H$$

So, we can use "A_H" in our "condition" expression and get:

$$\text{Condition to ensure separation: } \frac{Q}{A_H} \leqslant V_T$$

–This was an *analytical* proof of Hazen's principle.

Using Hazen's principle to size a separator

So sizing a separator requires that we first select a flow-rate to be processed and, then, a *critical* rise-rate based on our expectations for the oil water mixture to be separated. Dividing the first by the second gives us the *effective separation area* needed:

$$A_H = \frac{Q}{V_T}$$

A separator can, therefore, be sized to provide this separation area either as the plan area of its water surface or –much more efficiently– as the sum of the plan-areas provided by stacks of horizontally extending coalescing plates. This is outlined in more detail in the next section.

[†] In reality there will be some velocity variations with water depth in a separator chamber and hence the trajectory of a rising droplet will not be a straight line, but a curve. Accounting for this fact, however, significantly increases the complexity of the algebraic analysis needed, without altering the conclusions. The assumption that the horizontal velocity does not change with depth was therefore considered a reasonable simplification.

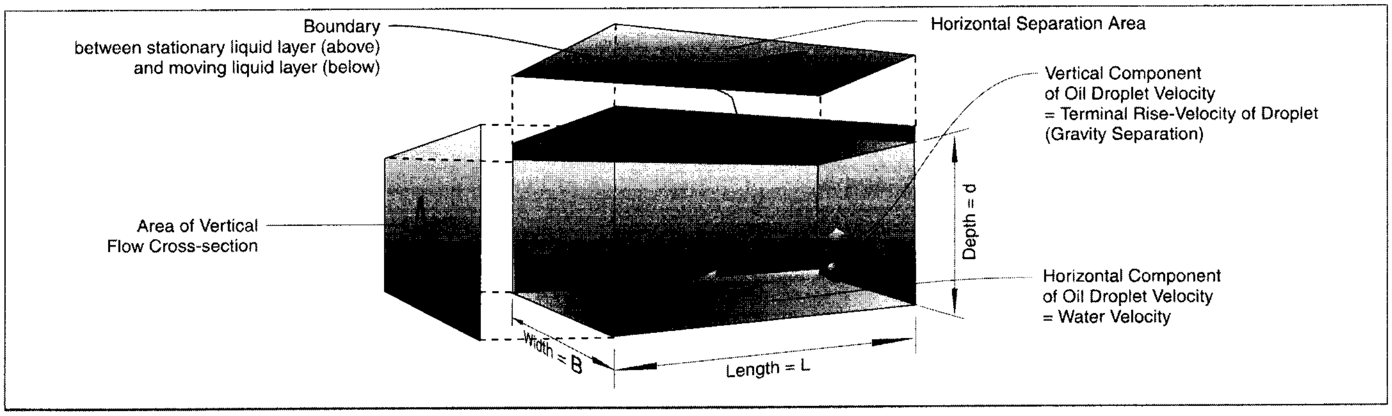


Figure 3 Model of a flow-through gravity separation process

Rating and Sizing Separators

Selecting an appropriate performance

In order to size a separator it is first necessary to know what kind of performance is necessary. The performance of a separator is measured in terms of the rise-rate of the slowest rising droplet the separator is certain to remove from water flowing at the separator's maximum operating flow-rate (or design flow-rate). This value is known as the *critical rise-rate* of the separator. See the section entitled, 'Understanding Separator Performance', for more information on this.

Determining the *design flow-rate*

The *design flow-rate* is the maximum *operating* flow-rate for the separator. In runoff applications, the flow-rate through a separator can be expected to vary over time. It is common therefore to design the separator for the maximum possible flow-rate. But this is not necessarily appropriate. If the main source of water is from washdown processes, the maximum flow-rate can be equated to the maximum water supply rate. If the main source of water is from rainfall, this cannot be done directly.

Stormwater Runoff

The most convenient method (known as the *rational method*), for calculating flow-rates of storm runoff from small areas uses the following simple equation.

$$Q = C\,i\,A$$

Q is the flow-rate

C is a dimensionless factor that accounts for the permeability and roughness of the surfaces (taken as 0.9 for paved areas)

i is the *design* rainfall intensity (usually expressed as inches per hour

A is the area of the site exposed to rainfall.

Note:

The design rainfall intensity value is carefully selected on the basis of local rainfall data (including times of concentration etc.) and also on the basis of providing the optimal economic design. A common method is to choose a rainfall intensity that would allow treatment of 90% or 95% of all the water leaving the site.

Because it is costly to treat large flows of water, it is recommended that only those areas that are at risk of contamination from oil and grease should be allowed to drain through the separator. Water quality devices are often designed for flow-rates substantially less than the flow-rates assumed for rest of the conveyancing system. It is seldom necessary (or feasible) to treat all of the water from very high intensity rainstorms. This is especially valid in areas where the majority of pollutants are transported during the *first flush*. Large water flows may be either detained upstream of the oil-water separator or allowed to by-pass it using suitable flow-splitting and recombination structures. Local guidelines for sizing should be consulted in any case.

Example:

Determine the design flow-rate for a separator on the basis of a one-hour, half-inch design rainfall intensity on a half-acre paved area:

$$\text{Paved Area} \Rightarrow C = 0.9$$

$$i = 0.5\text{ in.}/\text{hr} = \frac{0.5}{12\cdot 60}\text{ ft/min} = 0.000694\text{ ft/min.}$$

$$A = 0.5\text{ acres} = (0.5)\cdot(43560)\text{ sq. feet} = 21780\text{ sq. feet}$$

$$\therefore\ Q = (0.9)\cdot(0.000694)\cdot(21780)\text{ cubic feet / min}$$

$$= 13.61\text{ CFM}$$

$$1\text{ Cubic Foot} = 7.48\text{ gallons}$$

$$\therefore\ Q = (13.61)\cdot(7.48)\text{ GPM}$$

$$= 102\text{ GPM}$$

Determining the effective horizontal separation area required

Once suitable values for design flow-rate and critical rise-rate have been selected, it is easy to calculate the effective horizontal separation required. Just divide the first by the second (making sure that their units are compatible first) as follows:

Example:

What is the effective separation area required to ensure the removal of droplets with rise-rates of 0.033 feet/minute and greater at a flow-rate of 100 gpm?

