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Alaska State Legislature



Sen. Curt Menard, *Chair*
Sen. Lloyd Jones, *Vice-Chair*
Sen. Bettye Fahrenkamp, *Member*
Sen. Drue Pearce, *Member*
Sen. Dick Shultz, *Member*

P.O. Box V
Juneau, AK 99811
907 465-4921

Senate Transportation Committee

March 23, 1992

Scott Sterling, President
Regional Citizens' Advisory Council
Jensen, Harris & Roth
1029 West Third Avenue
Suite 600
Anchorage, AK 99501-1917

Dear Scott:

Congratulations on your election as President of the Regional Citizens' Advisory Council. If your past performance as Chairman of the TOEM Committee is any example, I am confident that you will provide the Council with the diligent and credible leadership necessary to effectively carry out the mission of this citizens' organization.

I also would like to invite you and Greg Winter from the TOEM Committee to participate in a joint Senate Oil & Gas and Transportation Committee hearing to be held in Juneau on Tuesday, March 31, from 1:30 - 3:30 p.m. in the Beltz Room of the Capitol.

The Committees would like to follow-up on the ballast water issues evaluated at length during the 1991 legislative session and review the status of your development of an environmental monitoring and testing program for the Ballast Water Treatment Facility at Alyeska.

Secondly, the Committees would like for you to discuss the status of your review of air quality issues related to the Alyeska Marine Terminal and the results and conclusions of any specific projects undertaken regarding airborne hydrocarbons, including the report recently completed by Dr. Yoram Cohen and released by the RCAC last week.

Page 2
Scott Sterling

I look forward to your presentation to the Committees. Please let me know if you have any questions or are unable to attend.

Warm regards,

A handwritten signature in black ink, appearing to read "Curt Menard", with a stylized flourish at the end.

Senator Curt Menard, Chairman
Senate Transportation Committee

cc: Sheila Gotterher
Greg Winter

Terminal Operations and Environmental Monitoring Committee (TOEM)

Quarterly Report to the RCAC, March 1992

Completed Projects

- Signed contract between RCAC and Alaska Department of Environmental Conservation to conduct review of testing and analysis used on effluent from the Ballast Water Treatment Plant at the Alyeska Marine Terminal, with a contingency for actual field sampling and testing if necessary.
- Compiled and submitted comments to government agencies and Alyeska Pipeline Service Co. regarding proposed revisions to the Best Management Practices Plan for Alyeska's ballast water treatment plant.
- Attended the Conference on Marine Vessel Emissions in Chantilly, VA, sponsored by the American Petroleum Institute.
- Met with EPA air pollution officials at EPA Pollutant Assessment Branch in Durham, NC, in order to enhance cooperation between RCAC and EPA on air pollution issues and become as current as possible on Clean Air Act Amendments rule making regarding vapor control requirements.
- Sponsored a fire protection workshop in Valdez with participants from RCAC, Alyeska, U.S. Coast Guard, City of Valdez, Prince William Sound Conservation Alliance, the Mayor's Ad Hoc Committee, etc.
- A Request for Qualifications seeking experts in the field of petroleum facility fire protection with the qualifications to conduct a review of fire protection and response at the Alyeska Marine Terminal in Valdez will be advertised and circulated in the near future.
- Completed the RCAC TOEM Committee's 1992 budget for total projected expenditures of \$825,000. Of this, \$525,000 is slated for direct program expense (the Committee's pollution-fighting projects) and \$300,000 is slated for operational expenses and overhead.
- Completed an upgrade of office space and equipment at the RCAC location in the Royal Center in Valdez. RCAC now occupies four offices and has the use of top of the line photocopying, fax, telephone and other equipment.

In Progress

- The TOEM Committee's review of sampling and test methods at the Ballast Water Treatment Plant continues, with funding assistance from DEC. The first phase of the TOEM Committee program, an examination of toxicity testing at the facility, is completed, and two other projects are underway:
 - a review by Beak Consultants of testing and analysis procedures used on BWTP influent;
 - a review by Investigative Science Inc. of methods used to sample and test effluent discharged from the plant.
- The TOEM Committee continues to track a number of ballast water issues with input from DEC, the Technical Advisory Group, and Alyeska, including:
 - Alyeska's request for a relaxation of state water quality standards or a redefinition of test methods;

- The company's bid to have EPA and DEC drop the requirement for a field verification study from its NPDES permit;
 - The likelihood that the state will exclude Port Valdez from its 1992 list of Impaired Waterbodies;
 - The TAG's call for a materials balance study at the BWT Plant.
- A report from TOEM consultant Dr. Richard Caldwell assessing toxicity testing of effluent from the ballast water treatment plant is near completion and is expected soon.
 - Valdez Air Study Review: the TOEM Committee continues to sponsor and fund this six-member peer review panel's examination of Alyeska's air studies and risk assessment in Valdez. The final step for the panel will be to review Alyeska's final report, expected in May.
 - Received draft report titled "Multimedia Fate and Effects of Airborne Petroleum Hydrocarbons in the Port Valdez Region" from TOEM consultant Dr. Yoram Cohen; the report will be reviewed, comments will be forwarded to Dr. Cohen, and the final report is expected to be available for the annual meeting in March.
 - The Committee continues to advocate the installation of technology to control volatile organic air emissions at the Alyeska Marine Terminal and is tracking government and industry dialogue and decision-making on this very important issue.
 - In the realm of fire protection, the TOEM Committee continues to work with the RCAC POVTS Committee, the City of Valdez, the Valdez Ad Hoc Committee, and Alyeska officials to assess fire protection and response capabilities at the Alyeska Marine Terminal. This effort is expected to include the hiring of an expert in the field petroleum facility fire protection.

Future

The TOEM Committee has budgeted for a number of projects that it hopes to initiate in the near future, including:

- A review of the effect of volatile air pollutants on the health and safety of workers at the Alyeska Marine Terminal;
- An investigation of sludge generation and disposal at the terminal
- An assessment of existing engineering and processes at the Ballast Water Treatment Plant and consideration of possible alternatives and improvements.

A Progress Report
on the
Independent Testing and Monitoring Program
at the
Alyeska Marine Terminal Ballast Water Treatment Plant
September 16, 1991

by the
Terminal Operations & Environmental Monitoring Committee
of the Regional Citizens' Advisory Council for Prince William Sound

I. Introduction

In May 1991, the Alaska State Legislature appropriated \$175,000 from the Oil & Hazardous Substance Release Response Fund to the Department of Environmental Conservation to fund a contract with the Prince William Sound Regional Citizens' Advisory Council for the development of an independent testing and monitoring program for the ballast water treatment facility operated by Alyeska Pipeline Service Company (Alyeska) in Valdez, Alaska. Governor Walter Hickel did not veto that appropriation.

Responsibility for developing this program lies with RCAC's Terminal Operations and Environmental Monitoring (TOEM) Committee, which is headquartered in Valdez. The TOEM Committee had already begun to develop such a program when the legislation was passed, recognizing that it is vital to the citizens of Prince William Sound regardless of whether the contract is ever realized.

The Independent Testing and Monitoring Program includes two major phases:

- Phase I. Research and design of independent testing and monitoring plans, and reviews of existing testing procedures at the terminal.
- Phase II. Implementation of the actual sampling and testing program to yield data from which broader and more accurate conclusions can be drawn.

In the legislators' letter to Commissioner Sandor, dated May 21, 1991, they suggest that this funding would enable ADEC to contract with RCAC to develop a plan for testing and monitoring influent, effluent, and "the long term effects on the biological system of Prince William Sound." The \$175,000 would probably cover little more than the first phase of the TOEM Committee's program. The committee will use the testing and monitoring plans designed under Phase I to initiate an independent testing and monitoring program or, if necessary, implement a plan to fill gaps in existing procedures.

influent and effluent, 2) critically review existing influent and effluent testing programs, 3) critically review existing toxicity testing programs, and 4) evaluate the combined results of the above studies.

This program complements and advances the recommendations of the Technical Advisory Group to ADEC on the BWTP (See IV.E. "Ballast Water Treatment Plant Concerns" in this report).

A. Influent and Effluent Reviews

For the reviews of influent and effluent testing, each consultant will design an ideal yet cost-effective sampling and analysis plan, using the highest scientific standards and best available technology. The consultants will then compare those plans with ADEC's influent sampling plan, or with the NPDES permit for the effluent analysis, and suggest improvements. The TOEM Committee will evaluate and, if appropriate, endorse those suggestions, and forward them to RCAC for approval. RCAC will then formally make recommendations to ADEC and Alyeska, and provide the information to the public.

Pursuant to the above reviews, the TOEM Committee is currently requesting proposals from qualified experts to design a random (unpredictable) sampling program for incoming tanker ballast water (influent). The final report is expected in January 1992. The committee is also drafting an RFP for design of a sampling plan for ballast water effluent. That report is expected to be completed in March 1992.

B. Toxicity Testing Review

Under the toxicity testing portion of the program, a qualified consultant will critically review the existing toxicity testing program at the terminal, including the NPDES permit requirements, make specific recommendations for expanding or improving those programs, and make recommendations for further studies. The TOEM Committee will evaluate and, if appropriate, endorse those suggestions, and forward them to RCAC for approval. RCAC will then formally make recommendations to ADEC and Alyeska, and provide the information to the public.

Pursuant to the above analysis, the TOEM Committee has selected experts to evaluate the toxicity tests and studies prepared by contractors for the Alyeska Pipeline Service Company. Their final report is expected in December 1991.

Phase II - Implementation

The result of Phase I of the Independent Sampling and Monitoring Program will be a body of reliable information about how to accurately assess the chemical composition of ballast water influent and effluent. The TOEM Committee will prepare a report based on those results and conclusions that:

adequately describe or characterize the wastes normally treated at the BWTP. ADEC began sampling and testing ballast water influent in April 1991.

Under the NPDES permit, ballast water effluent is monitored by a sampling and testing procedure scheduled in advance, which specifies substance to be tested, time, place, and testing method. Other waste streams are regulated or inventoried, but are not tested for water quality or monitored under the NPDES permit. Both EPA and ADEC agree that the presence or absence of hazardous or toxic substances in the influent can only be determined by a long-term testing and monitoring program.

There is still no "surprise" sampling program in effect at the BWTP which takes place without the prior knowledge of Alyeska officials. Alyeska controls the flow rate of the waste stream through the BWTP, has some control over tanker unloading, and arranges access and security escorts for ADEC and EPA officials there to take samples or inspect the facility. The TOEM Committee believes the Alyeska terminal should be subject to surprise sampling.

A. POSSIBLE DESIGN PROBLEMS WITH THE BWTP

As approved by Congress in 1977, the BWTP was designed to be built in phases corresponding to anticipated increased pipeline throughput. Alyeska promised, in the right of way lease covenants, to stay abreast of technological developments and to continually upgrade equipment. Since then, pipeline throughput has increased four-fold without the projected facility expansion.

The original plans called for an incinerator for disposing of oily sludge, real-time, continuous discharge monitoring instrumentation to control effluent quality, and two additional 430,000 barrel holding tanks. Presently, sludge is shipped out of state, continuous monitoring instruments are planned, but not yet in place, and additional holding tanks have not been built. It can be argued that Alyeska is currently operating with a BWTP that fails to carry out the original intent of Congress.

1. Flow Rate. Concerns have been expressed that the flow, or throughput rate (flow rate divided by volume) at the BWTP exceeds the rate for which the plant was originally designed, and that the facility is not operating effectively because of the alleged overload. Ballast water treatment effectiveness is determined by evaluating data regarding throughput rate, temperature, organism recycling, and nutrient sufficiency. Two important considerations when adjusting the throughput rate are 1) will the organisms suddenly wash out, or die off (called and "upset" by industry), and 2) is the degradation complete. Some say complete degradation requires a much slower throughput rate.

Another consideration which is not well understood is the mixing geometry. It is unclear how the system works: if biodegradation depends on recycling of organisms mixed upwards from the sediment and sludge on the bottom of the ponds, as driven by the aeration system. If that is the case, the throughput rate

B. UNIDENTIFIED TOXIC SUBSTANCES

Tank washings from dry dock cleaning of cargo areas, engine room diesel sludge, slops, and other toxic wastes have been known to be transferred to northbound TAPS trade tankers for discharge at BWTP in Valdez. This is not expressly forbidden by the NPDES permit, but neither is it authorized. EPA is currently investigating these practices, and until the investigation is closed, grants permission to unload ballast water in Valdez on a case-by-case basis. EPA has recently complained and proposed penalties against Alyeska, BP and Exxon for dumping unauthorized tank washings into the BWTP in Valdez.

Allegations have been made that this is a routine practice of TAPS tankers undertaken to avoid the substantial cost of discharging these loads at other west coast ports (up to \$200,000 per tankerload), and because the Valdez BWTP is the largest west coast facility. This practice undermines the original intention of having a "dedicated fleet" of tankers that haul only North Slope crude oil, thereby limiting the contents of ballast influent to the BWTP in Valdez.

There are two main problems 1) addition of foreign substances to the system, and 2) BWTP operations and effectiveness. If the plant operation is sound, foreign additions are not that serious; the wastes are going to remain somewhere.

C. QUESTIONS REGARDING OIL IN SEDIMENTS

Alyeska sediment studies required by the NPDES permit have recently shown increasing levels of aromatic hydrocarbons accumulating in the sediment of Port Valdez. These studies indicate the presence of sludge (i.e. toxic, carcinogenic, high molecular weight, polycyclic aromatic hydrocarbons) in the water column in increasing concentrations. Sediment concentrations are believed to be caused by the settling out of heavier chemical compounds from the water column (see TAG recommendations below). Therefore, in spite of the NPDES permit restrictions on effluent concentrations, ADEC's TAG group thought it reasonable to question whether, in fact, the BWTP is doing an adequate job of removing aromatic hydrocarbons from the effluent.

D. SELF-MONITORING

Harold Geren, Chief of Water Permits and Compliance Branch, EPA Region X, Seattle, in recent hearings before the Committee on Oil & Gas, stated that self-monitoring of discharges under wastewater discharge permits has been the foundation of the national compliance assurance program since the creation of the permit system under the federal Water Quality Act of 1972. In light of the Exxon Valdez spill and recent allegations regarding the BWTP, however, people want more than just assurances from the oil industry when it comes to pollution and environmental issues.

recommends that the first step in a mass balance study would be to look at the large amounts of data gathered by Woodward-Clyde, much of which was never reviewed or critiqued. He estimates 80% of the data needed already exists. Upon evaluation of the data, holes would be identified, and a plan established for filling in the missing information.

2) TAG recommends sampling, testing and analysis of the concentrations and concentration gradients of aromatic hydrocarbons in the Port Valdez water column (independent field verification). The 1985-86 Woodward Clyde study is admittedly flawed, yet modeling and extrapolation based on those results are the foundation of current estimates of water quality in Port Valdez, and the basis of the proposed removal of the port from the state's list of impaired waterbodies. To date there have been no field verification studies to show whether the BWT.V system currently in use by Alyeska results in compliance with state water quality standards outside the mixing zone.

Now that polycyclic aromatic hydrocarbons have been found in Port Valdez sediments by Alyeska's consultants, the TAG group feels it is critical that field testing and analysis be performed to verify the concentrations of oil in the water column. The most logical source of sediment concentrations of high molecular weight hydrocarbons is believed to be precipitation from the water column.

V. Background on the Regional Citizens' Advisory Council and Terminal Operations and Environmental Monitoring Committee

The Regional Citizens' Advisory Council (RCAC) of Prince William Sound (there is also an RCAC for Cook Inlet, the CIRCAC), is an independent, non-profit organization formed in the aftermath of the Exxon Valdez disaster to ensure the safe operation of the Trans-Alaska Pipeline Terminal and the crude oil tankers served by the terminal, so that the environmental impacts associated with the terminal and tanker fleet are minimized. The RCAC has 16 members who include representatives from municipalities, commercial fishing groups, Alaska Native interests, and environmental and business organizations.

RCAC is certified under the federal Oil Pollution Act of 1990 as the citizen advisory organization for Prince William Sound, and operates under a contract with Alyeska. The contract, which is in effect as long as oil flows through the pipeline, guarantees RCAC's independence, provides annual funding at \$2 million, and guarantees RCAC access to the terminal equal to that enjoyed by state and federal regulatory agencies.

The TOEM Committee is responsible for evaluating terminal operations in terms of their effect on the environment, identifying possible sources of chronic pollution, and making recommendations to RCAC in these areas. The TOEM Committee staff gathers information about the terminal through interaction with Alyeska, regulatory agencies, and the committee's consultants. Problems are usually approached by 1) identifying the relative seriousness and complexity of the situation, 2) determining how best to address the situation, 3) contracting

**Regional Citizens' Advisory Council
Terminal Operations and Environmental Monitoring Committee**

STATUS OF PROJECTS RELATED TO WATER QUALITY IN PORT VALDEZ

Mar. 31, 1992

TOEM remains focussed on ballast water treatment and monitoring practices at the Alyeska marine terminal. Past water quality violations and allegations of illegal ballast water transfers highlight the controversy surrounding this facility.

Port Valdez -- an impaired waterbody

- * Port Valdez appeared on Alaska's 1988 and 1990 lists of impaired waterbodies because aromatic hydrocarbons in the port were demonstrated to be in violation of state water quality standards.
- * More stringent effluent limits in the new permit should bring waters in Port Valdez back into compliance, however, a "mixing zone compliance study" has yet to be performed.
- * The Technical Advisory Group (TAG) and RCAC recommend such a study be conducted. RCAC feels strongly that Port Valdez should remain on the impaired waterbodies list until actual field verification verifies compliance with state water quality standards.

TOEM review of ballast water treatment testing and monitoring

Investigations launched last year and funded, by the \$175,000 appropriated by the legislature last year are starting to bear fruit in 1992. Based on the findings of three studies currently underway, TOEM will recommend changes or additions to the current ballast water treatment monitoring strategies.

Toxicity testing

- * Preliminary findings of the review of existing toxicity testing are generally positive. Our consultant reports that Alyeska is fulfilling, and in many ways exceeding, its NPDES requirements for toxicity studies at the present time.
- * Dr. Caldwell recommends that no significant reduction in required testing be allowed and suggests some refinements including a study of bottom fish to detect long term effects associated with hydrocarbons that have been detected in bottom sediment.
- * He also recommends that an effort be made to investigate the contribution of zinc to ballast water treatment plant effluent toxicity.

Influent testing

- * The TOEM Committee expects a draft review of Alyeska and ADEC ballast water treatment plant effluent in April, 1992.

Effluent testing

- * TOEM's contractor reviewing ballast water effluent testing is just getting started on this project, beginning with an Alyeska tour of the ballast water treatment facility and laboratory.

Revised "Best Management Practices Plan"

In February, TOEM submitted comments to the EPA on the proposed revised "Best Management Practices Plan" - a governing document in the operation of the ballast water treatment plant. We are waiting for EPA's response.

STATUS OF PROJECTS RELATED TO AIR POLLUTION IN PORT VALDEZ BASIN

Basic facts about air pollution in Valdez

- * Two categories of air pollutants are released from the Alyeska terminal. Levels of the so-called "criteria pollutants" are limited by federal and Alaska state regulations.
- * The other category is airborne hydrocarbons, also called VOCs (volatile organic compounds). The VOC group includes air toxics such as hexane, toluene, and benzene, a potent human carcinogen.
- * Alyeska's emissions comprise almost half of all VOCs emitted from marine loading operations nationwide. No existing regulations restrict the release of these gases from the terminal.

RCAC involvement -- Dr. Cohen's report

- * TOEM hired Dr. Yoram Cohen to identify specific air pollution issues the committee should address.
- * Dr. Cohen concludes that the expected lifetime cancer health risk due to benzene exposure is about 1 in 20,000. He also points out that the risk to terminal workers may be greater since their daily dose of benzene can be significantly higher than non-terminal workers.
- * Exposure to other chemicals of concern results in dose rates significantly below that which would cause health effects. However, it is pointed out that, like benzene, these other chemicals are found at much higher levels at and near the terminal.
- * Dr. Cohen found that the concentrations of some air toxics, including benzene, in Valdez air are typical of big cities like Los Angeles, Boston and Miami.
- * There is a need for a systematic program focused on ecological risks to the marine environment as a result of chronic exposure to low levels of hydrocarbons.
- * Convincing evidence needs to be presented to show whether or not the ballast water treatment plant is indeed biodegrading the chemicals of concern.

TOEM Committee's Valdez Air Studies Review Committee

In addition to commissioning Dr. Cohen's study, the TOEM Committee contracted with independent consultants to review the procedures being used by Alyeska's consultants in their health risk assessment study.

*Alyeska
Regulations
to respond*

- * Independent review will help insure that regulators and the public receive accurate and objective information from the Alyeska study.
- * Alyeska's study is comprehensive and utilizes state-of-the-art knowledge and current expertise.
- * The review committee, through RCAC, submitted recommendations for Alyeska's consideration in drafting the final report.
- * TOEM's consultants will review Alyeska's final report when it is issued this spring.

Vapor control at the Valdez marine terminal

- * TOEM continues to advocate installation of vapor control technology at the terminal, as well as, air quality regulations to require it.
- * Alyeska's ambitious efforts in the design of such technology have lead to the feasibility of a safe and effective hard piping system at the terminal.

Air pollution regulations

- * Federal rules are expected to require marine loading terminals to install hard pipe vapor control systems.
- * If Alyeska can demonstrate to the federal government that the Valdez terminal's VOC emissions do not pose a significant health or environmental problem, controls may not be required.
- * Alyeska is currently conducting a risk assessment study in Valdez to determine whether a health risk exists due to VOC emissions from the terminal. Alyeska expects to release its draft report this spring.
- * In the meantime, Alyeska has proceeded with preliminary engineering work for a vapor control system at the terminal; and has said, they may act to reduce or control these emissions even if the health studies are completely reassuring.



Official Business

Alaska State Legislature

P.O. Box V
State Capitol
Juneau, Alaska 99811

May 21, 1991

John Sandor, Commissioner
Dept. of Environmental Conservation
P.O. Box O
Juneau, AK 99811

Dear Commissioner:

Today, the House and Senate passed HB 75, the FY 92 operating budget. HB 75 appropriates \$175,000 from the Oil and Hazardous Substance Release Response Fund to the Department of Environmental Conservation to fund a contract with the Prince William Sound Regional Citizens Advisory Council (RCAC) to develop an independent testing and monitoring program for the ballast water treatment facility in Valdez.

This appropriation language is a result of extensive hearings in both the Senate and House on the ballast water treatment plant at the Valdez Marine Terminal. Those hearings documented substantial concerns regarding the adequacy of the monitoring at the plant by both the terminal operator and the agencies with regulatory responsibility.

It was our conclusion that state and federal agencies charged with oversight do not have sufficient information on the origins or composition of the ballast water being treated at the plant. Serious questions have been raised as to whether hazardous wastes, specifically tank washings, tank cleanings and diesel engine and other sludges, are being run through the system, whether the system is capable of treating these wastes and if the Port Valdez is in fact an "impaired waterway".

The funding provided for by section 20(e) of the operating budget will enable DEC to contract with RCAC to develop, in consultation with the Citizens' Oversight Council, a plan for testing and monitoring the ballast off-loaded to the ballast water facility, the effluent discharged into the Port Valdez and the long term effects on the biological system in Prince William Sound.

As articulated by the appropriation language, it is intended that RCAC should utilize 470 funds for the contract and that costs be recovered from Alyeska Pipeline Service Company. If the Department chooses to develop an alternative mechanism of direct payment or reimbursement from Alyeska, this would be consistent with the legislative intent of this appropriation section, provided the "direct billing" arrangement fully provides RCAC with the resources needed to adequately develop and implement the testing and monitoring program.

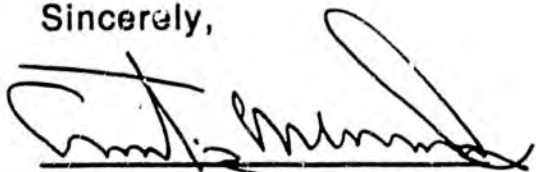
Regardless of the mechanism developed by the Department for recovery of the program costs, it is critically important to the fulfillment of the purpose of this appropriation that the study be performed without any perception of bias. Therefore, in forwarding this responsibility to the Department it is imperative that the testing and monitoring program developed and implemented by the RCAC in consultation with the Citizens' Oversight Council be free of any undue influence by Alyeska or the owner companies. In other words, Alyeska and the owners should not be allowed to direct or control the scope or depth of the program, the environmental consultant contract criteria or the contractor selection process.