Solution:

$$\text{Design flow-rate} = 100\text{ gpm} = 13.37\text{ cfm} = 13.37\ \frac{\text{feet}^3}{\text{minute}}$$

$$\text{Critical rise-rate} = 0.033\ \frac{\text{feet}}{\text{minute}}$$

$$\text{Effective horizontal separation area} = \frac{\text{design flow-rate}}{\text{critical rise-rate}}$$

$$\frac{13.37\ \text{feet}^3/\cancel{\text{minute}}}{0.033\ \text{feet}/\cancel{\text{minute}}}$$

$$= 405\ \text{feet}^2$$

In this example over 400 square feet of effective separation area is required to provide a separator with a design rise-rate of 0.033 feet / minute[†]. This implies that if a traditional retention vessel or pond is to be used, its area on plan will have to be of the order of 400 square feet. If it is not possible to properly control circulation (non-uniform distribution of flow through the unit), its area may have to be increased to more than five hundred square feet to make up for resulting inefficiencies. The other option is to use an efficient coalescing-plate oil-water separator.

Horizontal separation area of simple retention tanks and ponds

In traditional retention-tank systems, ponds and clarifies, the horizontal separation area is closely related to the area of the separation chamber measured on plan as shown in Figure 4. The flow through a retention tank is often not uniform and a design factor is usually necessary (See *Hazen's Principle of surface loading* – page 5). Baffles and vertical flow distributors may be included in the design of such units to limit turbulence and non-uniform flow distribution.

Note: vertical plates used for this purpose do not add to the amount of separation area in a separator chamber. Separation area can only be provided by continuous boundaries that project horizontally across the separator chamber.

Horizontal separation area of a coalescing-plate separator

In a coalescing plate separator the entire cross-section of flow through the separation chamber is divided into many thin water layers by horizontally extending plates. Each one of these layers acts like an individual separation chamber. The separation area of each of these layers is the same as the plan-area[†] of each plate as shown in Figure 5.

The easiest way to calculate the total area is to determine the *horizontal separation-area density* of the plate-stack first. This is the amount of horizontal area (square feet) found in one cubic foot of stack. If the average vertical spacing of the plates, s_p is known in inches –see figure 6– the horizontal separation-area density, a_H, can be found using the following rule:

$$a_H = \begin{array}{c}\text{Separation}\\\text{Area}\\\text{density}\end{array} = \begin{array}{c}\text{Horizontal area}\\\text{(square feet)}\\\text{in 1 cubic foot}\end{array} = \frac{12}{s_p}$$

The overall horizontal area, A_H is then found by measuring the total volume (based on its gross dimensions –see Figure 7) of the submerged plate-stack and multiplying it by a_H :

$$A_H = V_{gross} \cdot a_H = (B \cdot L \cdot H) \cdot a_H$$

In addition to providing a very large amount of horizontal separation area in a small volume, coalescing plate-stacks, when properly positioned, promote more evenly distributed flow throughout a flow chamber. It is usually assumed that the effective horizontal area provided by coalescing plates is simply the sum of their plan-areas (or projected areas). In other words, a value of 1.0 is assumed for the design factor, "F" (as explained on page 4).

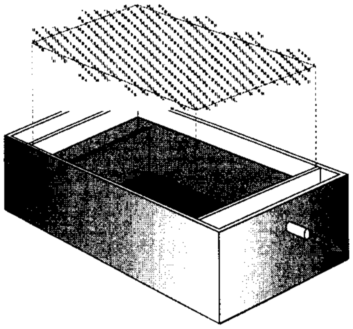


Figure 4 The horizontal separation area provided by a simple retention tank (baffle-type) separator.

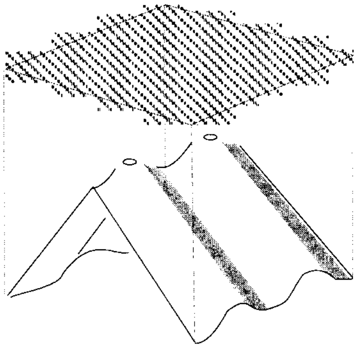


Figure 5 The horizontal separation area provided by an inclined and corrugated plate

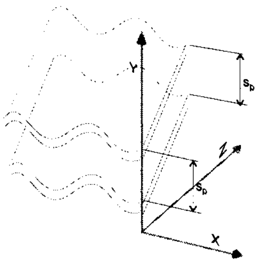


Figure 6 The vertical spacing of an inclined coalescing-plates

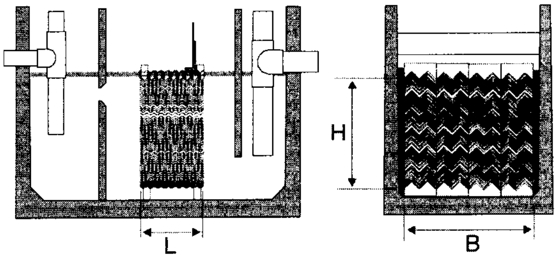


Figure 7 Gross dimensions of a stack of coalescing plates

[†] Inclinations and corrugations give strength and rigidity to coalescing plates and make them easier to maintain. However, while the plates themselves are neither flat nor horizontal, fluid continuity and the incompressibility of water means that each one still creates a horizontal separation area equivalent to the parallel-projection of its undersurface area onto a horizontal plane (its area "on plan").

Stokes' Law

Determining Critical Rise-rates

It is not always necessary to do a Stokes' law calculation in order to size a gravity separator or rate its performance. Appropriate *critical rise-rate* values may be obtained directly by experiment. Alternatively, if specific data about the likely oil-water mixtures entering the separator are unavailable, recommended values may be used. Experience and analysis can also determine the value chosen. Remember that the final choice of *critical rise-rate* assumed for any design will not only determine the ultimate effectiveness of the separator, but also its size and cost –especially when flow-rates through the separator are expected to be substantial.

It is common to actually list oil characteristics (such as density, droplet size etc.) when defining the performance of a separator. This would seem a practical approach except that many more variables controlling separator performance now need to be quoted with them (e.g. water viscosity and critical droplet size). Unless *all* of these values are provided, the separator *cannot* be assessed for performance. When they are provided, the equation known as Stokes' law can used to convert these variables into a *critical rise-rate* value. This value is the same regardless of the oil-water mixture characteristics. It is the value you can use to compare any two gravity separators.

Stokes' Law

The following equation, often referred to as Stokes' law, can be used to accurately calculate the rise-rate ('terminal rise velocity') of a droplet of oil of known density in water of known viscosity:

$$V_T = \frac{g \cdot (\rho_w - \rho_o) \cdot d^2}{18\,\mu}$$

The symbols used in the equation represent values as follows:

V_T = the rise-rate (or 'terminal velocity') of the oil-droplet (cm/s or ft/sec)
g = the acceleration due to gravity (in cm/s^2 or ft/sec^2)
r_O = the density of oil (g/cm^3 or lbm/ft^3)
r_W = the density of the water (g/cm^3 or lbm/ft^3)
d = the droplet diameter (in cm or ft)
m is the absolute viscosity of the water (g/cm.sec or lbm/ft-sec).