We also would like to encourage you to process the contract with RCAC as soon as possible as we believe that development and implementation of an independent testing and monitoring program is a first step toward resolving many of the questions surrounding the ballast water treatment facility and the effluent discharges into Prince William Sound.

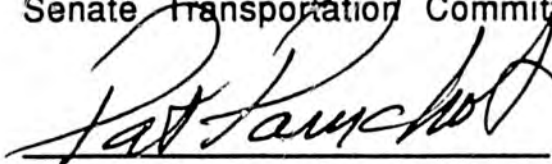
We look forward to working with you on development and implementation of this very important program and appreciate your recent efforts to step up oversight and investigation of tanker practices and operations.

Page 3
BWT Monitoring Program

Sincerely,



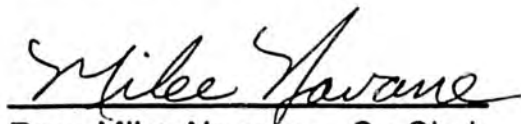
Senator Curt Menard, Chair
Senate Transportation Committee



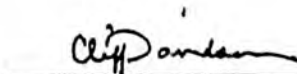
Senator Pat Pourchot, Co-Chair
Senate Finance Committee



Senator Bettye Fahrenkamp, Chair
Legislative Council



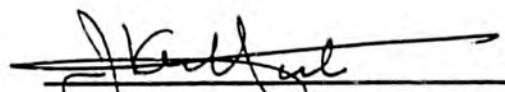
Rep. Mike Navarre, Co-Chair
House Committee on Finance



Rep. Cliff Davidson, Chair
House Committee on Resources



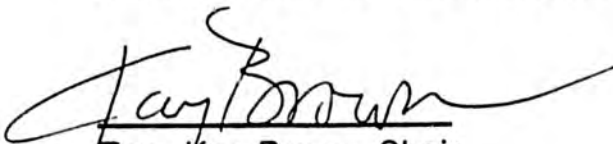
Senator Sam Cotten, Chair
Senate Oil & Gas Committee



Senator Jay Kerttula, Co-Chair
Senate Finance Committee



Rep. Bill Hudson, Chair
House Committee on Oil & Gas



Rep. Kay Brown, Chair
DEC Budget Subcommittee



Rep. Gene Kubina
District 6

SENATE CS FOR CS FOR HOUSE BILL NO. 75 (FINANCE)

IN THE LEGISLATURE OF THE STATE OF ALASKA

SEVENTEENTH LEGISLATURE - FIRST SESSION

BY THE SENATE FINANCE COMMITTEE

Offered:

Referred:

Sponsor(s): HOUSE RULES/GOVERNOR

A BILL

FOR AN ACT ENTITLED

1 "An Act making appropriations for the operating and loan program expenses of state
2 government and to capitalize funds; and providing for an effective date."

3 BE IT ENACTED BY THE LEGISLATURE OF THE STATE OF ALASKA:

4 * Section 1. Included within the general fund amounts appropriated in this Act, the following
5 amounts are from the unreserved special accounts in the general fund:

6 Highway Fuel Tax Account \$22,500,000

7 Aviation Fuel Tax Account 10,000,000

8 * Sec. 2. Federal or other program receipts as defined under AS 37.05.146 that exceed the amounts
9 appropriated in this Act are appropriated conditioned upon compliance with the program review
10 provisions of AS 37.07.080(h).

11 * Sec. 3. If federal or other program receipts as defined under AS 37.05.146 exceed the estimates
12 appropriated by this Act, the appropriation from state funds for the affected program may be reduced
13 by the amount of the excess if the reductions are consistent with applicable federal statutes.

14 * Sec. 4. Except as provided in sec. 5 of this Act, if federal or other program receipts as defined

1	PURPOSE	AMOUNT
2	State and regional contingency planning	\$ 395,900
3	Spill prevention, response, planning, safety,	
4	cleanup, and cost recovery	3,934,300
5	State Emergency Response Commission	299,900
6	Local emergency planning committees	600,000
7	Response office, depots, and corps	2,911,400
8	Hazardous Substance Spill Technology Review Council	296,100
9	Site investigation, safety, cleanup, and	
10	cost recovery	3,655,000
11	Kenai cleanup project	807,000
12	Exxon Valdez-spill cleanup	4,126,000
13	Exxon Valdez-assessment and restoration	12,474,400
14	Arctic Marine Resources Commission	100,000
15	Spill reserve	12,881,000
16	(c) The sum of \$490,900 is appropriated from the oil and hazardous substance release response	
17	fund (AS 46.08.010) to the Legislative Council for operation of the Citizens' Oversight Council on Oil	
18	and Other Hazardous Substances for fiscal year 1992.	
19	(d) The sum of \$3,653,100 is appropriated from the oil and hazardous substance release response	
20	fund (AS 46.08.010) to the Department of Law for the litigation costs associated with the Exxon Valdez	
21	oil spill for fiscal year 1992.	
22	(e) The sum of \$175,000 is appropriated from the oil and hazardous substance release response	
23	fund (AS 46.08.010) to the Department of Environmental Conservation for a contract with the Prince	
24	William Sound Regional Citizens' Advisory Council for a ballast water testing and monitoring program,	
25	to be developed in consultation with the Citizens' Oversight Council on Oil and Hazardous Substances,	
26	at the Alyeska terminal ballast water treatment facility.	
27	(f) The appropriation made by (a) of this section satisfies the appropriation requirements of	
28	AS 43.55.240.	
29	* Sec. 21. The sum of \$10,000,000 is appropriated from the general fund to the Alaska Student Loan	
30	Corporation, student loan fund (AS 14.42.210) to capitalize the fund.	
31	* Sec. 22. The sum of \$666,000 is appropriated from the general fund to the bulk fuel revolving loan	

**MULTIMEDIA FATE AND EFFECTS OF AIRBORNE
PETROLEUM HYDROCARBONS
IN THE PORT VALDEZ REGION**

FINAL REPORT

**REGIONAL CITIZENS' ADVISORY COUNCIL
Terminal Operations and Environmental Monitoring Committee**

March 14, 1992

Prepared by

**MULTIMEDIA ENVIROSOFT CORPORATION
9841 Airport Boulevard, Suite 900
Los Angeles, California 90045**

PLEASE NOTE

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**MULTIMEDIA FATE AND EFFECTS OF AIRBORNE
PETROLEUM HYDROCARBONS
IN THE PORT VALDEZ REGION**

FINAL REPORT

**REGIONAL CITIZENS' ADVISORY COUNCIL
Terminal Operations and Environmental Monitoring Committee**

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ABBREVIATIONS

BETX	- benzene, ethylbenzene, toluene, and xylenes
BTU	- biological treatment units
BWT	- ballast water treatment
BCF	- bioconcentration factor
DAF	- dissolved air floatation
MTD	- multimedia total dose
MW	- molecular weight
Receptor	- site at which concentration is monitored, object exposed to contaminants, or human or biological receptors (e.g., plants, animals) that are exposed to pollutants.
SMCM	- spatial-multimedia-compartmental
VOC	- volatile organic compound

UNITS

mg/kg	- milligram per kilogram
ppm	- parts per million
$\mu\text{g/kg}$	- micrograms per kilogram
GPM	- gallons per minute
GPD	- gallons per day
gallon	- (1 U.S. gallon = 3.79 liters)
ton	- equivalent to 2000 lb in the british system of units
metric ton	- 1000 kg
kg	- kilogram (1 kg = 1000 g)
mg	- milligram (1 mg = 0.001 g)
ppb	- parts per billion (e.g., 1 ppb (mass basis) = 1 $\mu\text{g/kg}$); Note - for air concentrations a volume basis is used (e.g., 1 $\mu\text{g/m}^3$ = (24.45/MW) ppb)
ppm	- parts per million (e.g., 1 ppm (mass basis) = 1 mg/kg)
ppt	- parts per trillion (e.g., 1 ppt (mass basis) = 1 ng/kg)
g	- gram
ng	- nanogram (1 ng = 0.000000001 g)
μg	- microgram (1 μg = 0.000001 g)
ml	- milliliter (1 ml = 0.001 liter)
l	- liter

MULTIMEDIA FATE AND EFFECTS OF AIRBORNE PETROLEUM HYDROCARBONS IN THE PORT VALDEZ REGION

EXECUTIVE SUMMARY

There is a concern that in Valdez, Alaska, hydrocarbons released to the environment from the Alyeska Marine Terminal at the southern end of the Trans-Alaska Pipeline may adversely impact the environment and the residents of Valdez. The primary function of the terminal is to load oil tankers, and to treat the ballast water from the tankers prior to discharge of the water into the bay water of Port Valdez. Approximately 1.8 million barrels per day of crude arrive at the Marine Terminal at Valdez via the Trans-Alaska Pipeline and approximately 16.4 million gallons of water per day are treated by the Ballast Water Treatment (BWT) facility.

Petroleum hydrocarbons are released to the Port Valdez environment primarily as the result of crude oil loading operations at the Alyeska Marine Terminal and the operation of the BWT facility. At the current level of crude oil production, the estimated tanker loading air emissions of total hydrocarbons are about 43,000 tons/year. The BETX (benzene, ethylbenzene, toluene, and xylenes) air emissions from tanker loading operations are about 797 tons/year. In addition, estimates of BETX air emissions from the BWT facility range from 75 tons/year to 293 tons/year. The discharge of BETX to the water column through the BWT diffuser pipe is estimated to be in the range of less than 0.4 tons/year to about 8 tons/year. Small quantities of spilled oil may also contribute to the input of hydrocarbons to both the atmosphere and water column at Port Valdez.

In order to assess the impact of the released hydrocarbons, the environmental distribution of chemicals selected for this study was evaluated using a simple (screening-level) analysis. Using the calculated environmental distribution of the study chemicals a subsequent estimate was made of the exposure of human and other ecological receptors to these chemicals.

Study Chemicals

Crude oil is a mixture of hundreds of chemicals, and thus it is neither feasible nor prudent to attempt to determine the environmental effects of each of these chemicals. From a practical viewpoint it is only the environmentally damaging compounds that are of interest in a screening-level analysis designed to elucidate the impact of emissions of volatile crude oil components. Therefore, in the first phase of the study, a simple ranking index was developed to determine which of the many petroleum hydrocarbons could be of concern from a human health risk perspective.

The ranking of the different crude oil chemicals according to their potential for volatilization and their potential human health hazard revealed that, of the carcinogenic volatile chemicals present in crude oil, benzene ranks at the top of the list of chemicals of concern,

followed by styrene. Although styrene is not normally present in crude oil, it has been found at a low concentration in the natural gas liquids (NGL) which are added on the North Slope to the Valdez-bound crude oil. Of the volatile non-carcinogens, *n*-hexane ranks as the chemical of most concern followed by toluene, xylenes (mixed), and ethylbenzene. Benzo(a)Pyrene, a semi-volatile polyaromatic hydrocarbon, is a carcinogen but with a significantly lower vapor emission rate relative to benzene and styrene. Among the semi-volatile non-carcinogens naphthalene ranks first followed by fluorene. It must be noted, however, that the above low ranking of semi-volatiles is based solely on considerations of vapor emissions and it does not consider direct discharge of semi-volatile hydrocarbons to the water of Port Valdez. Polyaromatic hydrocarbons are more persistent and tend to bioaccumulate to a greater degree relative to the more volatile components of crude oil.

It is important to note that polyaromatic hydrocarbons (PAHs) are also likely to enter the Valdez Port environment in the particle-bound form from exhaust emissions (e.g., from combustion engines), incineration, and wood burning, and due to direct discharge to the water column from the terminal ballast water treatment system, as well as from chronic or catastrophic oil spills. PAHs are present at 1-2 percent by weight in crude oil and thus it should not be unexpected to find these compounds in the environment surrounding the marine terminal. Indeed PAHs of crude oil origin have been detected in the Port Valdez sediment.

Although in this study the selection of the study chemicals (benzene, ethylbenzene, toluene, xylenes, and *n*-hexane) was based on their potential toxicity to humans, it should be noted that there are other important indicators of environmental hazard such as toxicity to aquatic life or plants, global warming potential, and ozone depletion potential. For example, if impact to the marine environment is of most concern, then a more appropriate evaluation should focus on toxicity to marine organisms. Different species can exhibit markedly different susceptibility to any one chemical. Also, observed effects due to chronic exposures at low concentrations are closely linked to the compound's ability to bioaccumulate. Consideration of bioaccumulation suggests that although air emissions of naphthalene, benzo(a)pyrene and fluorine are low, bioaccumulation for these compounds in the marine environment should be carefully examined.

Emission Sources

In the second phase of this study, the relative contributions of the various emission sources were evaluated in relation to the ambient air monitoring data reported by Alyeska¹ for the period 8/90 thorough 9/91. Another Alyeska study on air emissions of hydrocarbons due

¹ Alyeska Pipeline Service Company, "Valdez Air Monitoring System: Monthly Operational Data and Reports", prepared by CH2M Hill for Alyeska Pipeline Service Company, 8/90-9/91.

to the tanker loading operations² is indeed a detailed study that generated a voluminous data set on emissions. Unfortunately, the above study provided emission estimates only for a limited subset of specific compounds (i.e., BETX). For example, although air phase concentrations of *n*-hexane have been monitored, air emission estimates for *n*-hexane have not been provided by Alyeska. Estimates in this study suggest that the air emission rate for *n*-hexane due to tanker loading operations is about 623 tons/year. The estimates of tanker loading emission rates of benzene, ethylbenzene, toluene, and xylenes, as reported by Alyeska, are 450 tons/year, 16 tons/year, 262 tons/year, and 69 tons/year, respectively.

An analysis of the air emissions from other terminal operations revealed that the emissions of BETX from the ballast water treatment (BWT) facility are expected to be about 79 tons/year if the biological treatment units (BTU) are operating efficiently. However, reliable estimates of emissions from the biological treatment units (BTU) were not available. Thus, the above estimated emission rate from the BWT facility can only be regarded as an approximation. Although a clear demonstration of the effectiveness of the BTU is essential, such information was not made available by the Alyeska Pipeline Services Company. Therefore, the question of the effectiveness of the biological treatment units (BTU) in biodegrading BETX remains unresolved. If the BTU are not biodegrading BETX as claimed by Alyeska, then the volatilization of BETX from the BTU system could be as high as 293 tons/year which is about 26% of the total air emissions of BETX in Port Valdez. Clearly, if biotreatment is not as effective as it is claimed to be then the BTU facility may be a significant source of BETX emissions.

There are also non-terminal emission sources in Port Valdez. Such emissions have been linked to a number of commercial activities, fuel storage at the Valdez Airport, the harbor, roadways, residences, as well as emissions from the combustion of fuels and wood burning. The total of non-terminal sources of BETX is estimated to be about 23 tons/year³ which is about 2% to 2.5% of the total BETX air emissions in Port Valdez.

In a recent meeting of Alyeska officials and their contractors with RCAC representatives and their consultants⁴, it became clear that the estimated source emission rates will be used by Alyeska, in conjunction with the results of tracer studies using sulfur hexafluoride, to estimate

² Alyeska Pipeline Services Company, Report on Valdez Tanker Loading Vapor Emission Testing and Evaluation, Alyeska Pipeline Services Company, Doc. No. VVE-1990, Oct. 22, 1990.

³ Alyeska Pipeline Services Company, "Emission Inventory for Valdez Basin", Prepared by CH2M/Hill Northwest, Inc. (Alyeska Pipeline Services Company, Valdez, Alaska, December 1988, ANC 24595.CO.

⁴ Meeting of the RCAC Valdez Air Study Review Committee with Alyeska officials and Alyeska consultants, Denver, Colorado, 18 December, 1991.

the contribution of the air emissions from the Marine Terminal to the exposure of the residents of Valdez to ambient levels of BETX. Clearly, the apportionment of Alyeska's contribution to the total exposure of the residents of Port Valdez to airborne hydrocarbons depends upon the accuracy of the estimates of air emission for BETX and *n*-hexane as well as on the accuracy of the tracer studies. Currently, the uncertainties in the emission estimates are unknown and thus these uncertainties should be carefully evaluated.

Monitored Atmospheric Concentrations of BETX and *n*-Hexane

The data set of monitored concentrations reported by Alyeska for four monitoring stations, upon which part of the analysis in this study was conducted, represents an incomplete set. For the 8/90 - 9/91 sampling period, the average percentage of data not reported (including data not acquired during calibration periods) ranged from about 39.8% to 48.6%. The air monitoring study should be carefully examined in order to establish the level of confidence in the monitored results and to be able to place the appropriate error bounds on the reported monitoring data. As part of the above tasks, the correlation between the reported data, missing data, and the tanker loading activity logs must be established.

Examination of the monitoring data for BETX and *n*-hexane concentrations relative to the estimated sources revealed that there may be an inconsistency between the estimated emissions and the reported monitoring data. There is clearly a need to reconcile the estimated emissions with the monitoring data in order to determine the contribution of the terminal operations to the ambient levels of hydrocarbons in the Port Valdez area. This task will require that appropriate air dispersion models are used using the meteorological data base accumulated for Port Valdez and the available (or revised) emission estimates.

Analysis of the air monitoring data for Port Valdez, supplied by the Alyeska Pipeline Services Company, revealed that concentration levels of benzene, toluene, xylenes, and *n*-hexane at Port Valdez are typical of concentrations reported for urban atmospheres. It is useful to note that measured air concentrations for BETX and *n*-hexane in pristine atmospheric settings range from not detected to about 180 ppt (ppt denotes parts per trillion). In contrast, typical range of BETX and *n*-hexane concentrations in urban atmospheres is about 0.1 ppb to 40 ppb (ppb denotes parts per billion). Clearly, with respect to the atmospheric concentrations of BETX and *n*-hexane, Port Valdez cannot be considered to be either a pristine or a rural area.

Distribution of Study Chemicals in the Environment

In the third phase of the study, the environmental partitioning of the selected study chemicals were studied using the spatial-multimedia-compartmental (SMCM) model and available

monitoring data coupled with a multimedia total dose (MTD) model⁵. The SMCM and MTD models were developed specifically for the evaluation of multimedia distribution of pollutants and the associated exposures. This analysis served to estimate the concentration of the airborne petroleum hydrocarbons that partition into the air, water, sediment, suspended solids (in the water column), biota (in the water compartment), and vegetative cover. As part of this study, a screening-level exposure analysis was utilized to estimate the conservative upper limit level of exposure of human and ecological receptors to the selected study chemicals.

It is emphasized that pollutants which are released to the environment as the result of a variety of human-related activities (air emissions and/or direct discharge to surface water, etc.) move across environmental boundaries (e.g., via dry and wet deposition, volatilization, runoff, and infiltration) and are therefore found in most media. Chemical pollutants in the environment are also transformed via chemical and biological reactions, and they can be dispersed in the environment due to convective flows (e.g., winds and water currents). The environmental impact posed by chemical contaminants is proportional to their concentrations in the various environmental media. Pollutant concentrations can, in principle, be obtained by either pollutant fate and transport modeling or field measurements. The above tasks demand an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants among the different environmental media. Unfortunately, multimedia monitoring is a difficult task and requires a formidable expense for monitoring all potential air toxics. Thus, various estimation methods, which can be coupled with field monitoring, have been developed for the purpose of determining pollutant partitioning in the environment and human exposure to these chemicals.

Given the complexity of the issues involved, one should resort as a first step to a multimedia screening-level analysis in order to determine (or verify) the dominant pathways for pollutant distribution in the environment. Such a screening-level multimedia approach can be used to estimate the distribution of various chemicals in the environment (e.g., in air, soil, water, biota) and to conduct an overall mass balance analysis on the released contaminants. Multimedia concentrations of the study chemicals can then be used to estimate exposures of the human and other ecological receptors, to the released chemicals, via various exposure pathways (e.g., air, water, food). In this study, the spatial-multimedia-compartmental (SMCM) model was

⁵ Cohen, Y., Tsai, W., Chetty, S., and G. Mayer, "Dynamic Partitioning of Organic Chemicals in Regional Environments; A Multimedia Screening-Level Modeling Approach", *Environmental Science and Technology*, 24, no. 10, pp. 1549-1558, (1990).

Chetty, L. S., *Multimedia Total Dose Analysis*, M.S. Thesis, Department of Chemical Engineering, University of California, Los Angeles, Los Angeles, CA (1991).

utilized together with available monitoring data supplied by Alyeska to estimate the concentrations of the study chemicals in the air, soil, water, sediment, suspended solids (in water), biota, and vegetation, and to predict the transfer rates between the primary environmental compartments.

Analysis of the partitioning of BETX and *n*-hexane to the soil, water, sediment, suspended solids, biota (in water), and vegetation, revealed that over 95% of the amounts of these chemicals which are present in the Valdez environment are present in the air phase. About 1.7% to 4.78% of the BETX compounds that are present in the Port Valdez environment are present in the water column, and about 0.035% to 0.08% is present in the soil. The total mass of BETX (originating from air emissions) present in the sediment, suspended solids, and biota is negligible compared to the amount of these chemicals present in the atmosphere and water compartments. For all of the conditions studied, the calculated concentrations in the sediment and suspended solids were below or within the concentration range reported for pristine regions. Thus, it can be concluded that, relative to the atmospheric concentrations, volatile hydrocarbons such as BETX and *n*-hexane do not significantly accumulate in the sediment and in suspended solids.

The input of BETX and *n*-hexane to the soil and sea via precipitation scavenging (from the atmosphere) was found to be negligible relative to dry deposition. It is noted, however, that atmospheric removal of airborne pollutants is most significant for highly water soluble or reactive gases (e.g., sulfur dioxide) and for particle-bound pollutants (e.g., Benzo(a)Pyrene).

Accumulation of BETX and n-Hexane in Plants and Biota

The accumulation of BETX and *n*-hexane in vegetation is estimated to be in the range of 0.00013 to 0.0037 $\mu\text{g/kg}$ (i.e., micrograms per kilogram of plant matter). Benzene displays the highest accumulation in leafy plants followed by toluene, *n*-hexane, xylenes, and ethylbenzene. For root vegetables, *n*-hexane exhibits the highest accumulation followed by toluene, benzene, xylenes, and ethylbenzene. The above order of accumulation is expected consistent with the higher soil and air concentrations and bioconcentration factors for the chemicals exhibiting greater bioaccumulation. No documented adverse effects on vegetation due to low concentrations of BETX or hexane have been documented in the literature. It is known that adverse effects can occur when hydrocarbon emissions also affect ozone formation. However, this is not believed to be the case at Port Valdez given that the levels of ozone in the region are low.

The accumulation of BETX and *n*-hexane in fin fish and shell fish was estimated to be in the range of 0.14 to 13.3 $\mu\text{g/kg}$ (i.e., micrograms per kilogram of biota). Presently, it is not known if such low levels of bioaccumulation in fish can lead to adverse effects (on fish and other aquatic organisms) as the result of chronic exposure.

Although the accumulation of BETX and *n*-hexane (originating from air emissions from the Marine Terminal) in biota and vegetation appears to be at low level, data on toxicological and ecological impacts at such low concentration levels are unavailable. Obviously work is needed to establish the effect of chronic exposure of aquatic organisms and plants exposed to low concentration levels of hydrocarbons (both volatile organic compounds and polycyclic hydrocarbons).

Human Exposure to BETX and n-Hexane

The analysis of human exposure to BETX and *n*-hexane revealed that the dominant pathways of exposure to BETX and *n*-hexane is inhalation. Contaminant intake via the ingestion pathway is significantly less than the inhalation pathway. Also, the consumption of local both fin fish and shell fish has a negligible influence on the overall lifetime average daily intake of BETX and *n* hexane. Contaminant intake via the dermal absorption pathway is also insignificant when compared to the inhalation and ingestion pathways. The contribution of dermal absorption to the lifetime average specific intake rate is approximately six orders of magnitude less than that of inhalation and three to four orders of magnitude less than the contribution of ingestion.

Upper limit estimates of human exposure to outdoor BETX and *n*-hexane were obtained using a calculation that considered only chronic exposures to ambient concentrations (occupational and indoor exposures were not considered). The analysis revealed that human exposure to ethylbenzene, toluene, xylenes, and *n*-hexane results in a lifetime average contaminant intake ranging from 0.00031 to 0.0018 mg/kg/day (i.e., milligram per kilogram of body weight accumulated per day). These average intake rates are significantly below the EPA reference dose (RfD) at which adverse health effects may occur due to chronic exposures. However, it must be noted that higher daily intake, by a factor ranging from 2 to 10, can result from occupational exposure near and at the terminal as suggested by the higher concentrations of BETX and *n*-hexane reported from the East Gate monitoring station.

The estimate of human exposure to benzene revealed a lifetime average benzene intake rate of about 0.0021 mg/kg/day. At this exposure level, a conservative analysis of human health risk due to exposure to benzene, based on a basin-wide average concentration, revealed that the expected incremental lifetime cancer health risk is about 1 in 20,000. It is noted that the USEPA uses an acceptable risk of one in a million for a given chemical. In comparison, an equivalent analysis for the City of Los Angeles revealed that the incremental lifetime cancer health risk due to exposure to ambient benzene levels is about 1 in 10,000. It is important to note, however, that the daily dose of benzene for cigarette smokers (and those exposed through passive smoking) may be significantly higher compared to the dose received due to exposure to ambient levels of benzene. Obviously, a detailed analysis of exposure is required in order to assess the detailed health risks from all sources.

It is recognized that the above analysis is approximate and does not represent the actual risk to the population at Valdez. However, this study does demonstrate that the exposure levels to hydrocarbons in Port Valdez are comparable to those found in urban environments. Realistic exposure assessment that encompasses the actual exposed population in Port Valdez should be conducted. In fact, a detailed personal exposure modeling study was undertaken by Alyeska and a review of this study was recently undertaken by the Valdez Air Study Review (VASR) Committee convened by the Regional Citizen's Advisory Council (RCAC). It is hoped that the Alyeska study will provide the additional information required to assess the potential health risks associated with the operation of the Marine Terminal at Port Valdez.

Major Recommendations

Although there have been numerous studies concerned with the environmental impact of crude oil production on Port Valdez, the following major issues are yet to be resolved:

- There is a need to establish the level of confidence in the Alyeska ambient air monitoring data for specific hydrocarbons (e.g., BETX and n-hexane) in order to determine the appropriate error bounds on the reported monitoring data. As part of the above tasks, the correlation between the reported data, missing data, and the tanker loading activity logs must be established.
- There is a need to conduct a careful review of the tanker loading emission study in order to establish the uncertainty in the emission estimates reported by Alyeska. Such information is crucial if these emission estimates are to be used by Alyeska to establish the contribution of emissions from the terminal to exposure levels in various locations in Port Valdez.
- There is a need to establish the effectiveness of the biological treatment units (BTU) in the BWT facility. Convincing evidence should be presented by Alyeska to demonstrate that the BTU are indeed biodegrading BETX at the rate implied by Alyeska. If biotreatment is not as effective as it is claimed to be then the BTU can contribute significantly to air emissions from the BWT facility.
- Although polyaromatic hydrocarbons of crude oil origin have been identified in the Port Valdez sediment their sources have not been clearly identified. Since polyaromatic hydrocarbons tend to bioaccumulate, it is essential that their origin and potential impact on the marine environment is clarified.
- There is a need for a systematic program focused on the evaluation of ecological risks to the marine environment as the result of chronic exposures to low concentrations of hydrocarbons (both volatile organic compounds and polycyclic hydrocarbons).

2. INTRODUCTION

2.1 Problem Definition

There is a concern that in Valdez, Alaska, hydrocarbons which are released to the environment from the Alyeska Marine Terminal at the southern end of the Trans-Alaska Pipeline may adversely impact the environment and the residents of Valdez (ADEC, 1990; Tardiff et al., 1991; Alyeska, 1990). The primary function of the terminal is to load oil tankers and to treat the ballast water from the tankers prior to discharging the treated water to the bay of Port Valdez. The terminal is located on the south shore of Port Valdez approximately 4 km across the bay (Port Valdez) from the City of Valdez (Figure 1.1). The mountains on the south side of the terminal rise steeply from the bay to a height of about 100 m to 1500 m.

Approximately 1.8 million barrels per day of crude oil arrive at the Marine Terminal at Valdez via the Trans-Alaska Pipeline. Crude oil is transferred to oil tankers at the Marine Terminal at Valdez. It has been estimated that, at the current oil production rate, about 20,000 to 46,000 tons per year of hydrocarbon vapors, with a loading temperature range of 50°C to 100°C, are released to the atmosphere as the result of tanker loading and unloading operations. The Ballast Water Treatment (BWT) facility at the Terminal treats about 16 million gallons of water per day which consists primarily of ballast water containing a variety of organic chemicals which are primarily of crude oil origin. At the current level of crude oil production, total hydrocarbon emissions to the atmosphere from the BWT facility are estimated to be about 850 tons/year, with estimated total air emissions of benzene, ethylbenzene, toluene, and xylenes (BETX) from the BWT facility ranging from about 79 tons/year to 293 tons/year. Other emission sources include the direct discharge of trace levels of hydrocarbons to the water column through the BWT diffuser pipe with estimated effluent discharge of BETX ranging from less than 0.4 tons/year to about 8 tons/year. Small quantities of spilled oil may also contribute to the input of hydrocarbons to both the atmosphere and water column at Port Valdez.

In order to assess the potential for adverse environmental impacts associated with the marine terminal operation, this study was undertaken to evaluate the emissions of selected hydrocarbons, the distribution of the released chemicals in the various environmental media (e.g., air, water, soil, sediment), and the potential exposure of the human receptor and other ecological receptors to these chemicals. The study focused on obtaining basin-wide rather than site-specific estimates of environmental impact and thus the approach taken is classified as a screening-level analysis. The specific objectives of the study which was prepared for the Regional Citizens' Advisory Council are listed in section 2.2.

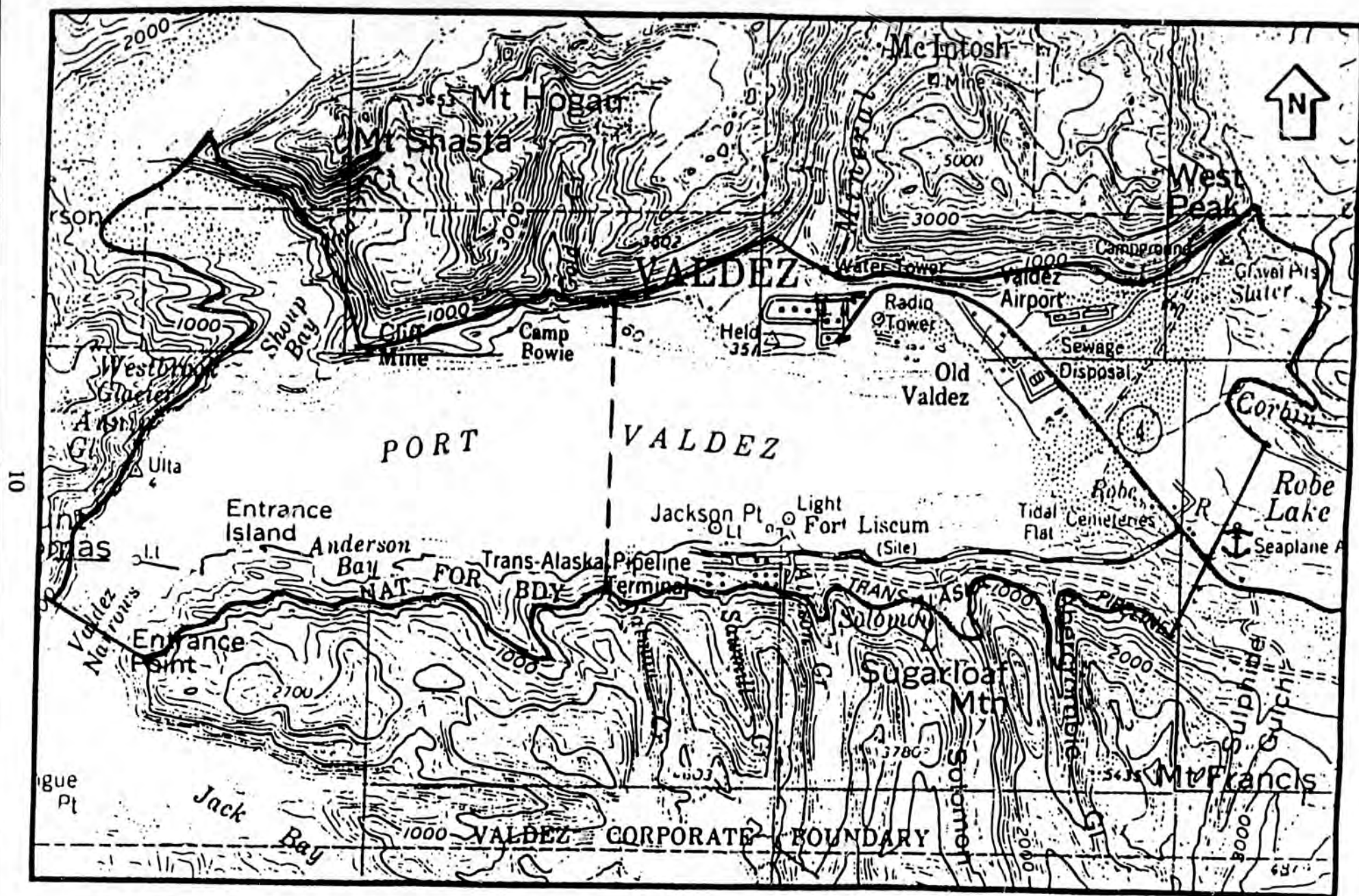


FIGURE 1.1 - Port Valdez and Approximate Borderz of the Study Area (The area to the East of the vertical Dotted line is defined as the Half-Port study area)

2.2 STUDY OBJECTIVES

1. Propose a rational approach to ranking hydrocarbons present in crude oil which may be most detrimental to human health and the environment.
2. Review the estimates of hydrocarbon emissions from the terminal operations in relation to available monitoring data and the likely fate and effects of the selected study chemicals.
3. Provide a discussion of the most likely fate and effects of the emitted hydrocarbons through appropriate diagrams, graphs, and tables to help convey their distribution in the environment.
4. Discuss the available monitoring data in relation to the need for evaluating the environmental multimedia distribution of released hydrocarbons.
5. Review the need for obtaining improved assessment of likely environmental impacts associated with the operation of the terminal and the available options for obtaining such assessment.

3. JUSTIFICATION FOR THE SELECTION OF STUDY CHEMICALS: A SCREENING-LEVEL METHODOLOGY

3.1 Overview

Crude oil is a mixture of hundreds of chemicals, and thus it is neither feasible nor prudent to attempt to determine the environmental effects of each of these chemicals. From a practical viewpoint it is only the environmentally damaging compounds that are of interest in a screening-level analysis designed to elucidate the impact of emissions of volatile crude oil components. It is not immediately obvious which of the many crude oil components may have the most potential to adversely impact human health and the environment. Thus, it is useful first to utilize a systematic screening-level ranking analysis that will allow the identification of target species that warrant a detailed analysis of their environmental impact.

The environmental impact of crude oil components released to the environment is strongly related to the emission rates of these chemicals. Thus, in this study an emission index (for vapor emissions) was determined in order to rank the various crude oil components according to their potential for volatilization. The emission index was correlated with available estimates of vapor emission rates. Subsequently, an emission hazard index defined as the product of the emission index and toxicity parameter was calculated. The ranking indices were determined for over 140 components of crude oil (see Appendix B) using the methodology described below.

3.2 Emission Index

At the crude oil/atmosphere interface one usually assumes that local equilibrium exists between the crude oil components in the liquid phase and the components in the vapor phase. Subsequently, based on the thermodynamic requirement that the chemical potential (or fugacity) of each component is equal in both phases (i.e., liquid crude oil and the vapor phase) one can write the following standard relationship between the mole fraction, for a given component, in the vapor and liquid phases. Accordingly (Sandler, 1989),

$$y_i \phi_i P_T = x_i \gamma_i P_i^s \quad (3.1)$$

in which y_i and x_i are the mole fractions in the vapor phase and liquid phase, respectively. The vapor phase fugacity coefficient is given by ϕ_i and the liquid phase fugacity coefficient is denoted by γ_i . Deviations from ideal mixture behavior for the vapor and liquid phases are corrected through the use of the parameters ϕ_i and γ_i . The saturation vapor pressure is given by P_i^s and the total pressure is denoted by P_T . At low pressures the mole fraction in the vapor

phase can be related to the saturation vapor pressure using the ideal gas law,

$$y_i = c_i^v \frac{RT}{P_T} \quad (3.2)$$

in which C_i^v is the vapor phase molar concentration (e.g., gmol/m³). After combining equation 1 and 2 the vapor phase molar concentration can be related to the mass concentration in the liquid phase (e.g., mg/l) by the following equation

$$C_{m,i}^v = C_i^v MW_i = \left(\frac{C_i^L P_i^s}{P_T \rho_o} \right) \left(\frac{\gamma_i P_T MW_{av}}{\phi_i RT} \right) \quad (3.3)$$

in which MW_{av} and MW_i are the average molecular weight of the crude oil and of the species of interest, respectively, and ρ_o is the mass density of the crude oil. The quantity in the square brackets is dimensionless and can be regarded as a volatility index for the chemical of interest. Accordingly, it is convenient to define E_i as the emission index given by

$$E_i = \frac{C_i^L P_i^s}{P_T \rho_o} \quad (3.4)$$

Compounds with greater values of E_i are expected to volatilize to a greater degree than compounds with a lower value of E_i . Thus, the emission rate is expected to correlate with the value of E_i . A more precise analysis would require knowledge of the parameters ϕ_i and γ_i for each component in the crude oil mixture leading to a modified emission index, $E'_i = E_i(\gamma_i/\phi_i)$. Alternatively, if K_i factors are available ($K_i = y_i/x_i$) then $E'_i = (C_i^L/\rho_o)(K_i P_i^s MW_{av}/RT)$. Since the goal of the present analysis was to obtain an approximate ranking of the various hydrocarbons, the approximate approach given by Eq. 3.4. was utilized.

In order to calculate E_i for the various crude oil components that are of interest the crude oil composition (in units of mg/l) were obtained from crude oil composition data supplied by the Alyeska Pipeline Services Company. It is important to note that although composition data were provided for approximately 150 compounds, detailed composition data for saturated alkanes in Alaskan crude oil were lacking. The available composition data included analysis data of cyclic compounds composition in crude oil (Core Laboratories, 1989), composition information in terms of volume percent for crude liquids (Ede, 1988), and molar composition data for natural gas liquids (NGL), which are added to crude oil to decrease its viscosity (Alyeska, 1988). The overall density of the crude oil and the NGL mixture was approximated from the following

simple linear volume averaged approximation

$$\rho_o = W_v(\rho_{NGL}) + (1 - W_v)\rho_{crude} \quad (3.5)$$

in which W_v is the volume fraction of NGL added to the crude oil. The amount of NGL in the crude oil stream is reported by Alyeska to be in the range of 3 to 4 percent by volume ("Report on Valdez Tanker Loading Vapor Emission Testing and Evaluation", Alyeska, October 22, 1990, page 19). The density of the NGL, ρ_{NGL} , was approximated to be 0.62 g/ml and with an assumed NGL content of 3.5% (by weight) the density of the crude was estimated to be about 0.9 g/ml.

Vapor pressures for the calculation of the emission index were compiled for a temperature of 20°C. For some compounds the vapor pressure at 20°C was calculated using the Clausius-Clapeyron equation (Grain, 1990; Reid et al., 1977; Weast, 1983; Stull, 1947). When Clausius-Clapeyron equation constants or vapor pressure data at 20°C were not available, the constants were determined using vapor pressure data near 20°C.

In order to illustrate the utility of the emission index, the vapor emission rates for benzene, ethylbenzene, toluene, and xylenes were correlated with the emission index values for these chemicals. The annual average vapor emission rates for BETX as the result of tanker loadings were obtained from the Alyeska study on tanker vapor emissions ("Report on Valdez Tanker Loading Vapor Emission Testing and Evaluation", Alyeska, October 22, 1990, page 19; see section 4.2). As Figure 3.1 illustrates the emission rates vary linearly with the emission index, E_i . This suggests that such an analysis can be used to develop reasonable correlations of the emission rates with the emission index for homologous series of compounds. It was not possible to construct an emission rate-emission index correlation for compounds other than BETX since the tanker loading vapor emission study conducted by Alyeska did not provide estimates of the vapor emission rates for specific hydrocarbons other than BETX. Specific tanker vapor composition for specific hydrocarbon species C_1 , $n-C_4$, IC_4 , $n-C_5$, $i-C_5$ were obtained but emissions estimates for the tanker fleet were not provided. In order to develop the type of correlation shown in Figure 3.1 for other homologous series, emission estimates from further analysis of the data available from the Alyeska emission study or from further additional modeling and/or monitoring of tanker emissions will be required.

3.3 Emission Hazard (EH) Index

The emission rate alone is obviously an insufficient indicator of the potential for a given compound to adversely impact the environment. The emission rate for a given chemical may be large, but if the chemical is not a toxic chemical, then it will not adversely affect the environment. Conversely, a very toxic compound emitted in small quantities could potentially

EMISSION INDEX VS EMISSION RATE

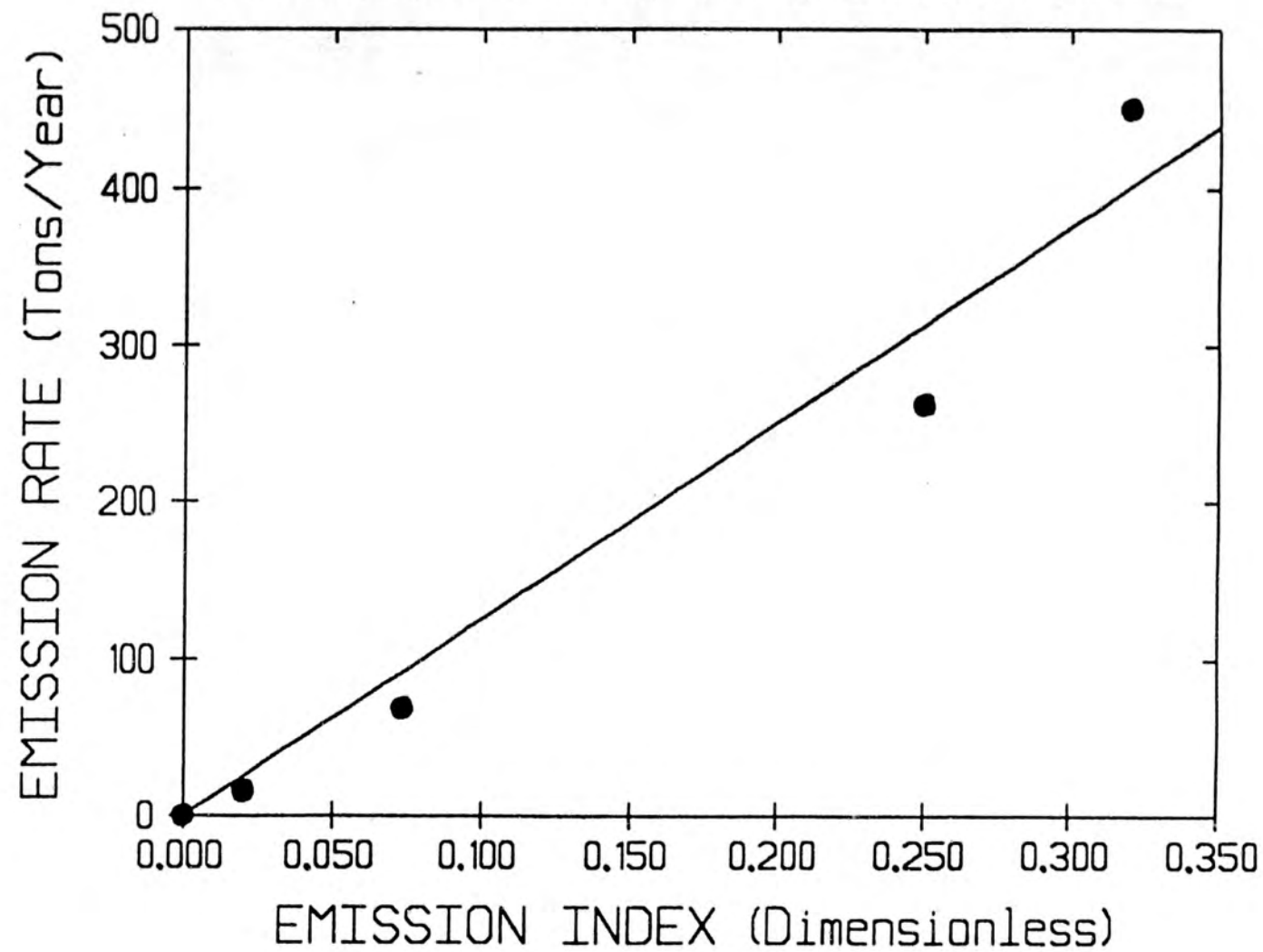


FIGURE 3.1

have significant adverse effects on human health and the environment. There are various measures of a chemical's toxicity. For example, the quantification of human health risks led to the development of the slope factor for cancer causing chemicals in humans and the reference dose (RfD) for non-carcinogenic effects. The slope factors and RfDs are usually obtained from animal studies and thus they are strictly applicable to animals although extrapolation to humans is usually carried out in health risk assessments. At present, carcinogenic and non-carcinogenic effects cannot be easily compared and must be ranked separately (EPA, 1991).

In order to provide for ranking of crude oil components which incorporates some measure of the potential toxicity of these components, one needs to modify the emission index (E_i) defined in section 3.2 (see Eq. 3.4). It is accepted that concentrations at a receptor site are proportional to emission rates. Also, it is accepted that human health risk will generally increase with increasing concentration of the toxic chemical of concern at the receptor site. Thus, one should expect that the product of the emission index and the slope factor for carcinogens will give an indication of the relative ranking of the potential of different carcinogens to lead to harmful health effects. For non-carcinogens, dividing the emission index by the RfD will yield a similar index for comparing non-carcinogens. The above indices are jointly termed here "emission hazard index" (EH_i).

In order to determine the EH_i index for both carcinogens and non-carcinogens, information was derived from the IRIS data base, searched via MEDLINE. Only officially recognized carcinogenic categories and RfDs were taken into account in the preparation of the list of study chemicals (EPA, Health Effects Assessment Summary Tables, OERR-9200.6-303 (91-1), NTIS# PB91-921199). For some compounds, separate slope factors and RfDs are available for the inhalation and ingestion routes. In such cases, the highest value for slope factor and the lowest value for the reference dose were used.

3.4 Discussion of Prioritization Analysis

The complete list of the emission index, E_i and the hazard emission index, EH_i , are given in Appendix B for crude oil components for which potency factors or RfD values have been reported by EPA. A partial listing of the E_i and EH_i values for the crude oil components including those that ranked highest among the group of compounds listed in Appendix B is given in Table 3.1.

From the analysis presented above (sections 3.2.1 and 3.2.2), as expected it is revealed that of the carcinogenic volatile chemicals present in crude oil benzene ranks at the top of the list of chemical of concern, followed by styrene. Although styrene is not normally present in crude oil, it has been found at a low concentration in the natural gas liquids (NGL) which are added on the North Slope to the Valdez-bound crude oil. Of the volatile non-carcinogens, *n*-hexane ranks as the chemical of most concern followed by toluene, xylenes (mixed), and

ethylbenzene. Benzo(a)Pyrene, a semi-volatile polyaromatic hydrocarbon, is a carcinogen but with a low emission hazard index relative to benzene and styrene. Among the semi-volatile non-carcinogens naphthalene ranks first followed by fluorene which has an emission hazard index several orders of magnitude lower than that of naphthalene. It must be noted, however, that the above statements regarding semi-volatiles are based solely on considerations of vapor emissions. It is important to note that polynuclear aromatic hydrocarbons (PAHs) are also likely to enter the Valdez Port environment in the particle-bound form (Junge, 1977) from exhaust emissions (e.g., from combustion engines), incineration, and wood burning, and due to direct discharge to the water column from the terminal ballast water treatment system, as well as from chronic or catastrophic oil spills. PAHs are present at 1-2 weight percent in crude oil and thus it should not be unexpected to find these compounds in the environment surrounding the marine terminal. Indeed both Fluorene and B(a)P have been detected, at concentrations as high as 35 $\mu\text{g/Kg}$ and 27 $\mu\text{g/Kg}$, respectively, in the Port Valdez sediment (Shaw, January 1992). Polynuclear aromatic hydrocarbons are more persistent and tend to bioaccumulate to a greater degree relative to the more volatile components of crude oil.