Note: *Metric units have also been given here because they are commonly used for Stokes' law calculations. You can use either metric (CGS) units or customary (FPS) units (but not both at the same time!).*

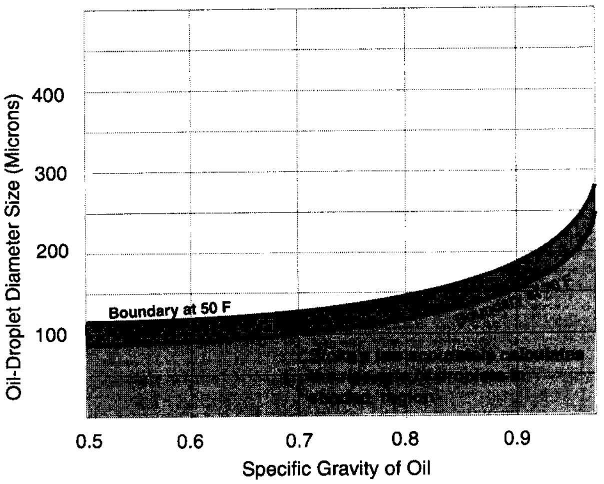


Figure 8: The curves represent the boundaries (for water 50 °F and 70 °F) below which Stokes' law is known to predict droplet rise-rate with negligible error.

How accurate is Stokes' Law?

Stokes' law is derived from Newton's laws of particle and fluid mechanics and it applies only to objects rising or falling in a fluid under certain conditions known as *Stokes' flow conditions*. These conditions are that the object must be spherical in shape, and sufficiently small and slow-moving so that microscopic turbulence and "boundary layer" effects do not come into play in the vicinity of the rising or falling object.

Fortunately, Stokes' law is almost perfectly suited to the design of most gravity oil-water separators. This is true for two reasons. First, because of oil's natural hydrophobicity and the phenomenon of surface tension, small droplets of oil *are* spherical in shape. Second, although there may exist a significant portion of larger droplets for which *Stokes' flow conditions* will not be satisfied as they rise, the smaller oil droplets <u>that are most critical to separator performance</u> nearly always lie within that range for which Stokes' law is known to be accurate (as illustrated in Figure 8 above).

Stokes' law will only be useful in predicting the rise-rates of droplets rising in still water or where the flow regime is *laminar*. Laminar flow is where the water moves as 'layers' with no vertical mixing, circulation or *turbulence*. The idea is simple. The droplet must be able to rise vertically –from 'layer' to 'layer' without interference. Turbulence and eddying simply undo the process of separation. Laminar flow is a prerequisite for any gravity separation process.

In summary, if the oil-droplet in question is within the range of sizes and densities shown in the shaded portion of the graph in Figure 8, and the flow regime is *laminar*, Stokes' law is accurate and reliable.

Stokes' Law - continued

Using Stokes' Law

Stokes' law is an equation of four variables. To calculate the rise-rate of an oil-droplet, all you need to do is plug in appropriate values for each of the four variables on the right-hand side of the equation: the density of the oil, the density of the water, the diameter of the oil droplet (which we know to be a sphere) and the absolute viscosity of the water. Care needs to be taken to ensure correct values are chosen for each of these using the correct units.

Viscosity:

The value for viscosity used in this version of Stokes' law is the *absolute viscosity* of the water. This is measured in poise, centipoise, g/cm.s (grams per centimeter-second), Pa.s (Pascal seconds) or lbm/ft-sec. Be careful with values given which are described as "kinematic viscosities" (measured in Stokes, centiStokes or slugs). These must be converted to the appropriate "absolute viscosity" value before this version of the Stokes' law equation can be used.

Values for the viscosity of water may be taken from Table 1 for most conditions. Notice how the viscosity of water changes dramatically with temperature. At higher temperatures, water becomes less viscous and therefore provides less resistance to the motion of particles - so that they separate more easily.

Temperature °F	Temperature °C	Absolute Viscosity Poise (=g/cm.s)	Correction factor for use with Figure 9
40	4.4	0.0155	0.85
45	7.2	0.0143	0.92
50	10.0	0.0132	1.00
55	12.8	0.0122	1.08
60	15.6	0.0113	1.16
65	18.3	0.0106	1.25
70	21.1	0.0099	1.33

Table 1: Relationship between viscosity and temperature of water

Shortcut method:

Figure 9 below was derived using Stokes' law. It may be used to estimate the rise-rate of a droplet of oil of a given size and density when the water is at a temperature of 50° F. For temperatures other than 50° F, the correct rise-rate value can be obtained by multiplying values taken from Figure 9 by the appropriate correction factor given in Table 1 (above).