Although the selection of the group of chemicals listed in Table 3.1 was based on their potential toxicity to humans, it is important to note that there are other important indicators of environmental hazard including toxicity to aquatic life or plants, global warming potential, and ozone depletion potential. For example, if impact to the marine environment is of most concern, then a more appropriate parameter may be the LC_{50} fish toxicity parameter (i.e., concentration lethal to 50% of a population in a three day period) or other toxicity indicators. As an illustration LC_{50} values for finned fish species for selected chemicals are given in Table 3.2. It is important to recognize that different species can exhibit markedly different susceptibility to any one chemical. Also, observed effects due to chronic exposures at low concentrations are closely linked to the compound's ability to bioaccumulate. The potential for bioaccumulation is quantified by the bioconcentration factor, BCF, which is defined as the equilibrium concentration in the organism divided by the concentration in the environmental medium where exposure occurs. As an illustration, the range of bioconcentration factors for fish and aquatic invertebrates are also given in Table 3.2. It is interesting to note that a ranking based on the bioconcentration factor alone, results in benzo(a)pyrene and fluorene being ranked at the top followed by naphthalene, with similar ranking for n-hexane, xylenes, toluene, ethylbenzene, and styrene, and the lowest ranking for benzene. It is emphasized that bioaccumulation is species-specific and thus any ranking based on bioaccumulation should be done for a specific species. Considerations of bioaccumulation suggests that although the emission hazard index values for air emissions for naphthalene, benzo(a)pyrene and fluorine are low, bioaccumulation for these compounds in the marine environment should be carefully examined.

TABLE 3.1
RANKING OF SELECTED CRUDE OIL AND NGL COMPONENTS

Compound	Estimated Concentration mg/l ⁽¹⁾	Volatility Index ⁽²⁾ (P_i^s/P_T)	Emission Index ⁽³⁾	Emission Hazard Index = Emission Index x Highest Value of		High Cancer Slope Factor, kg-day/mg	Low RfD, mg/kg/day ⁽⁴⁾
				Cancer Factor x 10 ³ (kg-day/mg)	Inverse RfD (day/mg)		
Benzene	2990	0.097	0.32	9.3	*	0.029	*
<i>n</i> -Hexane ⁽⁶⁾	2756	0.16	0.49		8.16		0.06
Toluene	6600	0.034	0.25		1.3		0.2
Styrene ⁽⁵⁾	16.8	0.0076	0.00014	0.0042	0.0007	0.03	0.2
Ethylbenzene	1610	0.011	0.02		0.20		0.1
Xylenes (mixed)	6570	0.010	0.073		0.37		0.2
Naphthalene	791	0.000066	0.000058		0.14		0.004
Fluorene	86.9	0.000011	0.000001		0.000025		0.04
Benzo(a)pyrene	9.7	0.0000026	0.000000028	0.00032	*	11.5	*

* No value was assigned to toxicity but harmful effects have been observed.

(1) Total concentrations in the crude oil delivered to the Marine Terminal.

(2) Vapor pressure was determined at 20°C

(3) Product of columns 2 and 3 divided by density of crude/NGL mixture.

(4) For noncarcinogenic harmful effects the lowest reported RfD was used.

(5) Present only in NGL

(6) The emission index for *n*-hexane and the concentration were estimated from the emission index-emission rate correlation (see Figure 3.1 and Table 4.2) and Eq. 3.4.

TABLE 3.2
FISH TOXICITY AND BIOCONCENTRATION VALUES^(a)

Compound	Fish Toxicity, ppm (96-hr LC ₅₀)	Bioconcentration Factor (BCF) ^(b)
Benzene	10	4-25
<i>n</i> -Hexane	-	170-180
Toluene	10	1.7-380
Styrene	10	13-130
Ethylbenzene	40	100-200
Xylenes	2	6-190
Naphthalene	2 ^(c)	~ 426
Benzo(a)Pyrene	-	~ 5000-20,000
Fluorene	-	1300-3000

^(a) Reported ranges for measured or estimated values.; ^(b) BCF = C_b/C₁; C_b - concentration in biota, C₁ - concentration in water; ^(c) 24-hr LC₅₀.

3.5 Overview of Typical Sources, Fate and Effects for the Study Chemicals

This study focused on the evaluation of the fate and effects of airborne petroleum hydrocarbons associated directly with emissions from the Alyeska Marine Terminal. Thus, only volatile compounds were considered for detailed study. The chemicals selected for detailed multimedia analysis consistent with the ranking criterion include benzene, ethylbenzene, toluene, xylenes, and *n*-hexane. This selection of study chemicals does not imply that the potential environmental impact of less volatile chemicals which may be released to the environment from other terminal related operations (e.g., emissions from tanker engines, incinerators) or other emissions in the area (e.g., wood burning, vehicular emissions) is of lesser significance. Prior to presenting a detailed multimedia analysis for the selected study chemicals, a brief review is provided for the selected study chemicals including the additional chemicals listed in Table 3.1, regarding their anthropogenic and natural source releases, the potential fate and toxicity of these chemicals and their reported presence in the environment.

Benzene is the simplest of the aromatic compounds. In addition to crude oil, natural sources include volcanos, forest fires, and some plants. Benzene is released during its own production and distribution. Other sources include automobile exhaust, solvents, nonferrous metal manufacture, ore mining, wood processing, and textile manufacture. Short term (acute)

exposure to benzene at ambient concentrations in the range of 10 ppm-100 ppm causes drowsiness, dizziness, and headaches, and can also affect the immune system. Benzene is acutely toxic to some fish at 10 ppm although it exhibits low degree of bioaccumulation. Long term (chronic) exposure to benzene causes leukemia, and possibly severe anemia and internal bleeding. Chronic exposure in animals has been shown to cause fetal damage at benzene air concentration levels as low as 10 ppm. Chronic exposures to benzene even at extremely low concentration (in the ppb range) can also lead to leukemia.

Toluene is an aromatic compound found not only in petroleum and petroleum related fuels, but also in automobile exhaust, solvents, and thinners. It is emitted during its own manufacture and distribution. Natural sources of toluene emissions include crude oil, volcanos, and forest fires, as well as *Tolu balsam*. Toluene can be smelled in air at levels as low as 0.16 ppm and tasted in water at levels as low as 0.04 ppm. In humans, short term exposure to high concentrations of toluene causes fatigue, confusion, weakness, memory loss, and nausea. Long term (chronic) exposure to toluene, at concentrations levels of 100 ppm - 600 ppm causes possible damage to the kidneys and brain, and may cause decreased resistance to disease. It is believed that chronic exposure to toluene can affect the central nervous system and impaired neuromuscular functions. Unfortunately, little dose-response data based on human exposure to toluene are available. In animals, long term effects due to exposure at the above concentration levels include liver, kidney, and lung damage, as well as fetal damage. Like benzene, toluene is acutely toxic to some fish at 10 ppm. It exhibits low to moderate bioconcentration.

Ethylbenzene emissions can result from its manufacture and use as an intermediate. It is a component of automobile exhaust and is emitted during biomass combustion. Short term (acute) exposure to high concentrations of ethylbenzene causes eye and throat irritation, decreased movement, and dizziness. In animals, ethylbenzene causes possible damage to the liver, kidney, nervous system, and blood. Long term (chronic) exposure in animals can result in birth defects and possibly tumors. Ethylbenzene is acutely toxic to some fish at 40 ppm and has a low bioconcentration factor.

Xylenes are a mix of three isomers; o-xylene, p-xylene, and m-xylene. Natural sources of xylenes include crude oil, forest fires, and plants. Anthropogenic sources include automobile exhaust, solvents, enamels, adhesives, pesticides, coal tar, and fugitive emissions during their own manufacture. Short term exposure to the xylenes, at concentration levels in the range of about 100 ppm - 1,000 ppm, can result in irritation of the skin, eyes, nose, and throat, as well as in difficulty breathing, impaired lung function, memory loss, stomach discomfort, and liver and kidney damage. Short and long term exposure causes headaches, lack of coordination, dizziness, confusion, and balance loss. In animals, xylenes exposure has resulted in spasms,

hearing loss, changes in organ weight and enzyme activity, and fetal death and damage. Xylenes can be acutely toxic to fish at 2 ppm and exhibit moderate bioaccumulation. In humans, chronic occupational exposure to xylenes has been associated with impaired pulmonary function and labored breathing, and impaired functioning of the cardiovascular system.

n-hexane is the only aliphatic compound among the study chemicals. It is a saturated straight chain alkane containing six carbon atoms. Emissions of this compound come from petroleum, petroleum derived fuels, and natural gas. Acute exposure to *n*-hexane can lead to nervous system disorders, vision problems, tingling of fingers and toes, muscular atrophy, and nerve degeneration in humans. In animals, exposure has been found to cause lesions in the membranes of the olfactory and respiratory system, abnormal posture and gait, and ocular irritation as well as nervous system disorders. Bioaccumulation of *n*-hexane is estimated to be moderate. EPA established a reference dose of 0.06 mg/kg/day for human exposure to *n*-hexane.

Styrene is made of an aromatic benzene ring with an unsaturated vinyl group. The only known natural source of styrene is *Storax balsam* and it has also been detected in the NGL which is added by Alyeska to crude oil. Styrene is released in automobile exhaust, from waste incineration, and during styrene and polymer manufacture. Styrene may be emitted from floor waxes, paints, adhesives, putty, metal cleaners, autobody fillers, varnishes, casting plastics, and fiberglass. Short term exposure to moderate to high styrene concentrations causes central nervous system problems and irritation of the eyes, nose, and throat. Long term exposure to moderate to high concentrations of styrene may cause low birth weights and spontaneous abortions. In animals, long term exposure has caused damage to the lungs, liver, blood, and kidneys. Styrene is acutely toxic to some fish at 10 ppm and bioaccumulates moderately. It has been suggested that in humans, given the limited human data and supporting animal studies, acute exposure to styrene at moderate to high concentrations can lead to adverse neurological effects. Styrene is a suspected carcinogen.

Naphthalene is a compound containing two aromatic rings. It is released from the burning of biomass, coal, liquid fuels, and during its own production. It is a constituent of coal tar and crude oil, and is emitted in automobile exhaust. Exposure to naphthalene results in blood cell damage. Nausea, vomiting, diarrhea, kidney damage, jaundice, liver damage, cataracts, and fetal damage are other ill health effects. Naphthalene is acutely toxic to some fish at 2 ppm and bioaccumulates significantly relative to the BETX group. Naphthalene is also readily metabolized by fish and mussels. Naphthalene rapidly degrades in the atmosphere with an atmospheric reaction half-life of about 3 to 30 hours. Naphthalene is the most volatile of the

PAHs and it can be smelled at concentrations as low as 0.08 ppm and it can be tasted in water at a concentration of about 0.02 ppm.

Benzo(a)Pyrene (B(a)P) is a polyaromatic hydrocarbon which forms during the incomplete combustion of fossil fuels and other organic substances. Benzo(a)Pyrene has a low vapor pressure and it is thus present mostly in the particle-bound form. Benzo(a)Pyrene has been shown to affect the reproductive system of mice and affect their offsprings. It has also been identified as a carcinogen which can also lead to skin disorders. Benzo(a)Pyrene is found to bioaccumulate in fish, shrimp and clams. Its atmospheric reaction half-life is several days and it degrades slowly in soils. The toxicology of B(a)P is the most widely studied among the PAHs.

Other polyaromatic compounds present in crude oil that have been identified as carcinogens include benzo(a)anthracene, benzo(b)fluoranthene, chrysene, dibenz(a,h)anthracene, pyrene, and anthracene. Fluorene which is also present in crude oil is not a suspected carcinogen but the EPA reports a reference dose for non-carcinogenic effects.

A summary of the observed environmental concentrations in fresh water, sea water, sediment, soil air, algae and aquatic fauna are given in Tables 3.3 and 3.4 for the chemicals listed in Table 3.1. Where possible, the character of the sampling site (urban, pristine, or source dominated) is indicated. It is important to recognize that the data in this table were compiled from the studies of a number of researchers who used different sampling techniques and analysis methods with equipment of varying sensitivity, making it impossible to attach a single value to the detection limit. It is useful to note that measured concentrations for BETX and *n*-hexane in pristine atmospheric settings range from not detected to about 180 ppt (ppt denotes parts per trillion). In contrast, typical range of average concentrations of BETX and *n*-hexane in urban atmospheres range from about 1 ppb to 30 ppb. Concentrations of BETX in pristine locations in seawater have been reported to be in the range of 5-400 ppt. The general observation is that concentrations of BETX and *n*-hexane are in the parts per trillion range for pristine locations and in the parts per billion range for urban regions. In contrast typical concentrations observed for the three PAHs, benzo(a)pyrene, fluorene, and naphthalene in natural soils and sediments (see Table 3.4) are higher than for volatile organics.

A discussion of the observed and predicted environmental concentrations of the study chemicals at Valdez relative to typical observed concentrations in pristine and urban environments is provided in Section 5.1 and Section 7.

TABLE 3.3
ENVIRONMENTAL CONCENTRATIONS OBSERVED
FOR THE SELECTED STUDY CHEMICALS ^(a)

Media	Concentration					
	Benzene	n-Hexane	Toluene	Styrene	Ethylbenzene	Xylenes
Fresh water	5.0 ppb ⁽⁴⁾		ND-5 ppb ⁽²⁾	0.1-4.2 ppb ⁽²⁾	<5 ppb ⁽²⁾	<2 ppb ⁽²⁾
Seawater	5-15 ppt ⁽¹⁾ 1-10 ppb ⁽²⁾	ND-7.8 ppt ⁽¹⁾	3-376 ppt ⁽¹⁾		400 ppt ⁽¹⁾ 5-15 ppb ⁽²⁾	ND-2 ppb ⁽¹⁾ 0.2-10 ppb ⁽²⁾
Sediment	<5 ppb ⁽⁴⁾			4.2 ppb ⁽²⁾	<5 ppb ⁽²⁾	
Soil	5 < - 191 µg/kg ⁽²⁾				0.067 ppm ⁽²⁾	
Air	ND ⁽¹⁾ 2.8 ppb ⁽²⁾ 3.2 ppm ⁽³⁾	61 ppt ⁽¹⁾ 1-28 ppb ⁽²⁾	57 ppt ⁽¹⁾ 4-35 ppb ⁽²⁾ 5.5 ppm ⁽³⁾	0.06-3 ppb ⁽²⁾ 1.69 ppm ⁽³⁾	13-156 ppt ⁽¹⁾ 0.3-12 ppb ⁽²⁾ 154.2 ppb ⁽³⁾	~30 ppt ⁽¹⁾ ~1-30 ppb ⁽²⁾ 19 ppm ⁽³⁾
Algae	20 ppb ⁽²⁾		5 ppm ⁽²⁾			
Aquatic fauna	220 ppb ⁽²⁾				0.8 - 10 ppb ⁽²⁾	0.05-0.12 ppm ⁽¹⁾

^(a) Source: HSDB, Hazardous Substances Data Bank, Bethesda, MD, National Library of Medicine, January, 1992; Toxicological Profiles for Benzo(a)Pyrene and Polyaromatic Hydrocarbons, U.S. Department of Health & Human Services, ATSDR/TP-88/05, 1990.

^(b) All values are mean values unless otherwise indicated.

ND: Not detected.

⁽¹⁾ Pristine, remote, or areas considered to be uncontaminated.

⁽²⁾ Urban, anthropogenic influences.

⁽³⁾ Source dominated.

⁽⁴⁾ Average or median of differing sites.

TABLE 3.4

**ENVIRONMENTAL CONCENTRATIONS
OBSERVED FOR SELECTED POLYAROMATIC HYDROCARBONS^(a)**

Media	Benzo(a)Pyrene	Fluorene	Naphthalene
Fresh Water	2-24 ng/L ^(a) 0.3-2 ng/L (treated surface water) 0.6-210 ng/L (untreated water)		1-10 µg/L ^(a)
Seawater		44 µg/L ^(a)	
Sediment	530-700 µg/kg ^(a) (total PAHs)		500-10,000 ng/L ^(a) (total PAHs) 300-4000 µg/kg ^(a)
Soil	40-1,300 µg/kg (rural) 100-1,000 µg/kg (typical soils)	9.7 µg/kg (agricultural soil)	
Air	0.1-1.2 ng/m ³ ⁽¹⁾ 0.2-19.3 ng/m ³ ^(a)		0.1-1.2 ng/m ³ (rural) 0.2-20 ng/m ³ ^(a) 10-1000 µg/m ³ ^(a) (vapor only) 0.1-4.4 µg/m ³ ^(a) (aerosol)
Aquatic fauna			1-10 mg/kg ^(a) (detected in fish)

^(a) Source: HSDB, Hazardous Substances Data Bank, Bethesda, MD, National Library of Medicine, January, 1992; Toxicological Profiles for Benzo(a)Pyrene and Polyaromatic Hydrocarbons, U.S. Department of Health & Human Services, ATSDR/TP-88/05, 1990.

⁽¹⁾ Pristine, remote.

⁽²⁾ Urban, anthropogenic influences.

⁽³⁾ Source dominated (in heavily polluted industrial areas or in the vicinity of hazardous waste sites).

⁽⁴⁾ Average or median of differing sites.

⁽⁵⁾ Valdez Harbor-Trans Alaskan Pipeline Terminal.

4. EVALUATION OF EMISSION SOURCES

4.1 Overview: Potential Sources of VOC Emissions

Emissions of volatile hydrocarbons can result from various activities at the Alyeska Marine Terminal as well as from sources such as automobile emissions and home heating at Valdez. Combustion engines and incinerators at the Port Valdez area could also contribute to the input of polyaromatic hydrocarbons to the atmosphere. In addition, direct discharge of chemicals to Port Valdez can result from runoff (e.g., during snow melt), or direct discharge of chemicals to the water column through the BWT diffuser. The release of chemicals at the Port Valdez region is the outcome of a variety of activities as summarized in Table 4.1.

TABLE 4.1
RELEASE OF HYDROCARBONS TO THE ENVIRONMENT
AT PORT VALDEZ

To the atmosphere:

- Fugitive emissions and leaks during tanker loading of crude oil
- Fugitive emissions from crude oil storage tanks
- Air Emissions from the BWT recovered crude oil tanks and ballast water tanks
- Volatilization of hydrocarbons from the DAF units of the Ballast Water Treatment (BWT) facility and from the weir
- Emissions from the biological treatment tanks
- Emissions from power boilers and incinerators (waste gas and solid waste) in the marine terminal
- Emissions from accidental spills
- Emissions from combustion engines (e.g., oil tankers, other marine vessels, and automobiles)
- Emissions due to home heating (e.g., wood burning)

To water:

- Direct discharge of hydrocarbons from the BWT through the diffuser
- Accidental spills
- Port activities including bilge pumping

To soil:

- Spills

There have been a number of studies conducted by the Alyeska Pipeline Services Company and its consultants which have focused on the estimates of emissions from the marine terminal and other non-marine terminal sources at Port Valdez. Based on these reported studies as well as monitoring discharge reports supplied by Alyeska a summary of the estimated emission rates and sources is presented in Tables 4.2 through 4.9. It is noted that in some cases approximate methods of estimating the emissions reported in Tables 4.2-4.9 were used while in others more accurate emission values were obtained. A brief discussion of the various emission estimates is given in sections 4.2-4.4 below.

4.2 Direct Emissions of VOCs from Tanker Loading Operations

Emissions during tanker loading were estimated during an extensive study conducted by Alyeska together with Arco, Exxon, and BP over the period 1988-1990. Extensive field monitoring of tanker emissions was conducted over a nine month period during 1990. Based on the above study it was determined that emissions due to tanker loading total about 43,000 tons per year with benzene emissions estimated at 450 tons per year ("Report on Valdez Tanker Loading Vapor Emission Testing and Evaluation", Document Number VVE-1990, October 22, 1990, Alyeska Pipeline Services Company). Emission rates were found to be functions of the amount of crude oil loaded, the temperature of the arriving crude, the hydrocarbon content of the crude, and the tanker size and configuration. It was also asserted that as the production of crude will decline past 1990, the temperature of the arriving crude will correspondingly decrease; correspondingly, the rate of hydrocarbon emissions was estimated to decrease with the projected future decrease of both crude oil production rate and temperature. The Alyeska study projected that the estimated emissions from tanker loadings will decrease by a factor of about 10 over the period from the year 1990 through the year 2010. This estimate was based on the assumption that the production of crude oil will decrease from 1.8×10^6 barrels per day in 1990 to 0.33×10^6 barrels per day by the year 2010. The estimated drop in the crude oil temperature for the same period was from 97°F to 50°F. Based on the Alyeska study, the current average annual emissions estimates as listed in Table 4.2 can be inferred.

Other emissions associated with the terminal operations are linked to emissions from the power boilers and vent gas incinerators at the terminal. In addition, emissions from tankers and tug boat engines also contribute a small fraction to the total volatile emissions. These other emission sources are given in Table 4.3. Clearly, BETX emissions from the power boilers and incinerators and oil tanker and tug boats engines are small compared to the total tanker loading emissions.

TABLE 4.2
ESTIMATED TANKER LOADING EMISSIONS FOR SELECTED HYDROCARBONS

Compound	Average Emissions ^(a) , tons/year	Range of Fleet Emissions Estimated from Tanker Emission Study at Crude Oil Temperature of 100°C (Tons/year) ^(b)	Estimated Emissions from the Emission Index Correlation ^(c) (Tons/Year)
Benzene	450	427-525	402
Toluene	262		314
Ethylbenzene	16		25
Para and meta xylene	57		
Ortho xylene	12		
Total Xylenes			91
Total BETX	797		
<i>n</i> -Hexane ^{(d), (e)}			623
Styrene			~0.2
Naphthalene			~0.07
Total C ₈ aromatics	~85		
Total Hydrocarbons	43,000	31,000-57,000	

(a) Based on Alyeska's estimate of benzene emissions of 450 tons/year

(b) Estimated crude oil production rate of 1.8×10^6 barrels/day

(c) Estimated based on the Correlation Emission (tons/year) = $1256E_i$ (E_i - emission index given in Table 3.1)

(d) Based on vapor phase composition of 0.54% by weight and benzene vapor phase composition of 0.16% by weight. Source: Dyreoft, G. V., Vapor Phase Analysis of Prudhoe Bay Oil, Prudhoe Bay Sample, Ref. No: 7323702, information attached to letter to Mr. R. Fritz, August 15, 1973, Esso Research and Engineering Company, Analytical and Information Division, Linden, N.J. Information on the concentration of *n*-hexane in crude oil arriving at the marine terminal was not available.

(e) Estimated emission of total hexanes ~2890 - 4270. Upper limit estimate is based on the correlation, Emission (tons/year) = $1256E_i$ (E_i - emission index given in Table 3.1); Lower limit estimate for the emission rate of total hexanes is based on the concentration ratio of total hexanes/benzene in crude oil (see Table 6.11)

TABLE 4.3
EMISSIONS FROM OTHER TERMINAL SOURCES ^(a)

	Alyeska Terminal: Boilers and Incinerators (Tons/Year)	Tanker and Tug Sources (Moving and Docked) (Tons/Year)
Benzene	0.1	0.5
Ethylbenzene	NA	NA
Toluene	0.1	0.5
Xylenes	0.01	0.08
Total BETX	0.201	1.08

^(a) Source: TRC Project Report No. 5885-T31, November 1989, "Emissions Inventory of Sources at Port Valdez".

4.3 Air Emissions from the Ballast Water Treatment Facility

4.3.1 Overview

The function of the Ballast Water Treatment (BWT) facility is to separate and recover hydrocarbons and treat separable and dissolved hydrocarbons, organic-based wastes, acids and caustics (Revised Best Management Practices Plan, Alyeska, November 12, 1991). Tankers that arrive at the terminal off-load their ballast and bilge water to the BWT facility where the residual oil is separated from the ballast water before it is returned to the waters in Port Valdez.

There are four primary sources of volatile organic emissions from the BWT facility. These are the ballast water storage tanks, the recovered crude tanks, the dissolved air floatation (DAF) basins and the biological treatment tanks.

4.3.2 Emissions from the Ballast Water Tanks and Recovered Crude Tanks

Total VOC emissions from the ballast water tanks were estimated, using the EPA AP42 method, to be in the range of 662 to 780 tons/year (see Table 4.4) and emissions from the recovered crude tanks were estimated to be approximately in the range of 9 to 13 tons/year (Table 4.4). The total BETX emissions from both the ballast water tanks and recovered crude tanks were estimated to be about 5.8 tons/year (Table 4.5). As Table 4.5 indicates emissions of BETX from the recovered crude tanks is negligible compared to emissions from the ballast water tanks.

TABLE 4.4
ESTIMATED VOC EMISSIONS
FROM THE BALLAST WATER TREATMENT HOLDING TANKS^(a)

	Estimated Emissions from the Ballast Water Tanks (Tons/year)	Estimated Emissions from the recovered crude tanks (Tons/Year)	Total Emissions from ballast water and recovered crude tanks (Tons/Year)
Breathing Losses	36.7 ^(a) 10 ^(b)	3.8 ^(a)	40.5 ^(a)
Working Losses	743.8 ^(a) 652 ^(b)	9.5 ^(a)	753.3 ^(a)
Total breathing and working losses	780.5 ^(a) 662 ^(b)	13.3 ^(a) 9.1 ^(b)	793.8 ^(a) 726 ^(b)

^(a) Source: Alyeska ANC24595.CO, 12/15/88, Tables D4 and D5 (Information Supplied by R. L. Mikkelsen, Alyeska memo dated December 13, 1991, File No. VR-16.00; see also Nelson, 1989).

^(b) Source: TRC Project Report No. 5885-T31, November 1989, "Emissions Inventory of Sources at Port Valdez".

TABLE 4.5
ESTIMATED BETX EMISSIONS FROM THE BALLAST WATER TREATMENT
SYSTEM HOLDING TANKS ^(a)

	Ballast Water Tanks (Tons/year)		Recovered Crude Tanks (Tons/year)		Total (Tons/year)
	Working Losses	Breathing Losses	Working Losses	Breathing Losses	
Benzene	3.7	0.05	0.018	0.0009	3.8
Ethylbenzene	0.016	0.0001	0.000085	0.0000045	0.016
Toluene	1.85	0.027	0.0124	0.0006	1.9
Xylenes	0.11	0.001	0.000727	0.000038	0.1
Total BETX	5.67	0.079	0.0312	0.0015	5.8

^(a) Source: TRC Project Report No. 5885-T31, November 1989, "Emissions Inventory of Sources at Port Valdez".

4.3.3 Emissions from the DAF Units

Air emissions from the dissolved air floatation (DAF) units of the BWT facility were estimated from data provided in the Discharge Monitoring Reports supplied by Alyeska (Mikkelsen, Memo VR-16.00, 1991). In these discharge reports, the flow rate of the influent into the DAF units was reported along with the concentration for BETX into and out from the DAF units. Thus, by a simple mass balance, assuming that biodegradation does not take place in the DAF units, one can determine the total amount volatilized from the DAF units

$$E_{DAF} = Q_{in}(C_{in} - C_{out}) \times 0.002194, \text{ tons/year} \quad (4.1)$$

in which E_{DAF} is the estimated emission rate (tons/year), Q_{in} is the inflow stream into the DAF units (gallons/minute), and C_{in} , C_{out} are the BETX concentrations (mg/l) in the influent and effluent streams, respectively. The estimated emissions based on data for the period 2/91 through 6/91 are presented in Table 4.6. The average BETX air emission rate from the DAF units is about 56.7 tons/year. It is interesting to note that the emission of BETX from the DAF units is about 7% of the estimated BETX emissions from the tanker loading operation and about a factor of ten higher than the combined BETX emission rate from the ballast water holding tanks and recovered crude tanks.

TABLE 4.6
PREDICTED ANNUAL EMISSIONS OF BETX FROM DAF UNITS^(a)

Month	DAF In ^(b) (mg/l)	DAF Out ^(c) (mg/l)	Flow Rate (GPM)	Projected Emissions (Tons/Year)
2/91	11.7	9.1	12412	70.8
3/91	12.0	9.9	12354	56.9
4/91	10.8	9.0	11969	47.2
5/91	11.2	8.8	10899	57.4
6/91	10.7	8.3	9606	50.6
Averages	11.28	9.02	11,448	56.7

^(a) Data Obtained from the Discharge Monitoring Reports for the given month (Monitoring Discharge Reports, supplied in LOTUS 123 format, Alyeska Pipeline Services Company Analytical Services, Valdez, 1990-1991)

^(b) Concentration of BETX in the inflow water stream

^(c) Concentration of BETX in the effluent DAF water stream.

4.3.4 Summary of Emissions from the Marine Terminal

Summaries of the various emissions from the marine terminal BWT facility is given in Table 4.7 and in Figures 4.1a and 4.1b. The estimated total BETX emissions is about 79 tons per year with the total estimated VOC emissions at about 848 tons per year. Reliable estimates of emissions from the biological treatment units (BTU) were not available. Information regarding the concentration of volatiles (e.g., BETX) in the BTU feed stream were not available and convincing data on biological degradation if such occurs in the BTU could not be located.

Thus, the estimated emissions from the BWT facility can only be regarded as an approximation. It is important to realize that since the concentration of BETX in the DAF effluent stream is about 9 ppm (see Table 4.6) an upper limit estimate of BETX emissions from the BTU, assuming that biodegradation does not occur, would be about 220 tons/year. If such a condition prevails then the maximum total BETX emissions from the BWT would be about 293 tons/year which is equivalent to about 36% of the tanker loading emission rate. The upper limit estimate for benzene emission from the BWT facility would probably be about half of the above total BETX emissions, i.e., about 147 tons/year. Clearly, the effectiveness of the BTU is central to the issue of emission estimates from the BWT Facility. Although a clear demonstration of the effectiveness of the BTU is essential such information was not made available by the Alyeska Pipeline Services Company.

4.4. Emissions from the Marine Terminal Relative to Non-Marine Terminal Sources at Port Valdez

Other emissions in the Port Valdez area have been linked to a number of commercial activities, fuel storage at the Valdez Airport, the harbor, roadways, residences, as well as emissions from the combustion of fuels and wood burning. The results from the emission inventory conducted by CH2M/Hill Northwest, Inc. (CH2M/HILL, 1988) are summarized in Table 4.8. Non-terminal sources of BETX emissions are estimated to be about 2% to 2.5% of the total BETX emissions in Port Valdez (including tanker loading emissions). In contrast, BETX emissions from the marine terminal (excluding tanker loading emissions) are about of 8% to 28% of the total BETX emissions in Port Valdez. The uncertainty in the estimated emissions from the terminal operations is linked to the lack of data regarding emissions from the biological treatment units in the BWT facility. The low estimate for the emission of BETX resulting from the operation of the marine terminal (excluding tanker loading emissions) is for the case of BTU operating at 100% efficiency while the high emission estimate is for the case of no biodegradation. The total estimated BETX emission rate from all sources is about 899 tons/year with an upper limit estimate of 1112 tons/year. A summary of the percent contribution of the different sources is shown in Figures 4.2a and 4.2b. Figure 4.2a and 4.2b illustrate the percent contribution of sources (including tanker loading emissions) for the case of an efficiently operated BTU and for the case of no biodegradation, respectively.

TABLE 4.7
SUMMARY OF EMISSIONS FROM THE BWT FACILITY^(a)

	Benzene	Ethylbenzene	Toluene	Xylenes	Total BETX	Total VOC
BWT Tanks (Breathing and Working Losses)	3.73	0.016	1.9	0.11	5.7	726
Recovered Crude Tanks	0.019	0.00009	0.013	0.00078	0.033	9.1
DAF Units	28.5 [20 ^(b)]	2.43 [1.6 ^(b)]	25.9 [18.2 ^(b)]	14.58 [16.9 ^(b)]	71 [56.7 ^(b)]	83.7 -
Weir	3.69	0.36	3.38	3.51	10.94	15.1
Biotreatment Lagoons	2.1	0.16	1.9	1.76	5.9 [18.6 ^(b)] 220 ^(d)	8.2 [20.6 ^(b)]
Total	27.5	1.93	23.6	20.7	79.5^(b)	~ 848^(b)

^(a) Source: TRC Project Report No. 5885-T31, November 1989, "Emissions Inventory of Sources at Port Valdez"; ^(b) Estimated from Discharge Monitoring Reports; ^(c) Marrs, D. R. and J. P. Scott, "Estimated Annual Air Emissions from Impound Basins at Alyeska Valdez Marine Terminal BWT Facility", July 31, 1989, Woodward-Clyde Consultants, Memo. 87200543s COT-1; ^(d) Assuming no biodegradation in the biological treatment units; ^(e) Biological treatment units (BTU) are assumed to be operating efficiently; also, emission from the DAF units taken to be 51.2 tons/year.

TABLE 4.8
OTHER NON-TERMINAL SOURCES RELATIVE TO EMISSIONS FROM THE BWT FACILITY AND LOADING EMISSIONS^(a)

Chemical	Point Sources (Tons/Year)	Area Sources (Tons/Year)	Emissions from Marine Terminal Operations Excluding Direct Tanker Loading ^(b) (Tons/Year)	Tanker Loading Emissions (Tons/Year)
Benzene	0.12	2.95	28	450
Ethylbenzene	-	0.71	1.9	16
Toluene	0.005	12.5	24.2	262
Xylenes	0.0008	6.4	21	57
Total BETX	0.13	22.5	~ 79.5 [~ 293 ^(d)]	797
Total Volatile Hydrocarbons	1.9	473	~ 848 ^(b)	43,000

^(a) CH2M/Hill Northwest, Inc., "Emission Inventory for Valdez Basin, Alyeska Pipeline Services Company, Valdez, Alaska, December 1988, ANC 24595.CO; ^(b) Biological treatment units (BTU) are assumed to be operating efficiently; ^(c) Assuming no biodegradation in biological treatment units (see section 4.3.3).

SUMMARY OF MARINE TERMINAL EMISSIONS AT PORT VALDEZ

(Excluding Tanker Loading Emissions)

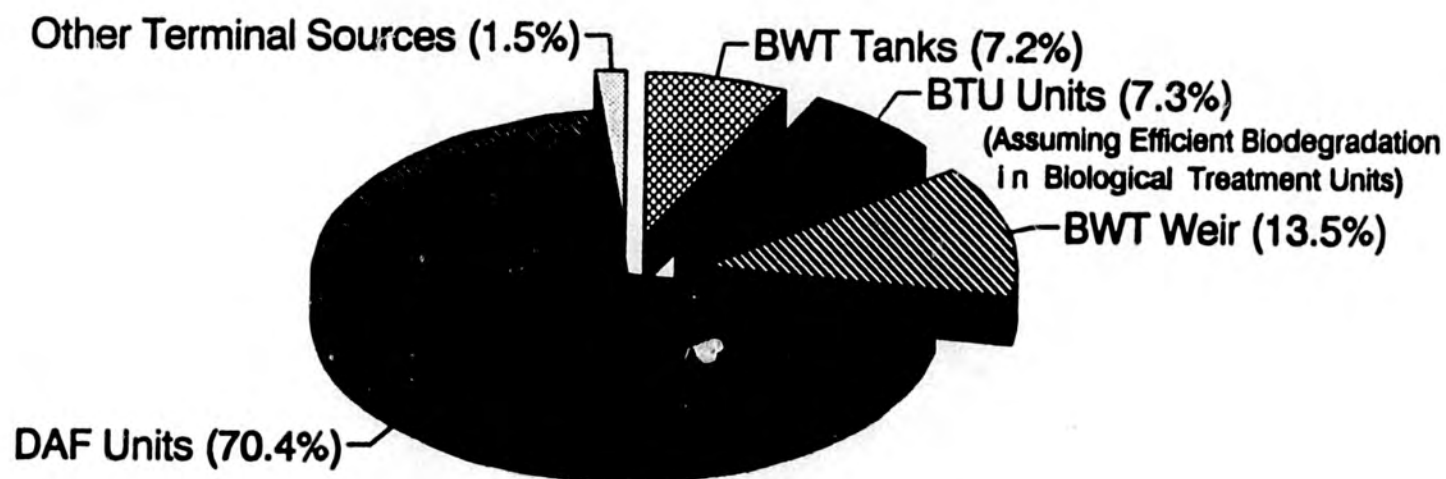


FIGURE 4.1a

SUMMARY OF MARINE TERMINAL EMISSIONS AT PORT VALDEZ

(Excluding Tanker Loading Emissions)

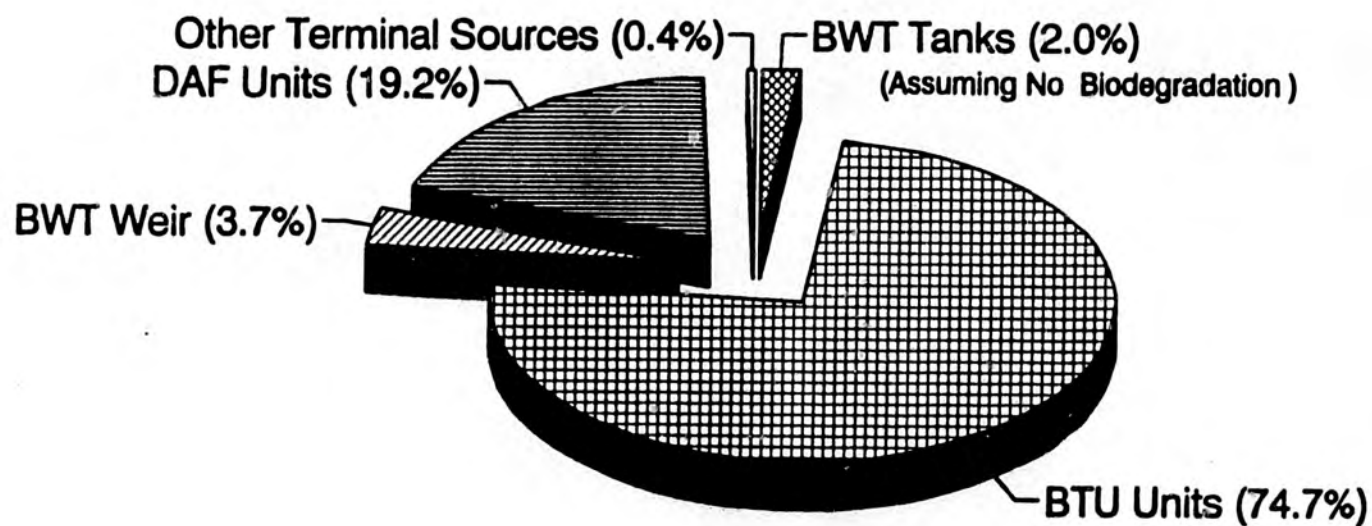


FIGURE 4.1b

SUMMARY OF EMISSION INVENTORY AT PORT VALDEZ

(Including Tanker Loading Emissions)

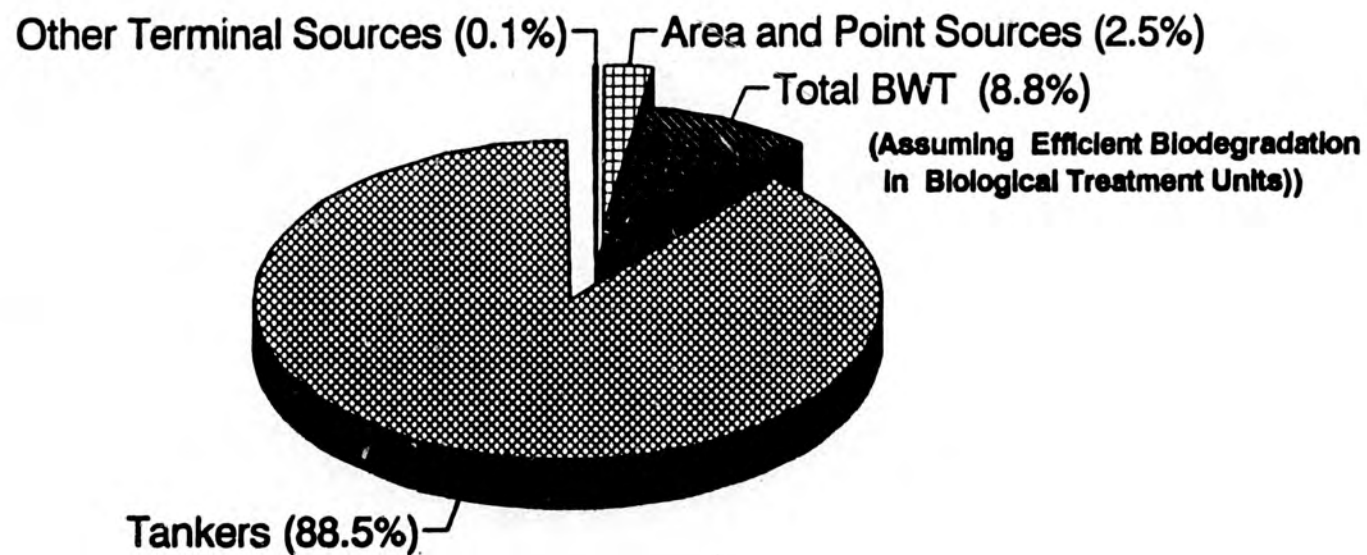


FIGURE 4.2a

SUMMARY OF EMISSION INVENTORY AT PORT VALDEZ

(Including Tanker Loading Emissions)

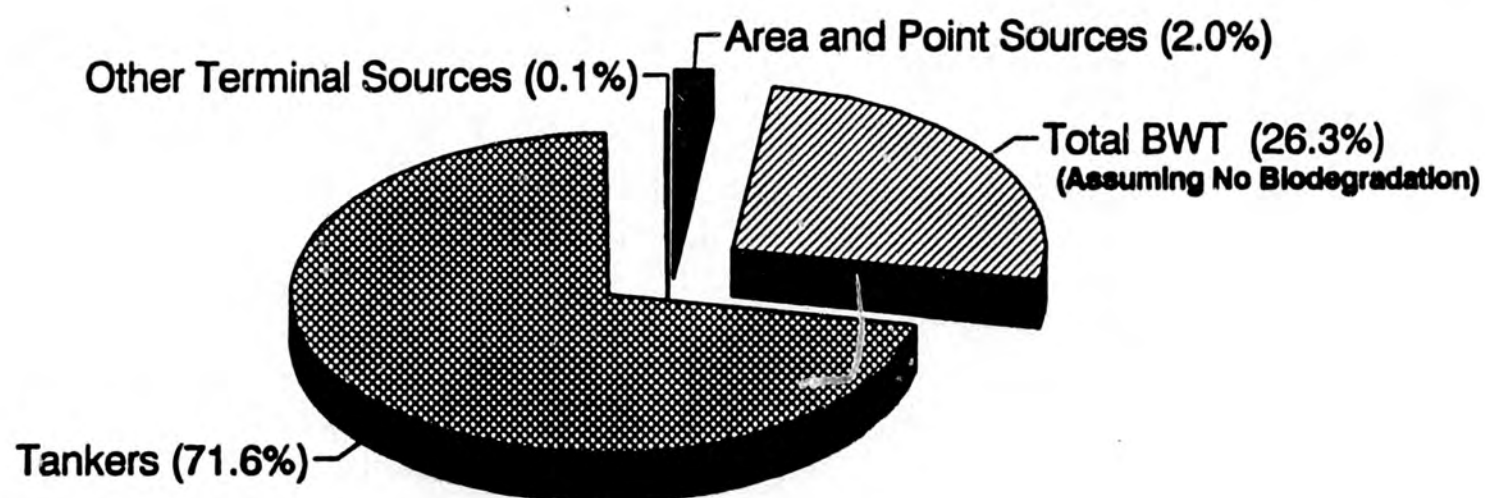


FIGURE 4.2b

4.5 Direct Discharge into the Water Column from the BWT

Direct discharge of chemicals into the water column can occur via the direct discharge of the BWT treated effluent water into the Port Valdez bay. Using information supplied in the Alyeska Discharge Monitoring Reports one can estimate the direct discharge given the average flow rate of treated water and the average concentrations of BETX in the discharged water. Estimates of the annual discharge of BETX, based on the period 1/91 through 6/91, are given in Table 4.9. In cases where effluent concentrations were below or at the detection limit the estimated discharge is shown as being at the level corresponding to or less than at the detection limit. Although there is a significant variability in the discharge of BETX through the diffuser, it appears that discharge of BETX to the water column as reported by Alyeska was reduced dramatically after 3/91. Continuous online monitoring data of BETX discharge were not available; thus, the reported discharge estimates are based on monitoring data based on the analysis of "grab" samples reported in the discharge monitoring reports provided by Alyeska.

TABLE 4.9
ESTIMATED DISCHARGE OF BETX (THROUGH THE DIFFUSER)
FROM THE BALLAST WATER TREATMENT FACILITY^(a)

Average Concentration in Effluent Discharge					
Month	Benzene (mg/l)	Toluene (mg/l)	Ethylbenzene (mg/l)	Xylenes (mg/l)	Projected Annual Emissions BETX (metric tons/year)
1/91	.0474	.0430	.0156	.0761	4.5
2/91	.047	.043	.016	.077	4.5
3/91	.13	.12	.012	.068	8.2
(4/91) ^(b)	.006	.006	.0029	.0115	.6
4/91 (5/91)	.0038	.0034	.0021	.0069	.4
(6/91)	.0117	.012	.003	.0085	.8
5/91	<.005	<.005	<.005	<.005	<.4
6/91	.012	.012	<.005	<.005	<.6

^(a) Data Obtained from the Discharge Monitoring Reports for the given month (Monitoring Discharge Reports, supplied in LOTUS 123 format, Alyeska Pipeline Services Company Analytical Services, Valdez, 1990-1991).

^(b) There are three sets of reported values for April of 1991. One set included in the report for April, one set included in the report for May and one set included in the report for June.

5. MULTIMEDIA DISTRIBUTION OF VOCs IN THE PORT VALDEZ AREA

5.1 Summary of Available Monitoring Data for VOCs

An extensive ambient air monitoring study has been conducted at the Port Valdez area since the spring of 1990 (Stophehagen et al., 1990; see also Valdez monitoring System -Monthly Operational and Data Reports, prepared by CH2M HILL for Alyeska Pipeline Services Company, Monthly reports 1990, 1991). The Valdez air monitoring system (VAMS) has been providing meteorological information and concentration data for criteria pollutants as well as BETX and *n*-hexane. Monitoring data for BETX, *n*-hexane and criteria pollutants have been collected at four sites as shown in Figure 5.1. The monitoring data (hourly measurements) from these sites were supplied by Alyeska on a computer disk in Lotus 123 format for the period 8/90 through 9/91. Data for *n*-hexane were available only for the period 4/91 through 9/91. The arithmetic averages of the hourly concentrations were computed, based only on reported data, and these are given in Tables 5.1-5.5. It is important to note that the concentrations presented in Tables 5.1-5.5 represent monthly and annual averages; therefore, these Tables do not reflect "peak" values of the monitored concentrations. For example, "peak" values of benzene concentrations have been reported at levels of about one to two orders of magnitude higher than the average concentrations.

It is interesting to note that the reported concentrations for benzene, toluene, xylenes, and *n*-hexane are in the range of typical concentrations reported for urban atmospheres (see Table 3.3 and section 7.3). This is a significant observation for it implies that the Port Valdez air basin is not pristine (despite its significant distance from major urban centers) and that the marine terminal operations lead to significant increase in the concentrations of these hydrocarbons.

Although the monitoring study was designed to provide hourly data, data were not available for a significant portion of the monitoring period. There are various plausible reasons for the lack of a complete data set and these include instrument failure, data rejected for quality control reasons, and data not collected during quality control, and instrument testing operations. Table 5.6 presents a summary of the number of missing data points (or hours not reported) for each month. Also, the percentage of the uncollected (or unreported) data is reported for the 1990 and 1991 periods as well as for the average of the entire present monitoring period. The percentage of unavailable data for the 1990 sampling period ranged from about 54.8% to 77.7% while during the 1991 monitoring period the percentage of unavailable data was in the range of 30.6% to 39.6%. The overall average percentage of missing data for the period 8/90 - 9/91 ranged from 39.8% to 48.6%. In general it is accepted that, for representative average values to be computed for a given time period, 75% of the values in the respective averaging period are required. Therefore, one is cautioned that due to the significant percentage of missing data the determination of average monitored concentrations should be regarded with caution. Presently it is unclear whether data are missing for periods of high or low emission rates. Thus,

it may be necessary to cross-reference the monitoring data with tanker loading activity if one desires accurate and meaningful average concentrations.