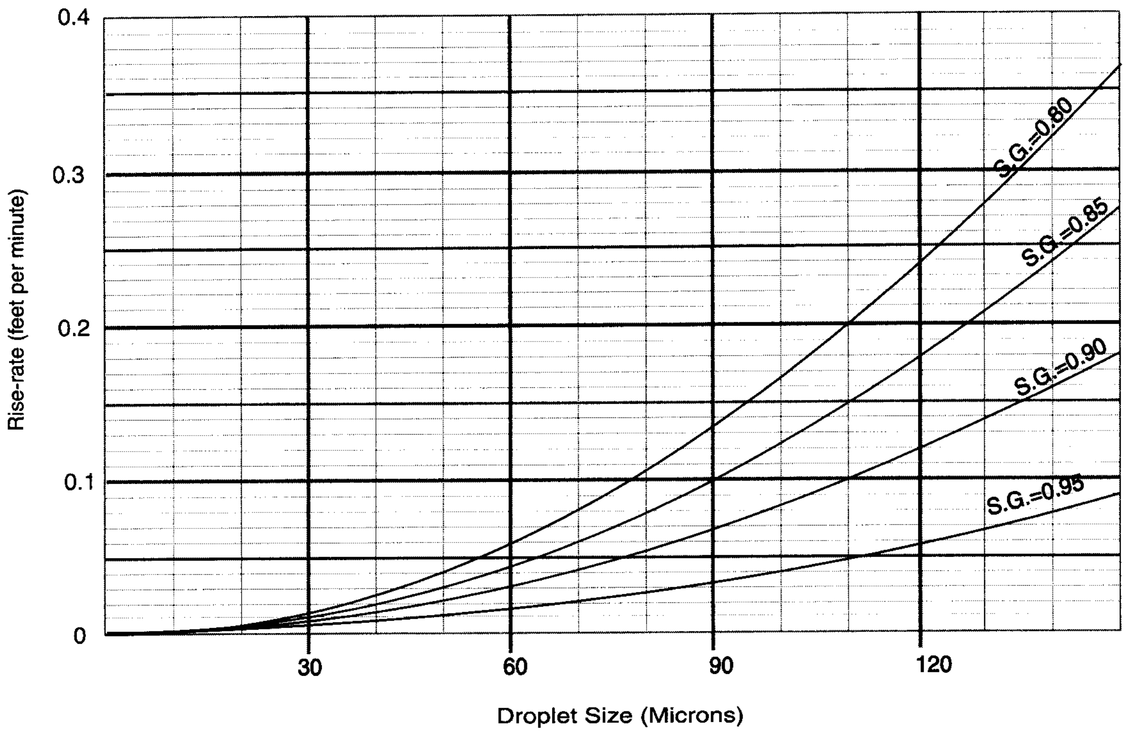


Figure 9: Rise-rate versus droplet size for oil-droplets of various specific gravities in water at 50 ° F

Example Calculations

Example 1

Calculate the rise-rate of a 60 micron droplet of oil that has a specific gravity of 0.888 in water at a temperature of 50 °F.

Solution:

$$d = 60 \text{ Microns} = 60\ \mu\text{m} = \frac{60}{(1000)(25.4)(12)} = 1.97 \times 10^{-4} \text{ feet}$$

Temperature = 50 °F

The viscosity of water is related to temperature. Table 1 (page 9), tells us that at 50 °F

Viscosity = 0.0132 poise

For Stokes' law we need to use compatible units

Since 14.882 poise = 1 lbm/ft-sec:

$$\mu = \frac{0.0132}{14.882} \text{ lbm/ft-sec.} = 8.87 \times 10^{-4} \text{ lbm / ft-sec}$$

Density of water = 62.4 lbm / ft^3 (= ρ_w)

Specific gravity of oil = 0.888

$$\text{Density of oil} = (0.888)(62.4) \text{ lbm / ft}^3$$
$$= 55.4 \text{ lbm / ft}^3 \ (= \rho_o)$$

Acceleration to gravity:

$$g = 32.2 \text{ ft / sec}^2$$

$$\text{Stoke's law:} \quad V_T = \frac{g(\rho_w - \rho_o)d^2}{18\mu}$$

$$\therefore V_T = \frac{(32.2)(62.4 - 55.4)(1.97 \times 10^{-4})^2}{(18)(8.87 \times 10^{-4})} \text{ ft / sec}$$

$$= 0.00055 \text{ ft / sec}$$

Example 2

Calculate the effective horizontal separation area required to capture all droplets with terminal velocities greater than or equal to that of a 60 micron droplet of 0.888 specific gravity oil in water at a temperature of 50 °F, flowing at 100 gallons per minute.

Solution:

In example 1, we already calculated the terminal rise velocity of this oil-droplet / water combination according to Stokes' law

$$V_T = 0.00055 \text{ ft / sec.}$$
$$= (0.00055)(60) \text{ ft / min.}$$
$$= 0.033 \text{ ft / min.}$$

Q = 100 gallons per minute

(1 cubic foot = 7.48 gallons)

$$\therefore Q = \frac{100}{7.48} \text{ ft}^3\text{/ min}$$
$$= 13.37 \text{ ft}^3\text{/ min}$$

Effective horizontal separation area required

$$A_H = \frac{Q}{V_T} = \frac{13.37}{0.033} = 405.2 \text{ ft}^2$$

Example 3

Size a suitable rectangular cross-sectioned retention tank (API oil-water separator) for a *critical rise-rate of 0.033 feet/min at its operating flow-rate of 100 gallons per minute. What size circular unit would be required to provide the same separation effectiveness?*

We will assume 20% inefficiency due to non-uniform flow distribution (short circuiting), turbulence etc.
In other words, we will use a design factor of 1.2[†]

$$\text{Effective horizontal separation area} = \frac{\text{Actual horizontal area provided}}{1.2}$$

$$\text{Require a plan-area} = 1.2 \frac{Q}{V_T}$$

$$\text{In example 2, we found } \frac{Q}{V_T} = 405.2 \text{ ft}^2$$

Actual plan area of separation chamber required

$$= (1.2)(405.2) \text{ ft}^2 = 486.3 \text{ ft}^2$$

Inside width of retention tank = 8 feet

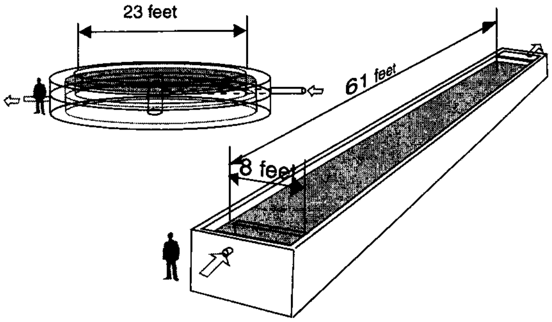
$$\therefore \text{Length required (at least)} = \frac{486.3}{8} \text{ feet} = 60.8 \text{ feet}$$

A circular unit (with central inlet and level perimeter discharge) can be assumed not to have any significant inefficiencies, because the flow is uniform radial.

The unit will have a circular inlet chamber at its center with a diameter (d in equation below) of approximately 2 feet which must be included when calculating the area of the circular chamber:

$$\text{Diameter required} = \sqrt{\frac{4}{\pi}\left(A + \frac{\pi d^2}{4}\right)}$$
$$= \sqrt{\frac{4}{\pi}\left(405.2 + \frac{\pi(2^2)}{4}\right)}$$
$$= 22.8 \text{ feet}$$

Clearly both of these approaches involve the creation of very large structures:

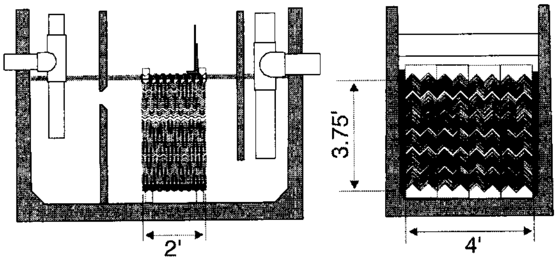


[†] This is similar to the design approach for this type of separator recommended by the American Petroleum Institute (Publication 421, 1990)

Example Calculations (continued)

Example 4

Check if the following Oldcastle separator is adequate for the same performance requirements of example 3 (Vertical plate spacing = 18.5 per vertical foot).



Solution:

Plate spacing: 18.5 / vertical foot

Vertical spacing between plate centers = $\frac{12}{18.5}$ = 0.649 in.

Horizontal area density = a_H = $\frac{12}{0.649}$ ft^2 per cubic foot of stack

= 18.5 ft^2 per cubic foot of stack

(This rule was given on page 7)

Notice how the number of plates per vertical foot is numerically identical to the horizontal area density in square feet per cubic foot. This is always the case (So it is not really necessary to do this calculation).

Total horizontal separation area

$= (18.5\ ft^2/ft^3_{stack})(4\ ft_{stack})(2\ ft_{stack})(3.75\ ft_{stack}) = 555\ ft^2$

$\therefore$ This separator exceeds the performance requirements

Additional margin of performance provided = $\frac{555 - 405.2}{405.2}$

= 36.9 %

Example 5

What is the design rise-rate of the Oldcastle separator in Example 4 at 100 gallons per minute? What size oil-droplet does this correspond to (oil specific gravity = 0.888, water temperature = 50 °F)? What is the maximum flow-rate that can be put through this separator for a design rise-rate of 0.033 ft/min.?

Solution:

Critical rise-rate = V_T = $\frac{Q}{A_H} = \frac{13.37}{555}$ ft / min.

= 0.024 ft / min

= 0.0004 ft / sec.

To calculate the size droplet to which this corresponds, we rearrange the Stokes' Law equation (see example 1):

$$d = \sqrt{\frac{18\,\mu\,V_T}{g(\rho_w - \rho_o)}} = \sqrt{\frac{(18)\,(8.87 \times 10^{-4})(0.0004)}{(32.2)(62.4 - 55.4)}} \text{ feet}$$

$= 1.68 \times 10^{-4}$ feet = 51.3 microns

Example 5 (continued)

For a critical rise rate, V_T, of 0.033 ft / min.

Maximum flow-rate, $Q = V_T \cdot A_H$ = (0.033 ft / min)(555 ft^2)

= 18.32 ft^3/ min

= (18.32)(7.48) GPM

= 137 GPM

Example 6

If the concentration of oil entering the separator was known to be 250 mg / liter and information about the droplet size distribution of the oil entering the separator revealed that typically 2% of the oil by volume in Example 1 is less than 60 microns, what would be the concentration of oil in the effluent from a separator operating to provide a design rise-rate of 0.033 ft / min.?

Solution:

At 50° F (0.888 s.g. oil), a separator operating to provide a design rise-rate of 0.033 feet per minute removes all droplets >60 microns in diameter

$\Rightarrow$ Fraction of original volume not removed < 2 %

$\Rightarrow$ Concentration of oil in effluent < (250 mg / liter)(0.02)

$\Rightarrow$ Concentration of oil in effluent < 5 mg / liter

With the limited information given, we can only use an inequality expression (i.e. one with '<') to describe the effluent concentration.

Installation

Planning for site-drainage and oil-water separator location

The Drainage Plan

Careful planning of paved areas and their drainage can significantly contribute to successful control of pollutants. See figure 10. Consider the following:

- *Vehicles, equipment and storage vessels and activities that pose a risk of oil-discharge should be limited to a single location if possible*
- *Drainage from roofs and green areas that are unlikely to have the same pollution problems should be routed separately* – This reduces flow-rates and treatment costs for contaminated water.
- *If occasional excessive flows of water are unavoidable, allow for by-passing of excess water to prevent flows from exceeding the maximum surge capacity of the separator unit and other treatment system components* – By-passing can be achieved with the help of detention structures and limited surface flooding as illustrated in Figure 13. Alternatively a flow-diversion and recombination structure can be constructed. Your local Oldcastle manufacturer may be able to provide a custom solution for you, such as a separator with integrated by-passing features, as illustrated in Figure 11.

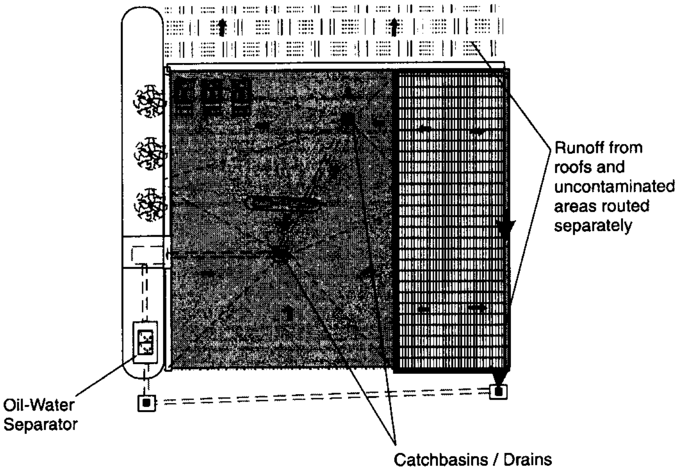


Figure 10: Example of site-drainage plan for runoff treatment (The area shaded in grey is identified where runoff from the pavement has the potential to be contaminated).

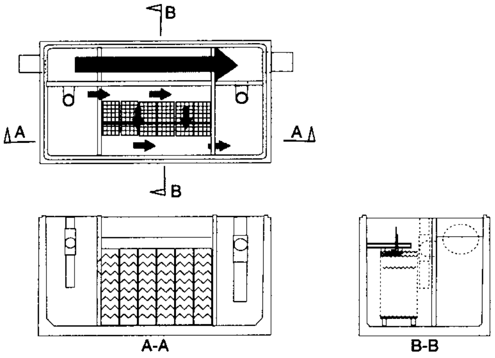


Figure 11: Oldcastle Separator with integrated by-pass.

Location of separator

When planning a suitable location for the oil-water separator, keep the following in mind

- *The top of the separator should be located at a ridge or crown in the pavement* – Risers can be provided to create tops to any grade level desired (See Figure 12).
- *When planning for on-site detention (controlled, limited flooding), the flow constriction must be placed upstream of the oil-water separator* – Do not position flow-constriction devices downstream of the separator or plan for any backup of flow in the separator chamber (See Figure 13.)
- *Make sure that there is room for access by maintenance vehicles to the separator* – To enable convenient, regular maintenance as necessary
- *Locate the separator where it may be conveniently accessed by personnel* – Where it is unlikely to become permanently covered by stored materials, vehicles or machinery

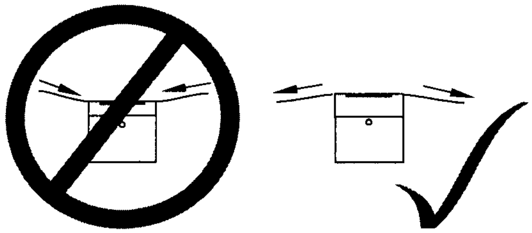


Figure12: Locate the separator at a crown in the pavement.