Despite the above concerns, in the present study, the average monitored ambient concentration of BETX and *n*-hexane were utilized to evaluate, through a simple mass balance, the estimated source strength for BETX and *n*-hexane at Port Valdez. Such an analysis can serve to ascertain whether the monitored concentrations match the emission rates estimated by Alyeska (see Chapter 7). In addition, the monitoring data can be used to estimate the multimedia concentrations of BETX and *n*-hexane as described in sections 6 and 7.

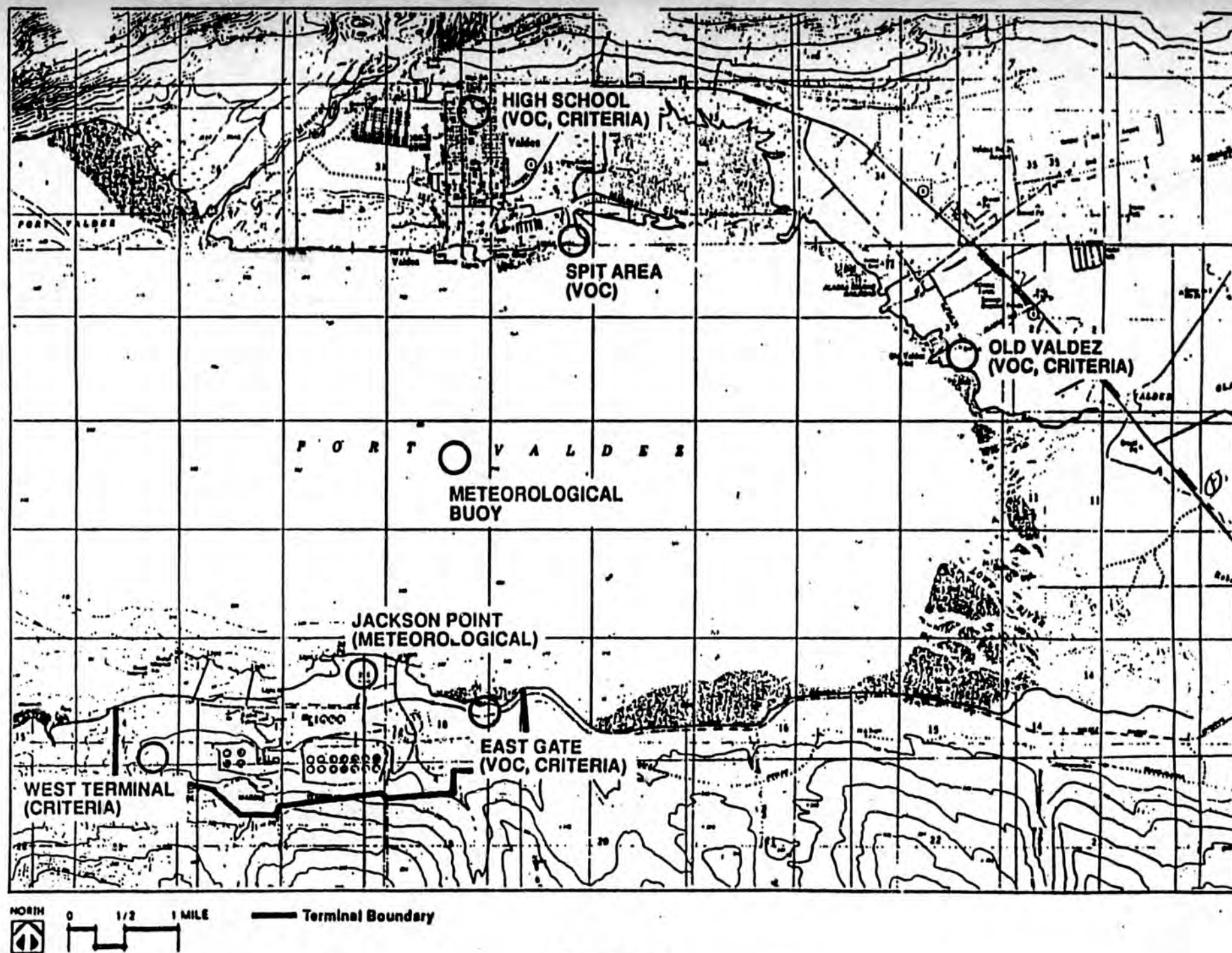


FIGURE 5.1

TABLE 5.1
Summary of Benzene Monitoring Data
for the Port Valdez Area
Source: ALYESKA VAMS MONTHLY REPORTS
Monitored Benzene Air Concentration
PPB (v/V)

Date	Old Valdez	High School	Spit	East Gate
8/90	.19	1.67	--	--
9/90	3.69	1.24	1.33	31.60
10/90	--	--	--	1.74
11/90	.23	.29	.24	.72
12/90	.79	1.28	.71	3.93
1/91	2.10	1.72	1.31	7.00
2/91	1.67	1.88	2.63	9.06
3/91	1.41	1.83	2.21	6.20
4/91	2.51	1.39	1.82	6.00
5/91	.79	.82	1.01	2.68
6/91	.73	.45	1.01	3.91
7/91	1.19	.22	1.87	12.31
8/91	1.09	.81	1.92	9.40
9/91	1.82	1.78	7.10	13.45
Average	1.40	1.18	1.93	8.21
1990	1.23	1.12	.76	9.50
1991	1.48	1.21	2.32	7.78

-- Indicates that the data files were not accessible.

TABLE 5.2
Summary of Ethylbenzene Monitoring Data
for the Port Valdez Area
Source: ALYESKA VAMS MONTHLY REPORTS
Monitored Ethylbenzene Air Concentration
PPB (v/V)

Date	Old Valdez	High School	Spit	East Gate
8/90	.15	.20	--	--
9/90	.18	.95	1.32	1.41
10/90	--	--	--	.39
11/90	.15	.15	.15	.18
12/90	.16	.40	.17	.38
1/91	.26	.48	.17	.55
2/91	.18	.43	.19	.62
3/91	.16	.39	.17	.35
4/91	.20	.29	.16	.42
5/91	.16	.28	.15	.24
6/91	.16	.17	.16	.31
7/91	.21	.15	.19	.97
8/91	.20	.20	.20	.81
9/91	.22	.28	.38	1.13
Average	.18	.34	.29	.60
1990	.16	.43	.55	.59
1991	.19	.30	.20	.60

-- Indicates that the data files were not accessible.

TABLE 5.3
Summary of Toluene Monitoring Data
for the Port Valdez Area
Source: ALYESKA VAMS MONTHLY REPORTS
Monitored Toluene Air Concentration
PPB (v/v)

Date	Old Valdez	High School	Spit	East Gate
8/90	.15	1.16	--	--
9/90	1.91	1.17	.96	24.40
10/90	--	--	--	1.03
11/90	.18	.17	.22	.38
12/90	.81	2.34	.66	2.73
1/91	1.93	2.78	1.01	4.87
2/91	1.30	2.65	1.78	6.77
3/91	.95	2.46	1.32	4.05
4/91	1.74	1.52	1.02	4.57
5/91	.54	.59	.51	2.01
6/91	.45	.64	.63	2.67
7/91	.77	.24	1.34	9.02
8/91	.73	.84	1.55	7.40
9/91	1.21	1.84	5.78	10.70
Average	.97	1.42	1.40	6.12
1990	.76	1.21	.61	7.14
1991	1.07	1.51	1.66	5.78

-- Indicates that the data files were not accessible.

TABLE 5.4
Summary of Xylenes Monitoring Data
for the Port Valdez Area
Source: ALYESKA VAMS MONTHLY REPORTS
Monitored Xylenes Air Concentration
PPB (v/V)

Date	Old Valdez	High School	Spit	East Gate
8/90	.15	.84	--	--
9/90	.74	1.90	.75	1.78
10/90	--	--	--	.60
11/90	.15	.16	.15	.21
12/90	.30	2.12	.27	.90
1/91	.70	2.42	.27	1.11
2/91	.33	1.98	.35	1.91
3/91	.22	1.80	.25	.64
4/91	.37	1.13	.21	1.33
5/91	.18	.71	.15	.58
6/91	.19	.43	.18	.53
7/91	.40	.15	.30	2.74
8/91	.38	.45	.36	2.50
9/91	.50	1.02	.98	3.65
Average	.35	1.25	.38	1.42
1990	.34	1.26	.39	.87
1991	.36	1.24	.34	1.67

-- Indicates that the data were not accessible.

TABLE 5.5
Summary of *n*-Hexane Monitoring Data
for the Port Valdez Area
Source: ALYESKA VAMS MONTHLY REPORTS
Monitored *n*-Hexane Air Concentration
PPB (v/V)

Date	Old Valdez	High School	Spit	East Gate
4/91	4.57	1.71	2.81	21.8
5/91	2.14	1.57	1.52	11.67
6/91	1.34	.75	.71	11.46
7/91	1.76	.36	1.82	29.81
8/91	1.48	.88	1.81	20.07
9/91	2.38	1.39	6.64	29.48
Average	2.28	1.11	2.55	20.72

TABLE 5.6
NUMBER OF MEASUREMENTS
AND PERCENT OF THE TOTAL POSSIBLE
HOURLY DATA NOT REPORTED

Date	Old Valdez	High School	Spit	East Gate	Total
8/90	665	572	744*	744*	744
9/90	619	445	473	635	720
10/90	744*	744*	744*	264	744
11/90	528	295	275	221	720
12/90	298	316	277	149	744
1/91	413	177	168	255	744
2/91	128	153	173	276	672
3/91	174	216	218	268	744
4/91	243	207	195	179	720
5/91	156	300	206	190	744
6/91	302	307	193	306	720
7/91	224	704	106	109	744
8/91	182	272	178	174	744
9/91	231	257	569	298	720
Total	4907	4965	4519	4068	10224
All Data	48.0%	48.6%	44.2%	39.8%	—
1990	77.7%	64.6%	68.4%	54.8%	3672
1991	31.3%	39.6%	30.6%	31.4%	6552

* Indicates that the data file was inaccessible. Unavailable data include those which were "Not Acquired", unreported values used to test "Quality Control", values "Rejected" for quality control reasons as well as those inaccessible. Unreported data were excluded from the calculation of the average concentrations. Note: there is a total of 24 possible hourly measurement values per day.

5.2 Availability of Multimedia Information

Although the major focus of this study is on the air emissions of volatile hydrocarbons, it must be recognized that airborne hydrocarbons can be transported from the atmosphere to other media (e.g., soil, water, vegetation) through intermedia transport processes such as dry and wet deposition. Monitoring data for VOCs in media other than the atmosphere are not available for the Port Valdez area; however, the distribution of VOCs in the multimedia environment can be obtained from appropriate transport and fate models. In this study a screening-level multimedia assessment was adopted as described in section 5.3 below.

5.3 The Multimedia Screening-Level Approach

Pollutants which are released to the environment as the result of a variety of human-related activities (air emissions and/or direct discharge to surface water, etc.) move across environmental boundaries and are therefore found in most media. The environmental impact posed by chemical contaminants is proportional to their concentration in the various environmental media.

Pollutant concentrations can, in principle, be obtained by either pollutant fate and transport modeling or field measurements. The above tasks demand an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants among the different environmental media. Unfortunately, multimedia monitoring is a difficult task and requires a formidable expense for monitoring all potential air toxics. Thus, various estimation methods, which can be coupled with field monitoring, have been developed for the purpose of determining human exposure to air toxics and subsequent pollutant intake. Given the complexity of the issues involved one should resort as a first step to a multimedia screening-level analysis in order to determine (or verify) which intermedia transport pathways are important (Cohen and Ryan, 1985b; Cohen, 1986b, 1986c, 1987). Such a screening-level multimedia approach can be used to estimate the distribution of various chemicals in the environment (e.g., in air, soil, water, biota) and to conduct an overall mass balance analysis on the released contaminants. Multimedia concentrations of the study chemicals can then be used to estimate exposures of the human and other ecological receptors, to the released chemicals, via various exposure pathways (e.g., air, water, food).

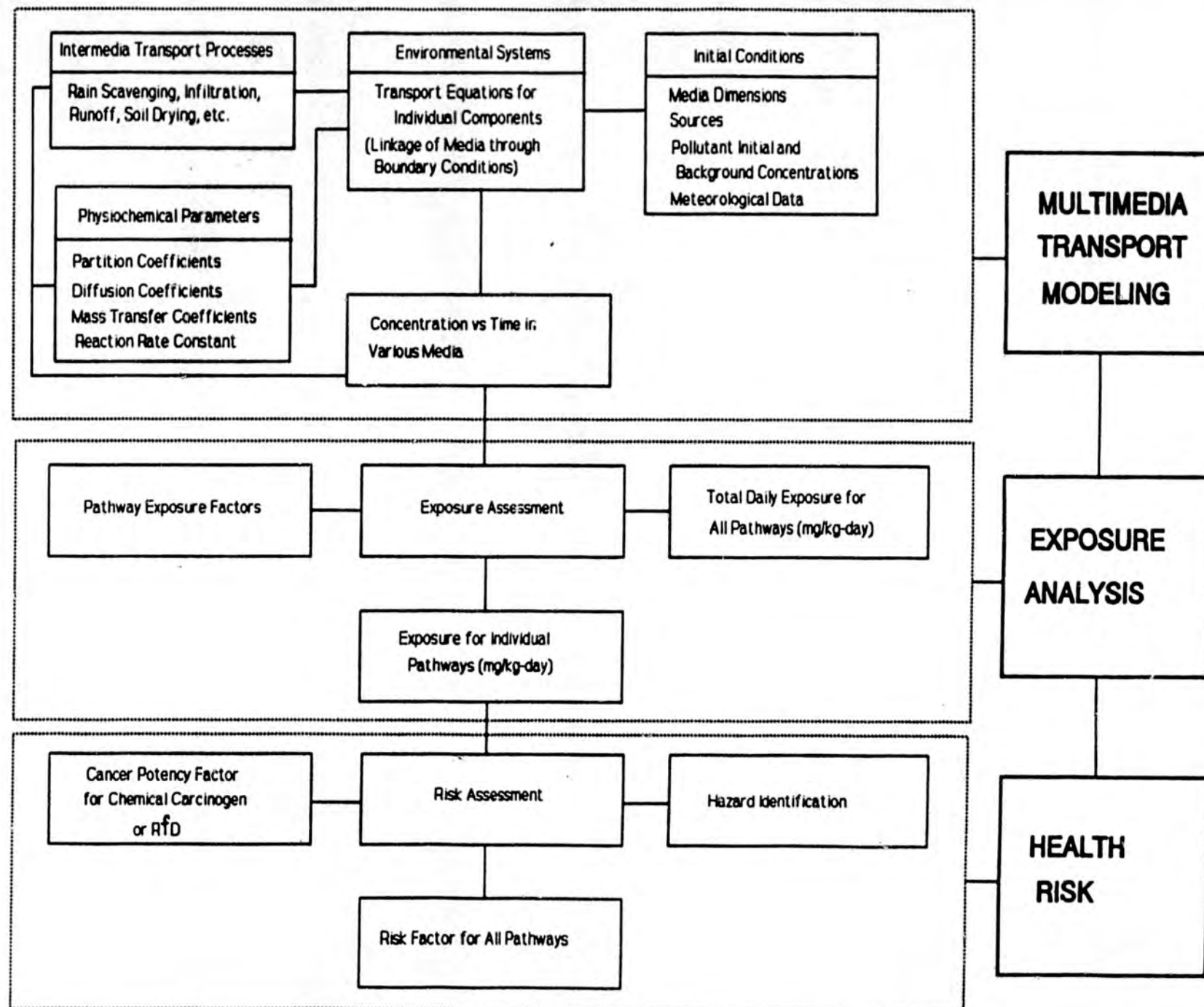
The movement of pollutants across environmental phase boundaries (e.g., air/water, soil/air) is the result of a variety of intermedia transport processes. As an illustration, a list of some of the major intermedia transport processes is given in Table 5.7. Detailed discussions of intermedia transfer processes can be found in a number of references on the subject area (Cohen, 1986a; Allen et al., 1989, Onishi et al., 1990).

TABLE 5.7
SUMMARY OF MAJOR INTERMEDIA TRANSPORT PROCESSES

- | |
|--|
| <ol style="list-style-type: none">1. Transport from Atmosphere to Soil and Water<ol style="list-style-type: none">a. Dry deposition of gaseous and particulate pollutantsb. Adsorption onto particle matter and subsequent dry and wet depositionc. Rain scavenging of gases and particlesd. Infiltratione. Runoff2. Transport from Water to Atmosphere, Sediment, Suspended Solids, and Biota<ol style="list-style-type: none">a. Evaporationb. Aerosol formation at the air/water interfacec. Sorption by sediment and suspended solidsd. Sedimentation and resuspension of solidse. Uptake and release by biota3. Transport from Soil to Atmosphere, Water, Sediment, and Biota<ol style="list-style-type: none">a. Volatilization from soil and vegetationb. Dissolution in rain water which is associated with infiltration and runoffc. Leaching to groundwaterd. Adsorption on soil particles and transport by runoff or wind erosione. Resuspension of contaminated soil particles by windf. Uptake by biomass such as microorganisms, plants, and animals |
|--|

The global scheme for the multimedia modeling approach is shown schematically in Figure 5.2. The input variables include media properties, physicochemical and thermodynamic properties of the pollutant under consideration, climatic conditions, and initial background concentrations. Additionally, intermedia transport as well as transformation processes must be specified. Finally, it is important to realize that the main driving force in any multimedia model is the source (or environmental emissions) of the chemical under consideration. Pollutants can be released from a variety of sources as summarized in Table 4.1.

FIGURE 5.2



6. THE MULTIMEDIA MODELING APPROACH

6.1 Overview

Multimedia models of pollutant transport and fate can be formulated as a collection of uniform (i.e., well-mixed) compartments, each representing a different sector of the environment, or they may involve detail modeling of temporal and spatial variations. In the alternative, they may be a combination of both uniform and non-uniform compartments (Cohen et al., 1991). Reviews of multimedia transport and fate models are available in a number of recent references (Allen et al., 1989; Cohen, 1986a-1986d; Onishi et al., 1990). Briefly, given appropriate source information, physicochemical properties, geographical information, and meteorological data, concentration fields can be determined, using appropriate multimedia transport and fate models and these can be coupled with exposure and risk-assessment models as is shown schematically in Figure 5.2.

Given the complex terrain of the Port Valdez area and the uncertainty in emission estimates, the variability in the meteorology, and uncertainty in chemical-specific parameters (e.g., environmental degradation rate constants), it was decided to evaluate the effect of the various model parameters in a screening-level analysis rather than conduct a detailed time-series analysis. The spatial-compartmental multimedia (SMCM) modeling approach developed by Cohen et al. (1990) was selected for the analysis of the distribution of hydrocarbons released from the Valdez Marine Terminal. The details of the modeling approach have been described in a number of references (Cohen et al., 1990; Onishi et al., 1990).

Briefly, the SMCM model makes use of both uniform (air, water, biota, suspended solids) and non-uniform compartments (soil and sediment). An illustration for a six compartment environment considered in the SMCM model is shown in Figure 6.1. The model equations of both the uniform and non-uniform compartments, the estimation methods of physicochemical parameters of pollutants, and source types for possible simulation scenarios, are discussed in Appendix A. In the SMCM model the soil and sediment compartments are treated using one-dimensional convective-diffusion equations which allow for degradation. The air compartment is treated as a uniform compartment with a correction for non-ideal mixing. The water compartment is also treated as a uniform compartment.

The SMCM model yields volume averaged concentrations in the modeled region. The source emission is allowed to disperse over the entire modeled region and thus, such a treatment provides a lower limit estimate of the volume averaged concentration. The important parameters associated with the air compartment include the mixing height, the atmospheric degradation rate for the compound under consideration, the average wind speed, and the convective atmospheric residence time. Although the above treatment is obviously an oversimplification of the situation prevailing in the Port Valdez area, it is expected to yield reasonable mass balance results as confirmed in a number of previous studies (Cohen et al., 1990; Cohen and Ryan, 1985b; Cohen,

1986c). One is cautioned that the SMCMM model is not a substitute for detailed dispersion modeling. However, the SMCMM model can be coupled with concentration estimates from dispersion models or monitoring data. For example, given air phase concentrations the SMCMM model can be used to calculate chemical distribution in the environment and intermedia transfers of released hydrocarbons (Cohen et al., 1990).

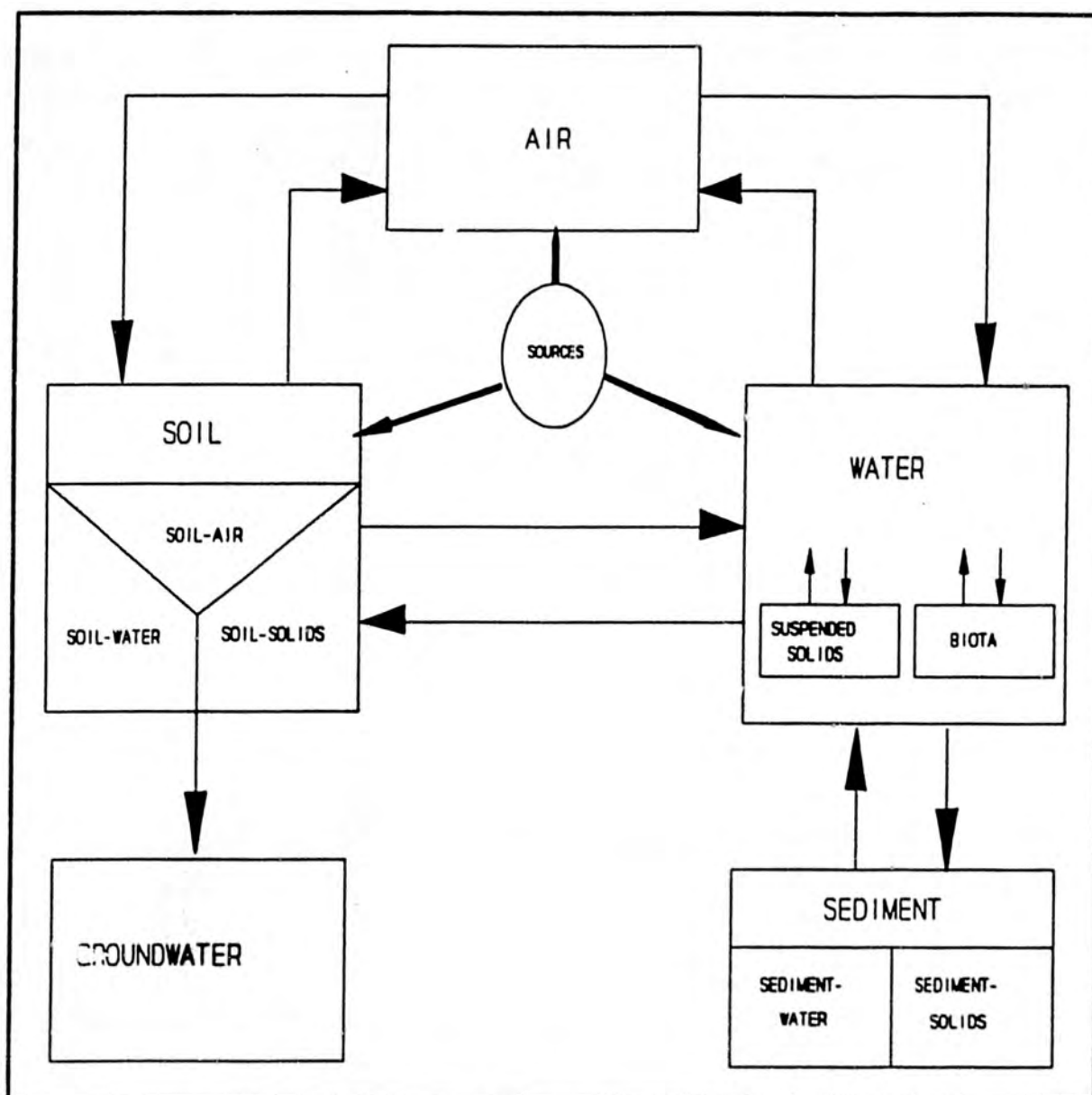


Figure 6.1 - Schematic Representation of the SMC Model Environment

6.2 Model Input Parameters

Multimedia analysis for airborne crude oil hydrocarbons requires knowledge of the source strength for the study chemicals or their atmospheric concentrations, physicochemical data for these chemicals, basic geographical data for the region, and meteorological data. The basic model parameters used in the study are described in the following sections.