Planning the Installation of separator

Oldcastle oil water separators require the same care with installation as any similar reinforced-concrete environmental structure. Contact your local Oldcastle representative for specific guidelines and equipment required to install a particular model. In any case, you should comply with applicable codes and regulations. Things to plan ahead for are:

. *Excavation*
  – In deep excavations, it is important that the excavation is kept properly shored. Clearance is required to allow for projecting pipe fittings as well as the concrete vault (See figure14).

. *Proper bedding preparation*
  –The installed separator unit must ultimately be supported by undisturbed or well-compacted soil that is unlikely to settle significantly. Care needs to be taken to ensure that the bedding material is properly screeded and compacted to provide a firm, level foundation for separator vault.

. *Use of proper lifting equipment*
  –Smaller Oldcastle units are installed by boom truck operators from your local Oldcastle Precast manufacturing facility. Larger sizes will require a crane to lower the unit in place.

. *Correct positioning of vault with respect to incoming and outgoing pipes*
  – Your Oldcastle Precast representative can advise you on suitable pipe-sizes and arrangements

. *Correct placement of gaskets between vault base, top-section and riser-sections*
  – Your local Oldcastle Precast manufacturer can recommend a durable, water- and oil-tight joint if necessary for your application. Special care needs to be taken in areas that are prone to high water-tables to prevent infiltration of water into the separator chamber. The joint between riser sections in a concrete vault must be clean before application of any gasket. Gaskets must be resistant to oil and hydrocarbon compounds. Check with the manufacturer to ensure that the gasket is suitable for the application. Ask your Oldcastle representative for advice in mounting gaskets between concrete sections.

. *Even backfilling before filling with water*

. *Protection of internal components during construction work on the surface*
  –During site construction work, sediments and debris should be kept out of the separator

. *Sealing of pipe connections at all points in the drainage system*
  Durable, non-corrosive water-tight seals are essential to the functioning of separators. Some special guidelines are given overleaf.

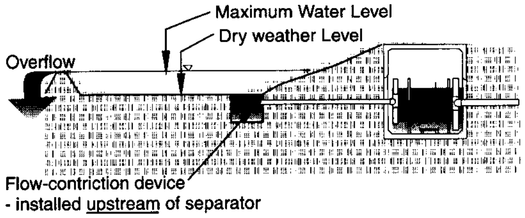


Figure 13: Surface detention to control flow-rates

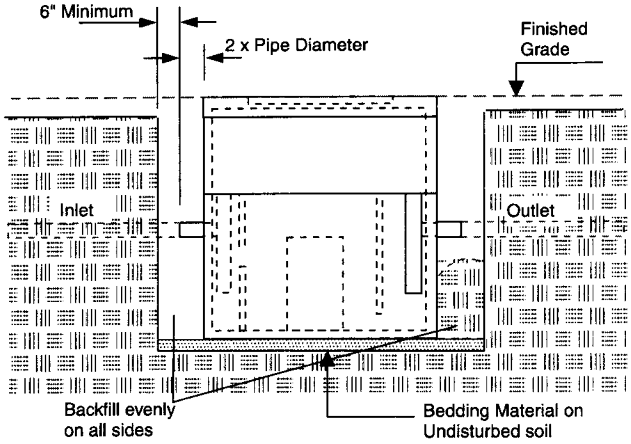


Figure 14: Planning separator installation

Installation (continued)

Connection of Pipe fittings:

Pipe fittings for oil-water separators must be oil- and water- tight. Where possible, Oldcastle Precast prefers to ship separators with tee-sections and pipes already installed and sealed, so that all the owner or contractor has to do is provide the external coupling to the outside drainage system. Occasions do arise, however, when it is necessary to leave the installation of pipes until after the unit has been installed. In this case the separator is shipped with cored or cast-in holes. In this case, it is the responsibility of the customer or contractor to provide an adequate seal that is both durable and flexible enough to function properly for the full range of allowed construction tolerances. Ask your local Oldcastle Precast representative for advice on this issue.

Pipe to Wall Seals

When installing pipes and tees into the separator vault, it is important to provide a good seal to reduce risks of liquid in-flow or out-flow at the pipe-wall seal. There are variety of methods for insuring a durable, well-sealed connection. Figure 15 shows two suitable ways to do it. Whatever method used, the integrity and durability of the seal depends on the quality of preparation, workmanship, the durability of the materials used as well as the provision of a rigid foundation under the vault-structure and piping.

Pipe-to-Pipe Seals

See Figure 16. Most pipe manufacturers have their own recommendations for how best to achieve pipe-to-pipe seals. Again, the key to achieving a good durable seal lies with the quality of surface preparation, workmanship, the durability of materials used and the provision of proper bedding material for the vault-structure and pipes. When you use proprietary methods, check with the manufacturer to make sure that the seal is durable and can withstand hydrocarbons and water. Follow the pipe-manufacturers instructions when using proprietary products.

Tees and Pipe-extensions inside vault

The tee-sections and pipe extensions play important roles in the functioning of the separator. They allow proper venting of incoming flow and controlled turbulence dissipation in the inlet chamber as well as providing additional containment for oil that becomes trapped in the separator. It is important, therefore, that they are attached using properly sealed, bonded (or mechanically joined) connections just like the external pipe fitting connections. They must be installed so that they extend to the correct elevations, providing sufficient freeboard and baffling of water flowing out of the separator. See Figure 17

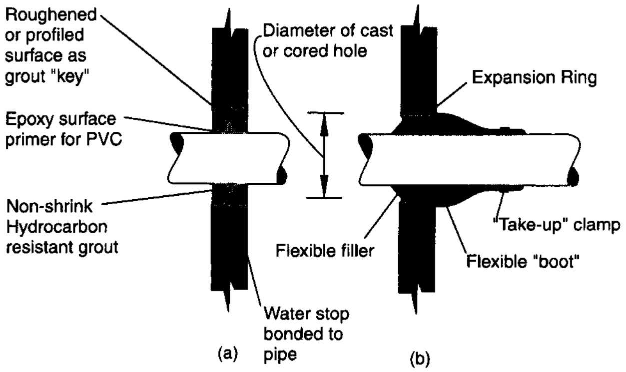


Figure 15: Typical pipe-wall seals for PVC pipe: (a) using a non-shrink grout and (b) using a proprietary "boot" system. In both cases careful preparation of surfaces of pipes and concrete and the choice of suitable adhesives and primers for each material is essential to the creation of a good seal.