6.2.1 Environmental Media

The environmental media can be categorized into two distinct groups: non-biological and biological environmental compartments, and the human receptor as a separate environmental compartment. The major non-biological and biological environmental media can be classified as given below in Table 6.1. The non-chemical specific information needed to describe the study area are listed in Table 6.2.

TABLE 6.1
MAJOR ENVIRONMENTAL MEDIA

<u>Non-Biological Compartment</u>	<u>Biological Compartment</u>
Atmosphere	Aquatic Fauna
Surface water	Terrestrial Animals
Sediment	Vegetation
Surface Water	Food (solid and liquid)
Soil	
Groundwater	

In the present study groundwater was not considered since it is not expected that airborne hydrocarbons will migrate to a significant extent down the soil column. Also, the biological compartments are not treated in detail within the SMCM model but they are considered separately in the exposure assessment analysis described in section 8. The effect of some of the pertinent parameters on the predicted environmental distribution of the released study chemicals listed in Table 6.2 are discussed in section 7.

TABLE 6.2
MAJOR SMCM MEDIA INPUT PARAMETERS

Compartment	Required Parameters
Atmosphere	● Mixing height ● Average Wind Speed ● Ambient Temperature (monthly average values)
Water	● Depth ● Concentration of suspended solids ● Flow Rate ● Temperature
Suspended Soils	● Average particle diameter ● Concentration of suspended solids ● Fraction of organic carbon ● Average density of suspended solids
Sediment	● Depth ● Fraction Organic Carbon ● Density of Sediment particles
Soil	● Soil Depth ● Soil type and usage of soil (e.g., type of vegetative cover) ● Fraction of Organic carbon ● Density of soil particles ● Soil slope (slope of the terrain in relation to surface water)
Other Parameters	● Interfacial areas: ● air/soil ● air/water ● water/sediment

6.2.2 Description of the Study Area and Associated Input Parameters

The Alyeska Marine Terminal is located near Jackson Point on the south shore of Port Valdez surrounded by the Chugach mountains. The city of Valdez is approximately four miles across the bay from the marine terminal. The City of Valdez and the Valdez Airport are located in a flat terrain near the shoreline of the bay. The flat glacial terrain is forested except for the town area, the tidal flats area along the northern and eastern shores, and the drainage area from the Robe and Lowe rivers to the east. The ridge lines surrounding the bay are about 200 to 4000 feet in elevation.

6.2.2.1 Area of Modeled Region

The modeled region was selected by following the 500 foot contour line on USGS maps of the area. As the area was steeply sloped at the 500 foot contour line, choosing a higher value would not have significantly altered the area. Robe Lake and Shoup Bay were not included in the water compartment to avoid the complexities involved in having three different water bodies in the same region. The above simplification is reasonable given the small size of the above water bodies relative to the entire bay. The entrance point to the Valdez narrows was selected to mark the beginning of the Port of Valdez. The air/water interfacial area was calculated to be 110.6 km². The air/soil interfacial area was calculated to be 75.3 km².

6.2.2.2 Air Compartment

Near the surface level, winds are channeled both along the Valdez bay and along the intersecting valleys. Up and down valley flows dominate the near surface winds. The topography of the Port Valdez area leads to an east-west channeling of the wind although complex wind patterns exist along the walls of the bay where outflow from the intersecting valleys can lead to local eddies (Peterson and Hoffnagle, 1990). The ventilation rates for the Valdez bay are significant; approximately 40 to 45 percent of the volume of the air basin is exchanged every six hours (See "Summary Report: Air Quality for the Trans Alaska Pipeline System: Terminal", Alyeska Pipeline Services Company, April 1974).

The mixing height in the basin can vary from about 100 meters to 600 meters⁽⁶⁾. Within the mixing height, often referred to as the thickness of the ground based convective layer, turbulence is generally high. It has been suggested⁽¹⁾ that a ventilation box-type model for the basin (essentially a fully-mixed basin model) is a reasonable approach to estimating the basin-

⁶ "Summary Report: Air Quality for the Trans Alaska Pipeline System: Terminal", Alyeska Pipeline Service Company, April 1974

wide impact of air quality due to terminal-related emissions in the Valdez area. According to this approach, given that sources are continuous and that a chemical in the atmosphere may undergo chemical transformation, and if one assumes a first order reaction kinetics with respect to the atmospheric chemical concentration, then the average-basin concentration, $C(t)$, is given by

$$C(t) = \frac{(S/V)(1 - e^{-(\tau^{-1} + k)t})}{\tau^{-1} + k} \quad (6.1)$$

where t is the time and τ is defined as the convective residence time (hr) given by

$$\tau = V/Q = 1/N \quad (6.2)$$

in which N is the number of air changes per unit time. The volumetric flow rate into/out of the basin is given by Q , V is the mixing volume (i.e., the mixing height multiplied by the area of the basin), k is the reaction rate constant (see section 6.3.3), S is the source strength (mass/time), and C_0 is the initial basin-wide average concentration of the pollutant. At steady state (i.e., $\tau^{-1} + k > 1$) the concentration, $C(t)$, is given by

$$C(t) = \frac{(S/V)}{\tau^{-1} + k} \quad (6.3)$$

Equation 6.3 assumes that the area outside Valdez is pristine and that intermedia transfers are negligible. Equation 6.3 can be used to approximate the basin-wide average annual concentrations knowing the ventilation rate (or τ), the reaction rate constant, and the volume of the air basin. The above approach is not appropriate for obtaining short-term average values, but for long term averages (e.g., annual averages) it should yield reasonable results. A discussion of the above approximate treatment in relation to the monitored concentrations is given in chapter 7.

As described in section 6.1 and Appendix B, in the current study a fully-mixed basin model was used for the air compartment since basin-wide impacts were of interest. The mixing height for the base case simulations was set to 350 meters and the effect of the mixing height was determined through a series of simulations. Finally, the average wind speed of 2.68 meters/second (~6 mph) (Valdez Coastal Management Program, Community Development Department, City of Valdez, Alaska, September, 1986) was used for the base case SMCM simulation. The effect of wind speed for the wind speed range of 1 to 6 meters per second was investigated through a series of simulations. Finally, the monthly average ambient temperature, precipitation, and snowfall were obtained from the National Oceanic and Atmospheric Administration, Local Climatological Data.

6.2.2.3 Soil Compartment

The organic carbon fraction in the soil in the Port Valdez region can reach values as high as 0.4 (Exploratory Soil Survey of Alaska). Low organic fraction is found in the porous and well drained lowlands while a high organic content is found in the vegetated higher areas. Data on the organic content of the soil in the Valdez region were not available. Thus, in the base case simulations a value of 0.6% organic carbon content was selected and the effect of different values of the soil organic content was investigated through a series of model simulations.

6.2.2.4 Water Compartment

Though precipitation, water run-off and tidal flow all contribute to exchange of water between Port Valdez and Prince William Sound, tidal flow was assumed to be dominant and was estimated from the difference between mean high and mean low tides. This value closely corresponds to the reported 1.6% tidal prism (Valdez Coastal Management Program, Community Development Department, City of Valdez, Alaska, September, 1986) assuming two high tides per day. The estimated tidal flow value was for the half port simulation and $2.67 \times 10^7 \text{ m}^3/\text{hr}$.

6.2.2.5 Sediment

Port Valdez is described as having a, "remarkably flat horizontal bottom". Thus, the water/sediment area was assumed to be equal to the air/water interfacial area. The overall mean depth of the water column is about 180 meters with a maximum depth of about 247 meters (Valdez Coastal Management Program, Community Development Department, City of Valdez, Alaska, September, 1986). The water temperature for the base case was estimated to be about 2°C. The effect of variations in the water temperature from the value used in the base case was investigated in a number of simulations. The concentration of the suspended solids in the water column varies widely and a representative concentration of 5×10^{-5} volume percent was used for the base case (Sharma and Burbank, 1973).

The fraction of organic carbon in the surface sediment of Port Valdez was reported to be in the range of .001 and .006 (Hood et al., 1973). A value of .4% organic carbon content was chosen as a reasonable value for the base case and the effect of varying the organic carbon content relative to the base case value was investigated. The same organic content was assumed for the suspended solids in the water column.

6.3 Chemical-Specific Transport and Fate Parameters

6.3.1 Physicochemical Properties

Physicochemical properties for the pollutants of interest are needed for both the analysis of intermedia transport parameters (e.g., mass transfer coefficients) as well as for the prediction of parameters such as partition coefficients, biotransfer factors when partition coefficient information is not available. A compilation of the basic physicochemical properties for the study chemicals is given in Table 6.4. In addition to the basic physicochemical parameters listed in Table 6.4, the aqueous solubility, the octanol/water partition coefficient, the organic carbon/water partition coefficient, and the Henry's law constant are given in Table 6.5 for the study chemicals.

The Henry's law constant ($\text{Pa}\cdot\text{gmol}/\text{m}^3$) relates the partial pressure of the chemical in the air phase to the aqueous phase concentration, under equilibrium conditions,

$$H_i = P_i / C_i \quad (6.4)$$

where P_i is the partial pressure of the chemical in the air phase (units of Pa) and C_i is the concentration in the water phase (gmol/m^3).

The octanol/water partition coefficient is defined as

$$K_{ow} = C_o / C_w \quad (6.5)$$

in which C_o is the solute concentration in the octanol phase (mg/m^3) and C_w is the solute concentration in the water phase (mg/m^3). K_{ow} indicates the tendency of a chemical to partition into an organic phase (e.g., lipid phase or other hydrophobic organic phase). Thus, the bioconcentration factors and K_{oc} are often correlated with K_{ow} . Also, it is interesting to note that K_{ow} itself can be correlated with various physicochemical properties (e.g., solubility). For example, K_{ow} for aromatic compounds (benzene and benzene derivatives) can be estimated from the following correlation (Hansch et al., 1968)

$$\text{Log}(1/S) = 0.996\text{Log}K_{ow} - 0.339 \quad (6.6)$$

in which S is the aqueous solubility in units of gmol/L . A similar correlation is available for polynuclear aromatics (Yalkowski and Valvani, 1979)

$$\text{Log}(S) = -0.88\text{Log}K_{ow} - 0.01T_m - 0.012 \quad (6.7)$$

in which S is the aqueous solubility in units of gmol/L and T_m is the melting temperature. If T_m is less than 25°C then as recommended a value of 25 should be used for T_m .

The organic carbon/water partition coefficient is defined as

$$K_{oc} = \frac{(\text{mg solute/g organic carbon})}{(\text{mg solute/ml solution})} \quad (6.8)$$

The organic carbon/water partition coefficient is used to determine the soil solids/water and sediment solids/water partition coefficient (Kenaga, 1980; Karickhoff et al., 1979; Lyman et al., 1990). This partition coefficient designated by H_{ow} is defined as

$$H_{ow} = C_s/C_w = K_{oc}\chi_s\rho_s \quad (6.9)$$

in which C_s and C_w are the solid phase and water phase concentrations, respectively, χ_s is the mass fraction of organic carbon in the soil or sediment, and ρ_s is the density of the soil or sediment particles.

In the absence of experimental data the organic carbon/water partition coefficient can be estimated from a number of available correlation. For example, Karickhoff et al, (1979) proposed the following general correlation

$$\text{Log}K_{oc} = \text{Log}K_{ow} - 0.21 \quad (6.10)$$

A more recent correlation was proposed by Brown et al. (1990)

$$\text{Log}K_{oc} = -0.54\text{Log}(S) + 0.44 \quad (6.11)$$

where S is the solubility in mole fraction.

Bioconcentration factors (BCFs) serve to estimate the accumulation of the pollutant in biota given estimates of the aqueous phase concentration or the concentration of the chemical in the sediment. The bioconcentration factors are defined as

$$BCF = C_b/C_w \quad (6.12)$$

in which C_b and C_w are the concentrations of the chemical in biota and in the aqueous phase (in identical units), respectively. A number of correlations for BCF which are useful in estimating the bioconcentration factors are given below.

A general correlation for BCF (based on studies with flathead minow, bluegill sunfish, rainbow trout, and mosquito fish) was proposed by Veith et al. (1980)

$$\text{Log}(BCF) = 0.76\text{Log}(K_{ow}) - 0.23 \quad (6.13)$$

Another correlation which is applicable for shell fish was developed by Southworth et al. (1978)

$$\text{Log}(\text{BCF}) = 0.819\text{Log}(K_{ow}) - 1.146 \quad (6.14)$$

and a correlation for bioconcentration in sessile marine organisms was proposed by McFarland (1984)

$$\text{Log}(\text{BCF}) = 0.98\text{Log}(K_{ow}) - 0.063 \quad (6.15)$$

A specific correlation for benzene derivatives was proposed by Lu (1974)

$$\text{Log}(\text{BCF}) = 0.206 + 0.6669\text{Log}(K_{ow}) \quad (6.16)$$

and a correlation which applies to the bioconcentration of PAHs in *Daphnia Pulex* was reported by Beauchanp and Schmieder (1978)

$$\text{Log}(\text{BCF}) = 0.752\text{Log}(K_{ow}) - 0.4362 \quad (6.17)$$

Bioconcentration factors are chemical-specific and organism-specific. Bioconcentration factors may also vary with environmental conditions such as temperature, pH, and salinity. Nonetheless, when experimental or field values are unavailable, correlations such as the ones given above can be used to obtain estimates of the expected level of contaminants accumulation in marine species. The BCF value listed in Table 6.5 represent reasonable mean values derived from both available data and the correlations presented above (Lyman et al., 1990; Howard, 1989, 1990; ATSDR, Toxicological Profiles for the study chemicals).

TABLE 6.4
PHYSICOCHEMICAL PROPERTIES OF HYDROCARBONS
CONSIDERED FOR THE VALDEZ MULTIMEDIA STUDY ^(a)

Chemical	Chemical Type	Molecular Weight (g/mol)	Boiling Point (K)	Molal Volume at Boiling Point (cm ³ /gmol)
Benzene	Aromatic	78.11	353.25	96.5
Ethylbenzene	Aromatic	106.16	409.40	123
Toluene	Aromatic	92.13	383.75	107
Xylenes (mixture)	Aromatic	106.16	411.65	140.4
n-Hexane	Alkane	86.17	342.15	139.4
Styrene	Aromatic	104.16	418.35	—
Naphthalene	Aromatic	128.19	491.15	147.6
Fluorene	PAH	166.2	568.15	187.9
Benzo(a)Pyrene	PAH	252.3	495	—

^(a) The above properties were obtained from the following sources:

- (1) Agency for Toxic Substances and Disease Registry Toxicological Profiles;
- (2) Reid, R.C., Praunitz, J. M., and T. K. Sherwood, The Properties of Liquids and Gases, McGraw-Hill Book Company (1987).

TABLE 6.5
PHYSICOCHEMICAL PROPERTIES (CONTINUED)

Chemical	Solubility (mg/l)	Partition Coefficients	Henry's Law Constant (Pa·m ³ /gmol)
Benzene	1780 @ 25 °C	Log K _{ow} = 1.9 K _{ow} = 60 BCF = 23, 3 ^(a)	550
Ethylbenzene	140 @ 15°C 161 @ 20°C	Log K _{ow} = 3.23 K _{ow} = 247 BCF = 198, 32 ^(a)	670 @ 20°C 800 @ 25°C
Toluene	515 @ 20°C	Log K _{ow} = 2.79 K _{ow} = 295 BCF = 97, 14 ^(a)	674.8
Xylenes (mixture)	130-200 @25°C	Log K _{ow} = 3.2 K _{ow} = 260 BCF = 190, 30 ^(a)	532
n-Hexane	16.4 @ 4°C 15.2 @ 14°C	Log K _{ow} = 4.11 BCF = 834, 166 ^(a)	99620 ^(b) @ 2°C
Styrene	300 @ 20°C	log K _{ow} = 2.95 K _{ow} = 550 BCF = 126, 19 ^(a)	264.5
Fluorene	1.7 - 2.0	Log K _{ow} = 4.12 K _{ow} = 7.3 x 10 ³ BCF = 1000, 170 ^(a)	0.65
Naphtalene	31.7 @ 20°C	Log K _{ow} = 3.44 K _{ow} = 933 BCF = 426	46.6
Benzo(a)Pyrene	3.8x10 ⁻¹²	Log K _{ow} = 6.06 K _{ow} = 5.5x10 ⁶ BCF = 20,000	0.049

^(a) Estimated BCF values for shell fish using the correlation of Southworth et al. (1978); ^(b) Estimated assuming ideal solution ($H = P^{\text{sat}}/C_s$, where P^{sat} is the saturation vapor pressure and C_s is the solubility); ^(c) The above properties were obtained from the following sources: (1) Lyman et al., 1990; (2) Howard, 1989, 1990; (3) ATSDR, Toxicological Profiles for the study chemicals; (3) IUPAC, Solubility Data Series vol. 37, Hydrocarbons with Water and Sea Water, Part 1, C5-C7; (4) Tewari, Miller, Wasik and Martire, "Aqueous Solubility and Octanol Water Partition Coefficients of Organic Compounds at 25 °C", Journal of Chemical Engineering Data 1982, 27, 451-454.

6.3.2 Transport Parameters

Interfacial mass transfer coefficients are required to be able to predict the flux of the chemical across the various interfaces and thus the accumulation of the pollutants in the environmental medium of interest. The intermedia transport coefficients are calculated internally in the SMCM model using the various approaches as listed in Table 6.6.

TABLE 6.6
TRANSPORT PARAMETERS ^(a)

Mass Transfer Coefficients	
a. Overall mass transfer coefficients (K_{aw})	Lewis et al. (1924)
b. Gas-side mass transfer coefficient at the atmosphere-soil interface ($k_{a,sm}$)	Fernandez de la Mora et al. (1982)
c. Overall volumetric water/biota mass transfer coefficients	Cohen and Ryan (1985)
d. Water-side mass transfer at the water/suspended solid interface	Rowe et al. (1965)
e. Sediment-water mass transfer coefficient (water-side)	Thibodeaux et al. (1982)
f. Air-water mass transfer coefficient (air-side)	Brutsaert (1975)
g. Liquid side mass transfer coefficient at the water-air interface	Cohen and Ryan (1985)
Diffusion Coefficients	
a. Air phase diffusion coefficient (D_a)	Chapman-Enskog method (1979)
b. Water phase diffusion coefficient (D_w)	Wilke-Chang correlation (1979)
c. Effective diffusivity in the soil matrix (D_{sm})	Jury et al. (1983)
d. Air and water phase tortuosities (τ_a and τ_w)	Sallam et al. (1984)
e. Effective diffusivity in the sediment (D_{sm})	Apply Eqns. 30-32 with $\theta_w = 1 - \theta_a$, (i.e., saturated soil).
Transport Parameters Associated with Rainfall	
a. Infiltration rate (V_w)	Clay (1992)
b. Runoff rate (R_a)	Clay (1992)
c. Soil drying rate	Van Bavel (1966)

^(a) Adapted from Cohen et al. (1990)

6.3.3 Reaction Rate Constants

The degradation of the compounds in the various environmental media as the results of chemical, photochemical, or biochemical reactions must be considered in the analysis of the transport and fate of the study chemicals. In the current approach first order degradation constants with respect to the concentration of the chemical in the environment have been utilized. The degradation rate constants are given in Tables 6.7-6.10.

The atmospheric degradation of the study chemicals is the key process affecting the persistence of the emitted hydrocarbons in the atmospheric compartment at Port Valdez. For the study chemicals considered in this work the reaction with atmospheric hydroxyls was considered to be the dominant reaction (Atkinson, 1989) and thus the degradation rate was expressed as

$$R_i = k_i[OH][C_i] \quad (6.18)$$

in which R_i is the reaction rate, k_i is the reaction rate constant, and $[OH]$ and $[C_i]$ are the concentrations of the hydroxyl radical and the chemical of concern, respectively. It is often convenient to combine the rate constant k_i and the concentration of the hydroxyl free radicals $[OH]$ such that the reaction rate is expressed by

$$R_i = k'_i[C_i] \quad (6.19)$$

in which

$$k'_i = k_i[OH] \quad (6.20)$$

The values of the rate constant k_i for the study chemicals were obtained from the temperature-dependent rate constants given by Atkinson (1989) and the computed pseudo-first order rate constants k'_i are given in Table 6.7. It was found that the rate constants published by Howard et al. (1990) differed to some extent from the values calculated from the expressions given by Atkinson (1989). The values given in the critical review by Atkinson (1989), however, are considered more reliable. Also, since the actual concentration of the hydroxyl free radicals in the Port Valdez atmosphere was not available, reasonable average values for k_i were utilized (see Table 6.7 and 6.11).

TABLE 6.7
RATE CONSTANTS FOR ATMOSPHERIC REACTION WITH HYDROXYL RADICALS

Compound	High [OH] High T	High [OH] Low T	High [OH] Average T	Low [OH] High T	Low [OH] Low T	Low [OH] Average T	Average [OH], T
Benzene	.004301	.004084	.004189	.00043	.000408	.000419	.002094
Ethylbenzene	.02556	.02556	.02556	.002556	.002556	.002556	.01278
Toluene	.022644	.024751	.023693	.002264	.002475	.002369	.011846
Xylenes	.054	.054	.054	.0054	.0054	.0054	.027
Naphthalene	.089027	.111414	.099797	.008903	.011141	.00998	.049898
n-Hexane	.019382	.01815	.018744	.001938	.001815	.001874	.009372

- The above rate constants are in units of hr^{-1} . The High concentration of the Hydroxyl ions ([OH]) is 10^6 ions/ cm^3 , the low concentration is 10^3 ions/ cm^3 , the average concentration is 5×10^3 ions/ cm^3 . The High temperature (T) is approximately 52°F ; the low temperature is 19°F ; the average temperature is 34°F .
- Typical Hydroxyl radical concentrations data were obtained from Lyman et al., Handbook of Chemical Property Estimation Methods, American Chemical Society, Washington, D.C. (1990).
- The rate constant expressions were obtained from Atkinson, R., Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds, Journal of Physical and Chemical Reference Data, Monograph No.1, (1989).

Degradation of the study chemicals in the aquatic environment is primarily due to photolysis, photooxidation, and biodegradation. Degradation of the study chemicals in the soil is expected to occur primarily via biodegradation. At the expected low environmental concentrations, the reaction kinetics for both the soil and water media were expressed by a simple first order kinetics

$$r_s = k_s [C]_s \quad (6.21)$$

in which k_s is the reaction rate constant (hr^{-1}) and $[C]_s$ is the concentration of the given chemical in the either the soil or water compartments (e.g., $\mu\text{g}/\text{m}^3$), and r_s is the degradation rate per unit volume (e.g., $\mu\text{g}/\text{m}^3 \cdot \text{hr}$).

Suggested high and low values of aquatic degradation rate constants and the degradation rate constants for soils are presented in Tables 6.8 and 6.9. In both Tables 6.8 and 6.9 the geometric mean values and the arithmetic average of the high and low reported degradation rate constant are given. Clearly, there is a variation in the rate constants depending on a variety of environmental conditions. It is difficult to determine the precise degradation constant which is applicable to a particular location without carrying out actual laboratory or field studies designed for the specific media properties for the region of interest. Thus, regardless of which average value is used, these values should only be regarded as estimated values for the region of study.

TABLE 6.8
AQUATIC DEGRADATION RATE CONSTANTS ^(a)

Compound	Aquatic Reaction Rate Constant Maximum (hr ⁻¹)	Aquatic Reaction Rate Constant Minimum (hr ⁻¹)	Aquatic Reaction Rate Constant Geometric Mean (hr ⁻¹)	Aquatic Reaction Rate Constant (Arithmetic Mean) (hr ⁻¹)
Benzene	.0058	.001805	.00323	.00379
Ethylbenzene	.009627	.002888	.00527	.00626
Toluene	.00722	.001313	.003079	.00427
mixed Xylenes	.004126	.001031	.002063	.002579
Styrene	0.002	0.00103	0.0014	0.0015
Naphthalene	.057702	.001444	.009128	.02957
Fluorene	0.063	0.011	0.026	0.037
Benzo(a)Pyrene	0.0005	0.000067	0.00018	0.00028

^(a) Howard, H. P., Handbook of Environmental Degradation Rates, Lewis Publishers, Chelsea, Michigan (1991).