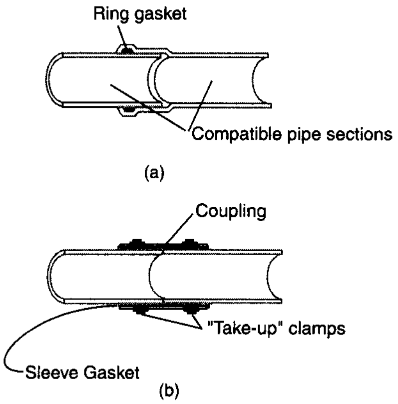


Figure 16: Pipe to pipe seals outside separator and for connecting internal "tees" and extensions: (a) using proprietary 'bell' ends or pipes and (b) a typical sleeve coupling arrangement.

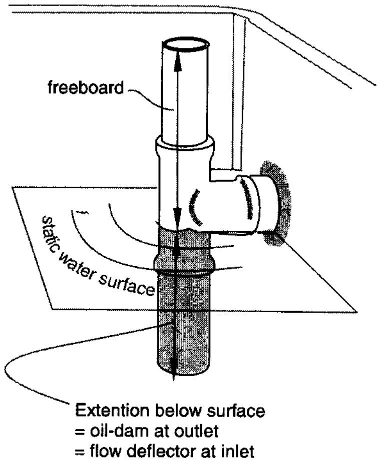


Figure 17: Tee-sections required at inlet and outlet

Operation and Maintenance

Note on Safety

Always exercise caution when dealing with underground installations, oil and other hazardous substances. The details of all necessary safety precautions cannot be covered in detail here. Remember, however, that the following may be necessary:

- *Precautions when handling oils and other substances* – Some oils are potentially hazardous substances
- *Fire-prevention measures around oil*
- *Measures to avoid accidents when inspecting or entering underground installations* – Seek advice from a health and safety expert if you are in doubt about correct safety procedures
- *Compliance with local, state and federal safety regulations*

Role and function of a separator

Oldcastle's oil-water separator may be thought of simply as a highly efficient gravity-separation device, that is capable of removing extremely small droplets of oil that would otherwise be carried on through the drainage system. The separator does not destroy the oil or other pollutants it captures. It traps and provides temporary storage for them.

The use of an oil-water separator is recognized by the EPA, state and local environmental agencies as a Best Management Practice (BMP). The separator will serve its purpose best when seen as a component of a larger strategy to protect runoff water quality. An oil-water separator is a part of the site drainage system and will only do its job well if the other parts (i.e. catchbasins, grit-chambers, pipes etc.) are performing their functions properly too.

Though a separator for the most part requires little human intervention to work, it does need periodic inspection, cleaning and preventive maintenance. The amount of maintenance required will vary with each application. It is the responsibility of the separator owner to ensure that his separator inspection and maintenance plan suits the application requirements and that this plan is properly carried through. The owner can reduce maintenance costs by making changes to work practices that generate excessive quantities of sediments and oil releases.

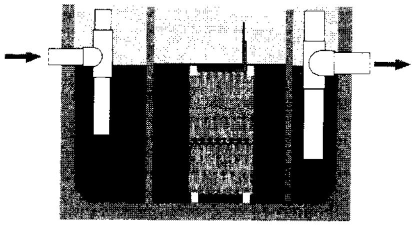


Fig 19: Gravity (or buoyancy) causes droplets of oil dispersed in the water to rise up and separate from water. The film of oil that develops on the surface must be removed periodically.

Inspection

Regular inspection is the key to ensuring that an oil-water separator does its job well. The internals of Oldcastle's separators are easily viewed simply by opening the large access doors and looking inside. Doing so, in most cases, takes only a minute.

The inspection frequency required for separators varies from application to application. It depends on the quantities of oil released at the site. During the first few months of operation, it is advisable to inspect the separator once a week to determine the rate of accumulation of solid material and oil in the unit. If the activity on the paved area which drains through the separator is fairly consistent, then the frequency of inspection can be reduced to as little as once every three months.

1. Oil Buildup
   Measure the thickness of the layer of oil that has built up on the surface of the separator. It should be removed before it reaches a depth of two inches.
2. Solids Accumulation
   Use a long pole to determine sludge build-up on the bottom – judged by the resistance felt when you attempt to push the pole to the bottom of the separator chamber. If more than six inches of sludge has accumulated at the bottom of the unit, it requires cleaning out.
3. Presence of debris and floatable materials in the inlet chamber
   The inlet chamber must be kept clear. This chamber and its openings are important for dissipating turbulence and distributing the flow of water through the separator. The inlet chamber also acts as a last line of defense for the separator against heavy grit, floating and settling debris. Excessive amounts of these in the separator is an indication of problems with the system upstream that should screen out these materials.
4. Water Level in the unit
   Check that the water level has not risen excessively inside the unit. The water level inside the separator should never rise more than twelve inches above its standing level (unless the separator has been designed to allow for additional *freeboard*). The static water level should be the same as the level of the invert of the outlet pipe (or outlet weir – if one is present). An excessive rise in water level during operation is an indication of blockage either downstream of the separator or within the coalescing plates themselves.
5. The Whole System
   Inspect catch-basins, other units and drained areas upstream of separator. The level of the top of solid material in the base of grit chambers and catchbasins should be well below the level of the *invert* of the pipe leaving the catch basin. Make sure that paved

Operation and maintenance (continued)

Inspection (continued)

areas draining to the catchbasins are free of large quantities of sand and dirt and other materials that could interfere with the system such as detergents, solvents, and antifreeze agents. These substances cause oils to become more thoroughly mixed with water so that greater quantities of the oil are dispersed as extremely small droplets (< 10 Microns), emulsions and even solutions. While in this state, oils have little tendency to separate.

Servicing and Maintenance

Periodic cleaning and preventive maintenance is essential to the proper functioning of oil-water separators.

Oil Removal from the surface

Oil that is removed from a separator should be stored separately as a potentially hazardous material. If possible, store it safely with other used oils and recycle it. Oil can be removed from the surface of the water in oil-water separators by a number of means:

. *Wet vacuuming*
This is the quickest and most convenient method for frequent oil-removal from a separator. Most industrial wet/dry vacuum cleaners are suitable for this. Entry into the separator is not necessary and special extensions and skimming attachments are available for doing this job.

. *Using skimming devices*
Many skimmer devices are available that have low energy requirements. The simplest is a rope or belt skimmer where an adsorbent belt (or looped rope) is fed continuously through the oil/water surface in the separator. Skimmers are useful only in situations where there is constant oil-buildup in the separator. They are slow and require frequent inspection and maintenance.

. *Bulk pumping of the entire separator contents*
In some cases (especially after an accidental bulk spill of oil), it is best to obtain the services of a professional tank cleaning company, who usually removes a separator's entire contents (oil, water and solids) using special vacuum trucks. This material is then delivered to a licensed treatment facility where the oils, solids and classifiable materials can be extracted and recycled or safely stored.

Solids Removal from separator chambers
Bulk pumping of sludge that collects at the bottom of the oil water separator is recommended if the level of solids buildup inside the separator chamber exceeds six inches. This is best achieved using the services of a professional tank cleaning company. This type of cleaning should not be expected to be necessary more than once a year. If excessive sludge buildup is a problem, it may be due to problems with catchbasins and grit-chambers upstream of the separator

Maintaining the coalescing plates

The coalescing plates in an Oldcastle separator are designed to operate for long periods without requiring maintenance. Inclinations and channels in the plate stacks enable solid particles to settle out of the system and oil to gradually flow to the water surface.

In the event of the separator receiving a heavy silt load, it may be necessary to clear the plate-stacks of this material with a hose (high-pressure if necessary). This can be accomplished without moving the plate-stacks. It is not necessary to completely clean the plates in order for them to work properly.

Removing and Installing Coalescing-Plates
Sometimes it is desirable to completely remove the plate-stacks for closer inspection of the chamber or intensive maintenance if nuisance substances were introduced into the separator or if the plates become damaged. The plate-stacks Oldcastle uses are modular and may be lifted easily through the separator access doors. Take care to ensure that they are replaced correctly with the proper components securing them in place in their correct positions like those shown in Figure 19 below.

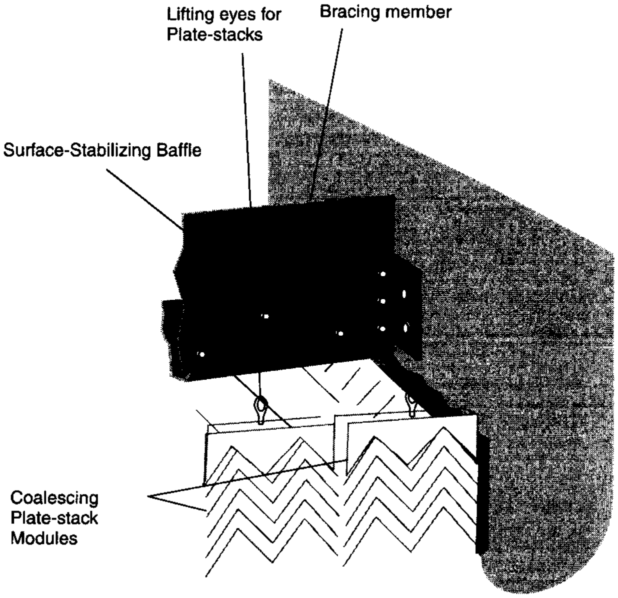


Figure 19: Internal components need to be properly positioned in the separation chamber

10 essentials
for a successful and cost-effective
oil-pollution prevention plan
for surface runoff from your site

1. **Start now** —Don't wait until a neighbor or environmental official raises their concerns with you. Investigate your work practices. As time goes on people are becoming less and less tolerant of avoidable runoff pollution and penalties for non-compliance are becoming more and more severe.

2. **Install an oil-water separator**
—which provides reliable, measurable performance, maintainability and durability

3. **Create a contingency plan for dealing with small and large releases of oils and polluting substances**
— You can start by looking up local tank-cleaning companies and enquiring about their services and how quickly they can respond. When a spill or accident occurs that poses a potentially hazardous situation, **your priority is to minimize damage**. Implement a suitable cleanup procedure promptly and document the incident. Chances are you will have completely averted the risk of any serious environmental damage. Instead of seeing the incident as a "disaster", take pride in the success of your contingency clean-up plan.

4. **Get tough on all liquids and materials that could be carried into your drainage system** —Maintain a clean shop. Keep litter, sand, soil, etc. off paved areas. Also, keep a close watch for the following liquids that can damage the functioning of an oil-water separator: **antifreeze agents, degreasers, detergents, alcohols and solvents.**

5. **Pay attention to your oil-water separator <u>and the rest of the drainage system</u> and clean and maintain it promptly when necessary** —Inspect your oil-water separator regularly (it should only take a minute). Also check your catchbasins and other structures. Find the safest, most convenient method you can use to clean them out as needed.

6. **Service your drainage system promptly** —Do not wait until the system is full of oil or solids. Oil should be removed before it reaches a level of 2 inches. Do not use a separator or any other part of the drainage system as a receptacle for used oil. Do not leave the separator or other parts of the drainage system full of large quantities of oil for long periods of time[†].

7. **Store used oil and oil removed from separator together in a safe, well contained location for hazardous wastes and have it sent to a licensed recycling facility** —In parts of the country, people are profiting from the sale of waste oil. There may be similar opportunities in your area.

8. **Inspect your machinery and liquid storage regularly and undertake preventive measures for early detection and prevention of leaks from corroded or worn parts** —Preventive maintenance of your vehicles' equipment saves you money by reducing costly repairs and downtime. It also reduces the cost of maintaining your runoff treatment system and enhances its reliability.

9. **Reduce risks that help you reduce costs** —When more environmentally sound work-practices and source control measures are adopted, the separator and other components of your treatment system require less and less maintenance. Regular separator servicing should not be a time-consuming or costly activity. Maintaining your separator this way reduces the need for more costly and intensive overhaul at a later stage.

10. **Take responsibility for your own effluent** —No-one else has the power you have to control runoff pollution from your site. So it is your responsibility. Oldcastle's oil-water separator represents the state of the art in gravity-separator design, but it is still only a *tool* to help you control your water quality. There is no technology that can automatically take care of all of your water quality worries. Avoid over-reliance on oil-level sensors and alarms, leak detection equipment etc. Such devices may be unreliable in the long run and may provide you with a false sense of security. There is no substitute for visually inspecting your drainage system on a regular basis (which should only take a minute anyway).

[†] Storing large quantities of oil and other potentially hazardous liquids in an open hydraulic system is strongly discouraged and illegal in many parts of the country. As well as creating a fire and safety hazard, environmental risks remain. Double-walled containment of oil-water separator chambers does *not* constitute secondary containment of liquids because the system is open. Oil and other materials can be re-entrained into the effluent as a result of blockage-induced surge or turbulence, the accidental release of interfering substances (e.g. detergents) into the separator and the occurrence of other unpredictable physical, chemical or microbiological reactions at the oil-water interface.