TABLE 9
DEGRADATION RATE CONSTANTS IN THE SOIL ^(a)

Compound	Aquatic Reaction Rate Constant Maximum (hr ⁻¹)	Aquatic Reaction Rate Constant Minimum (hr ⁻¹)	Aquatic Reaction Rate Constant (Geometric Mean) (hr ⁻¹)	Aquatic Reaction Rate Constant (Arithmetic Mean) (hr ⁻¹)
Benzene	0.0058	0.0018	0.0032	0.0038
Ethylbenzene	0.0096	0.0029	0.0053	0.0061
Toluene	0.0072	0.0013	0.003	0.0042
mixed Xylenes	0.0041	0.001	0.002	0.0025
Styrene	0.002	0.001	0.0014	0.0015
Naphthalene	0.0017	0.0006	0.001	0.0011
Fluorene	0.0002	0.000065	0.00011	0.00013
Benzo(a)Pyrene	0.0005	0.00005	0.000016	0.00027

^(a) Howard, H. P., Handbook of Environmental Degradation Rates, Lewis Publishers, Chelsea, Michigan (1991).

6.4 Description of Simulation Scenarios

6.4.1 Sources

The SMCM simulations were conducted so as to obtain the development of the concentrations in the various environmental compartments as a function of time. The relevant reported results, however, are the annual average concentrations (or "steady state" concentration). Although emissions from the terminal operations are unsteady, since annual average concentrations were sought, the source strength due to the terminal operation was taken to be constant and approximately equal to the annual estimated emissions. The emission rate of *n*-hexane was not reported by Alyeska (see section 4.2) and thus the value estimated in this study was utilized. The source emissions used for the base case study are given in Table 6.11 below.

Although accurate data on the amount of VOC discharged through the diffuser were not available, the effect of discharge through the diffuser on the water column concentration was investigated. As per the discharge permit, diffuser discharge of BETX concentrations are not allowed to exceed 1.3 ppm (Yearsley, 1978; Mikkelsen, 1991). Given a yearly annual flow rate through the diffuser of $2.3 \times 10^7 \text{ m}^3/\text{yr}$ and the discharge limit of 1.3 ppm translates into a source of approximately 24 metric tons per year or approximately 30 gmol/hour (assuming the molecular weight of benzene). Since the reported discharge BETX concentrations ranged from 0 to 8 ppm, diffuser emissions were not considered in the base case simulation. However, the effect of including the discharge of BETX through the diffuser was considered in a number of simulations.

TABLE 6.10
AIR EMISSIONS USED IN THE BASE CASE SIMULATIONS

Compound	Mass Compound ^(a) Mass Benzene	Emissions (tons/yr)	Emissions (gmol/hr)
Benzene	1.0	450	650
Ethylbenzene	.035	16	16.8
Toluene	.583	262	324
Xylenes	.152	69	74
<i>n</i> -Hexane	1.384	623 ^(b)	825.3

^(a) Source: Report on Valdez Tanker Loading Vapor Emission Testing and Evaluation, Alyeska Pipeline Services Company, Doc. No. VVE-1990, Oct. 22, 1990; also see section 4.2.

^(b) Estimated based on vapor phase composition (see Table 4.2).

6.4.2 Base Case Simulations

The modeled region described in section 6.2.2.1 was selected for the base case simulation. The air/soil interfacial area was set to 75.3 km², the air/water interfacial area (equal to the sediment/water interfacial area) was set to 110.6.1 km², and the water flow rate was set to 1.04 x 10⁷ m³/hr. The emissions for the base case simulations are given in Table 6.10 and the atmospheric reaction rate constants for the base case simulations are given in Table 6.11. The mass balance results describing the distribution of the chemicals in the Port Valdez Environment and the transfer rates among the various compartments were also calculated for the half-port area. The half-port region includes the Port Valdez region east of Saw Island (see Figure 1.1) with a soil/atmosphere interfacial area of 58.9 km² and an atmosphere/water interfacial area of 43.1 km². The half-port region was selected for this representation since it is more representative of the region which encompasses the City of Valdez and the Alyeska Marine Terminal.

TABLE 6.11
BASE CASE ATMOSPHERIC REACTION RATE CONSTANTS

Compound	Atmospheric Reaction Rate (hr ⁻¹)
Benzene	0.0021
Ethylbenzene	0.0128
Toluene	0.0118
Xylenes	0.0270
n-Hexane	0.0093

(a) see Table 6.7

Since the main interest in this study was to evaluate the effect of emissions associated with the marine terminal, the contribution of sources outside of the Port Valdez area to the distribution of the study chemical in the modeled region were not considered.

Several preliminary precipitation scavenging simulations indicated that although precipitation has some effect on the fluctuations of the concentrations in the soil compartment, it has little effect on the annual average atmospheric concentrations of BETX and n-hexane. Thus, the input of BETX and n-hexane to the soil and sea via precipitation scavenging (from the atmosphere) is negligible relative to dry deposition. It is noted, however, that atmospheric removal of airborne pollutants is most significant for highly water soluble or reactive gases and for particle-bound pollutants (Ligocki et al., 1985; Tsai and Cohen, 1991).

6.4.3 Evaluation of the Effect of Model Parameters on Predicted Multimedia Distribution of BETX and *n*-Hexane

A number of scenarios were simulated for different model parameters in order to investigate the effect of these parameters on the predicted concentrations in the various compartments relative to the base case predictions. The parameters varied in the above series of simulations are listed in Table 6.12.

TABLE 6.12
PARAMETERS VARIED IN THE SMCM MODEL SIMULATIONS

MODEL PARAMETER
Size of Modeled Region
Emissions Rate
Mixing Height
Wind Speed
Organic Carbon Content of Soil, Sediment, and Suspended Solids
Water Temperature

6.4.4 Evaluation of the Multimedia Distribution of BETX and *n*-Hexane Based on Reported Atmospheric Concentrations

In this part of the analysis the emission rates for BETX and *n*-hexane were approximated based on the reported monitoring data for these compounds. This was accomplished by setting the atmospheric concentration in the SMCM model to the monitored concentrations and determining the accumulation of BETX and *n*-hexane in the Port Valdez environment (see section 7.4). It is important to note that the average concentrations were derived by averaging the concentrations reported by the monitoring stations (section 5.1). Given the uncertainty in the monitored concentrations and the expected spatial variability of the concentration fields, the calculations of the emission rates using the SMCM model should only be regarded as approximations. Nonetheless, as discussed in section 7, such analysis does portray potential incompatibilities between the reported emission rates and the monitored concentrations.

7. THE DISTRIBUTION OF BETX AND N-HEXANE IN THE PORT VALDEZ REGION

7.1 Overview

The concentrations of BETX and *n*-hexane in the air compartments were evaluated based on both the monitoring data and a simple mass balance approach (see section 6.2.2.1). Based on the average monitored concentration data, the partitioning of the study chemicals into the soil, water, suspended solids, and sediment compartments was determined using the SMCN model (see section 6 and Appendix B). The effect of various assumed model parameters on the calculated concentrations in the various compartments and in relation to the estimated sources are presented in sections 7.2 - 7.5. Finally, the distributions of the BETX and *n*-hexane in the Port Valdez environment and the ~~intermedia~~ fluxes are presented in section 7.6.

7.2 Atmospheric Compartment

Several test cases have shown that for the study chemicals and the range of environmental conditions at Port Valdez, the transfer of airborne hydrocarbons to the water and soil environment has a negligible effect on the air phase concentration. This conclusion is supported by the recent study of Cohen et al. (1990, 1991) on the multimedia distribution of refinery emitted hydrocarbons. Given the above findings it is instructive to explore the mass balance on the emitted BETX and *n*-hexane using the simple box-model given by Eq. 6.3. At steady state (i.e., the case representing annual averaged basin-wide concentrations) one can determine from Eq. 6.3 the atmospheric chemical concentrations for a given volume and the mean convective residence time for the basin. The resulting concentrations relative to the averaged monitored concentration (for the sites excluding East Gate; see Tables 5.1), using the approximate reported convective residence time of 13.3 hours (see section 6.2.2.2) and the average atmospheric degradation rate constants (see Table 6.12), are shown in Table 7.1 and Figure 7.1. The results given in Table 7.1 which were obtained based on the estimated emission rates for BETX (see Table 4.2) indicate that the estimated concentrations for benzene and *n*-hexane are higher by about a factor of two relative to the averaged reported concentrations. The predicted concentrations for xylenes and ethylbenzene are lower by factors of about 2.4 and 3.8, respectively, than the average of the reported concentrations. Finally, the predicted concentrations for toluene are only 11% higher than the average of the reported concentrations,

Using Eq. 6.3 one can also estimate the source strength for each of the chemicals that would be required to yield the average of the monitored concentrations. As shown in Figure 7.2 (see also Table 7.2), the calculated sources are different from the reported estimated emissions (see Table 4.2). It is noted that the emission rate estimate for *n*-hexane was not available from the Alyeska Tanker Loading Emission Study (Alyeska, 1988, 1990). Thus, the emission rate for *n*-hexane was estimated based on vapor phase analysis data for Prudhoe Bay Crude oil (see

Table 4.2). The above analysis, although approximate, does suggest that there is a need for a detailed modeling effort to determine the suitability of the monitoring data to provide a representative view of the distribution of released hydrocarbons in the Port Valdez basin.

TABLE 7.1
PREDICTED VERSUS OBSERVED CONCENTRATIONS
AT PORT VALDEZ^(a)

Chemical	<i>Predicted Concentration</i> <i>Measured Concentration</i>
Benzene	2.13
Ethylbenzene	0.26
Toluene	1.11
Xylenes	0.41
<i>n</i> -Hexane ^(b)	1.85

^(a) $Q/V = 0.075 \text{ hr}^{-1}$; The measured concentrations represent the average of the monitored concentrations (excluding the East Gate site).

^(b) based on estimated source emission of 623 tons/year (see Table 4.2)

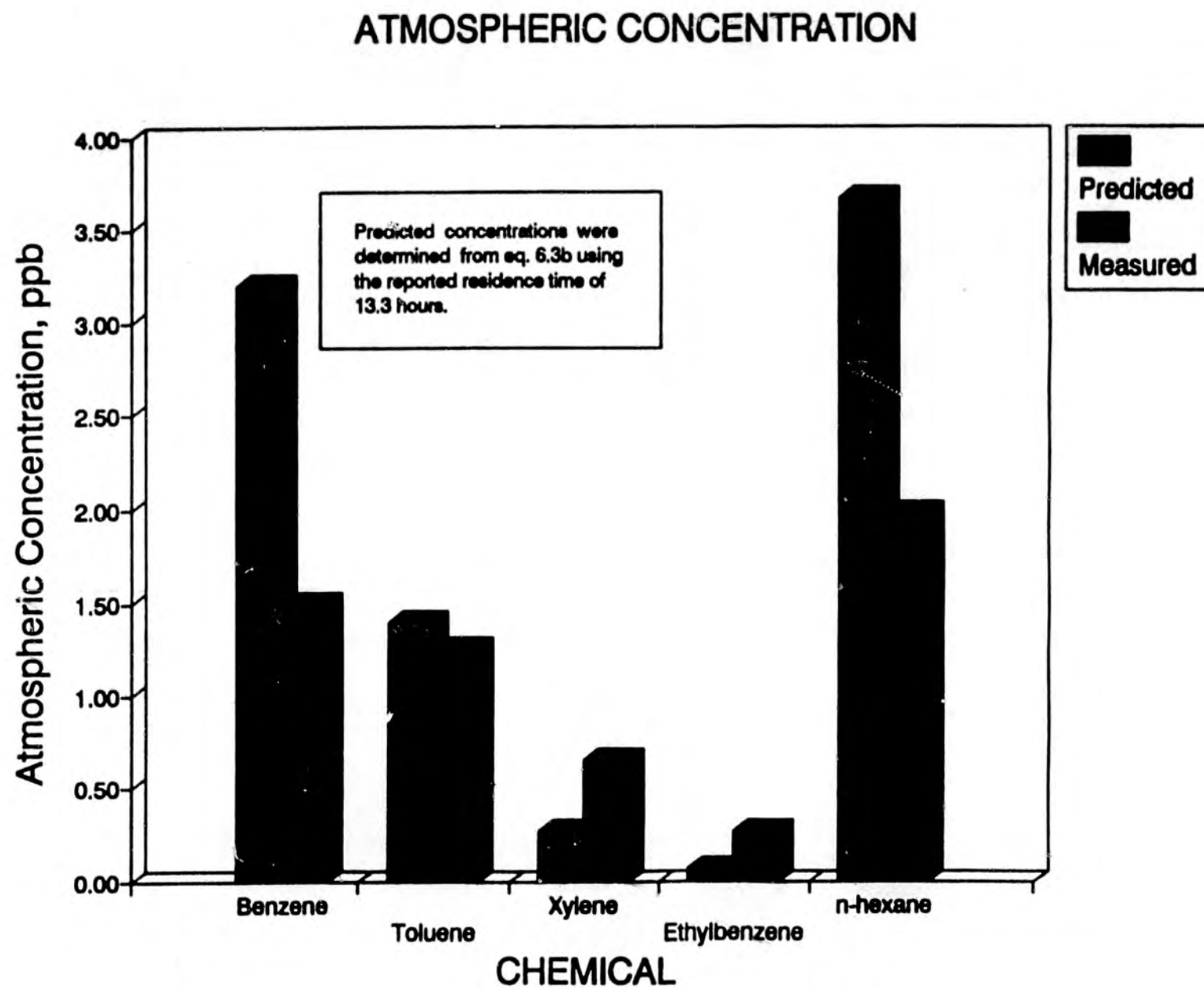
TABLE 7.2
Emissions Calculated From Eq. 6.3 Compared with Emissions Estimated
from the Alyeska Tanker Loading Emission Study

Chemical	Average Monitored Concentrations (Excluding East Gate) (ppb)	Calculated Emission Rate (Tons/Year) (Based on Eq. 6.3)	Emission Rate Estimated by Alyeska (Table 4.2) (Tons/Year)
Benzene	1.5	211	450
Ethylbenzene	0.27	58.7	16
Toluene	1.26	237	262
Xylenes	0.66	57	69
<i>n</i> -Hexane	1.98	336	623 ^(a)

^(a) Estimated based on vapor phase composition (see Table 4.2).

^(b) Emission rates determined based on the average monitored concentrations (excluding East Gate).

FIGURE 7.1



EMISSION RATES (Based on Reported Concentration Data)

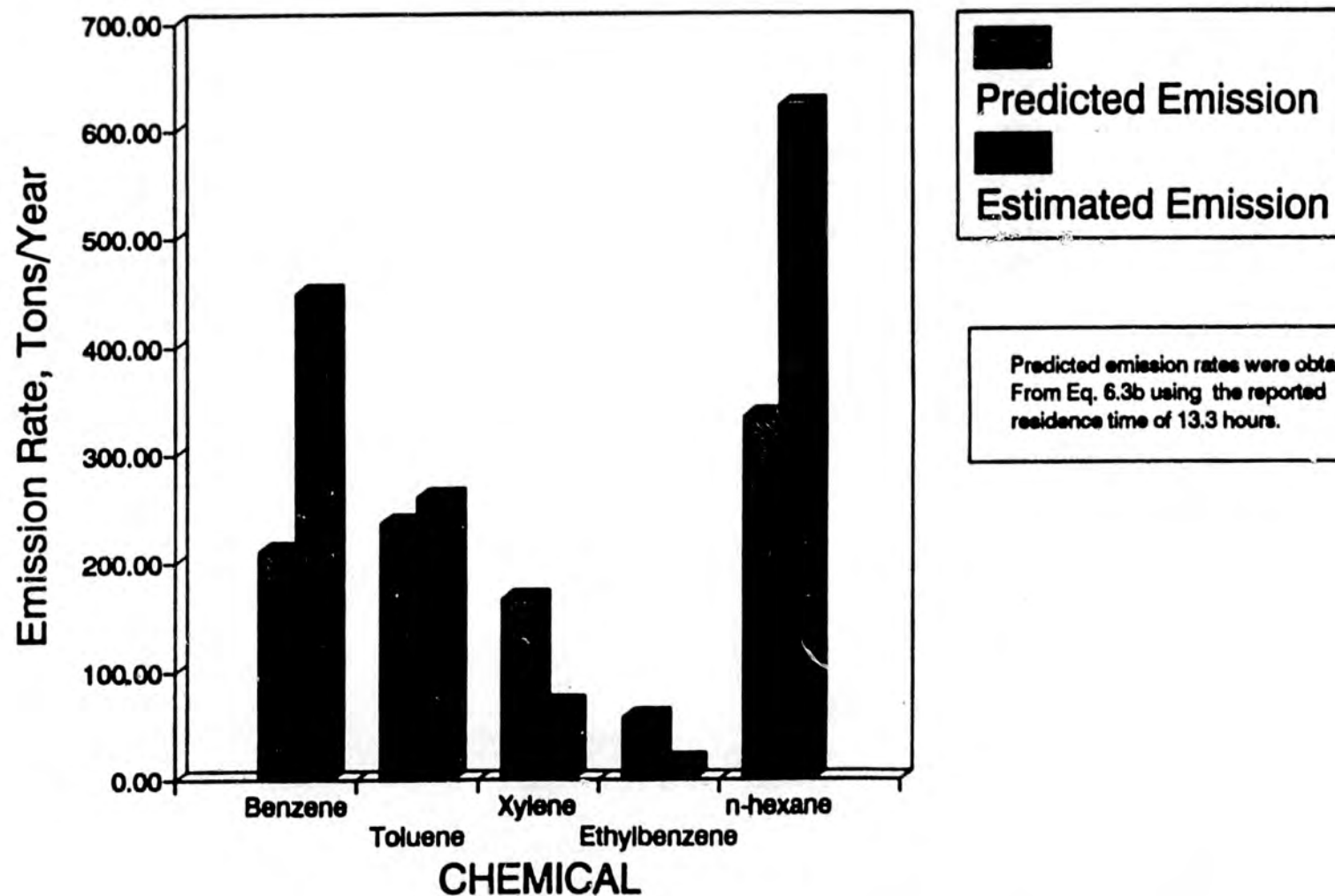


FIGURE 7.2

Wind dispersion leads to the spreading of the emitted pollutants in the region and generally higher wind speeds lead to a greater degree of dilution and consequently lower observed concentrations. The degree of wind mixing on a basin-wide scale can be approximated by the convective residence time (see eq. 6.3) the higher the convective residence time, for a given air basin volume, the lower the observed concentrations. One would expect that if equation 6.3 is used as an empirical equation to calculate the convective residence (i.e., using the monitored concentrations) then a single convective residence time should be expected for the air basin. The results of such an analysis is presented in Figure 7.3. Clearly, in order to match the predicted and average reported concentrations different convective residence times must be used for each chemical. This representation of the simple mass balance approach suggests that a closure of the mass balance must be sought in order to assure that the monitored concentrations can indeed be quantitatively related to the estimated emissions from the marine terminal and other sources at Port Valdez.

The mixing height has a direct influence on the predicted atmospheric concentrations. A higher mixing height leads to a larger mixing volume for the air basin and thus a lower concentration for the released pollutants (i.e., the pollutants are dispersed in a larger volume). Similarly, as mentioned above a higher wind speed will lead to increased dispersion (or dilution) and thus a lower concentration. As an illustration the change in the atmospheric concentration of benzene relative to the base case (mixing height=350 m, wind speed = 2.68 m/s) as a function of the mixing height and wind speed is depicted in Figure 7.4. Clearly, the mixing height can have a significant effect on the atmospheric concentration and as a result also on the concentration in the water column in the bay (due to atmospheric input; see section 7.4.3). The mixing height does change diurnally (and seasonally) and thus fluctuations in the air-basin concentrations of the emitted chemicals are to be expected. Real-time data for the mixing height at Port Valdez were not available⁷, but it is believed that the range of average mixing heights depicted in Figure 7.4 is representative of typical mixing heights expected for the Port Valdez area (see "Summary Report: Air Quality for the Trans Alaska Pipeline System: Terminal", Alyeska Pipeline Services Company, April 1974).

⁷ Mixing height monitoring data were obtained by Alyeska but these data were not available at the time of preparation of this report.

ATMOSPHERIC CONVECTIVE RESIDENCE TIME (Based on Reported Concentration Data)

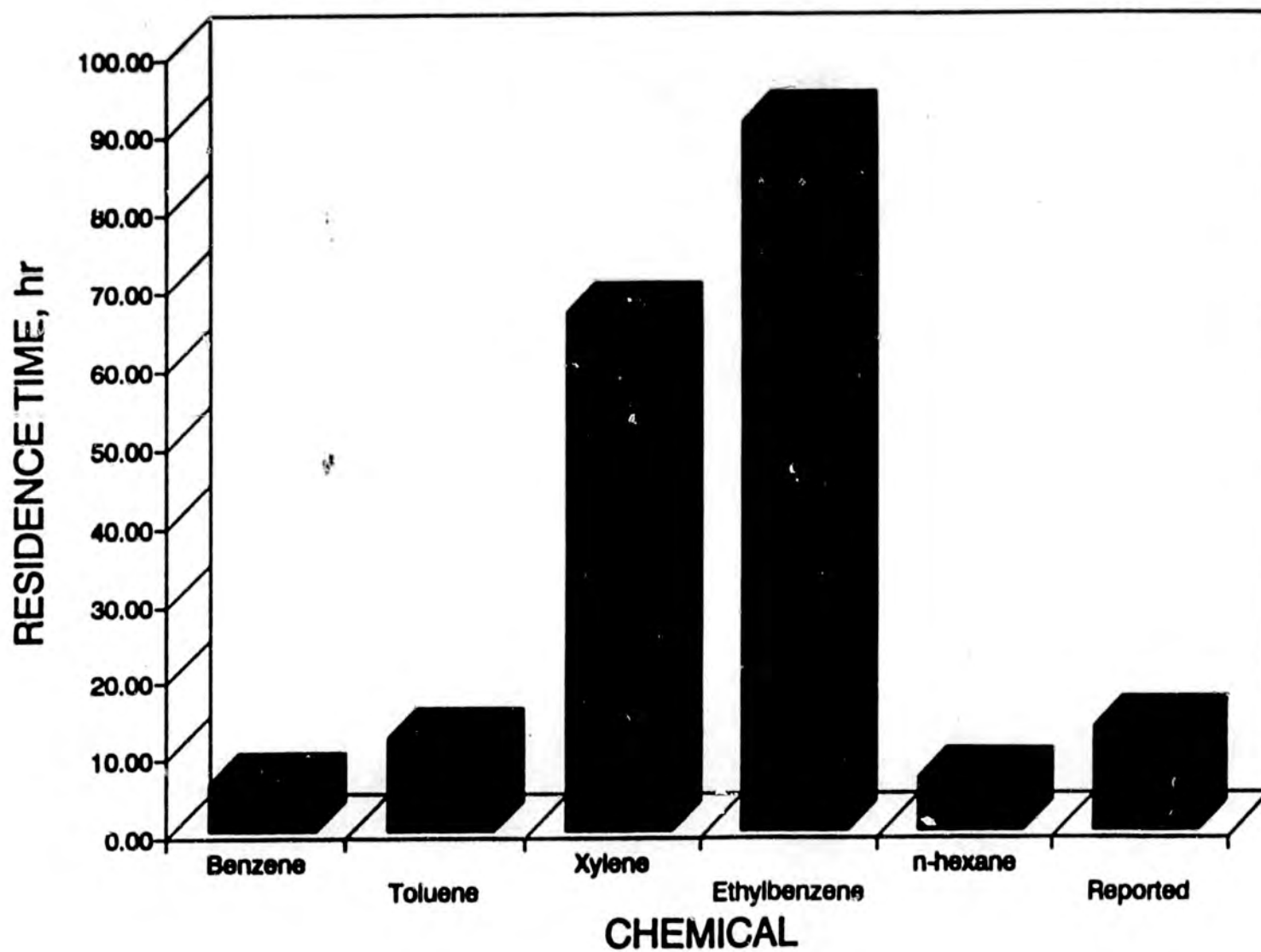


FIGURE 7.3

EFFECT OF WIND SPEED AND MIXING HEIGHT ON BENZENE CONCENTRATION IN ATMOSPHERE

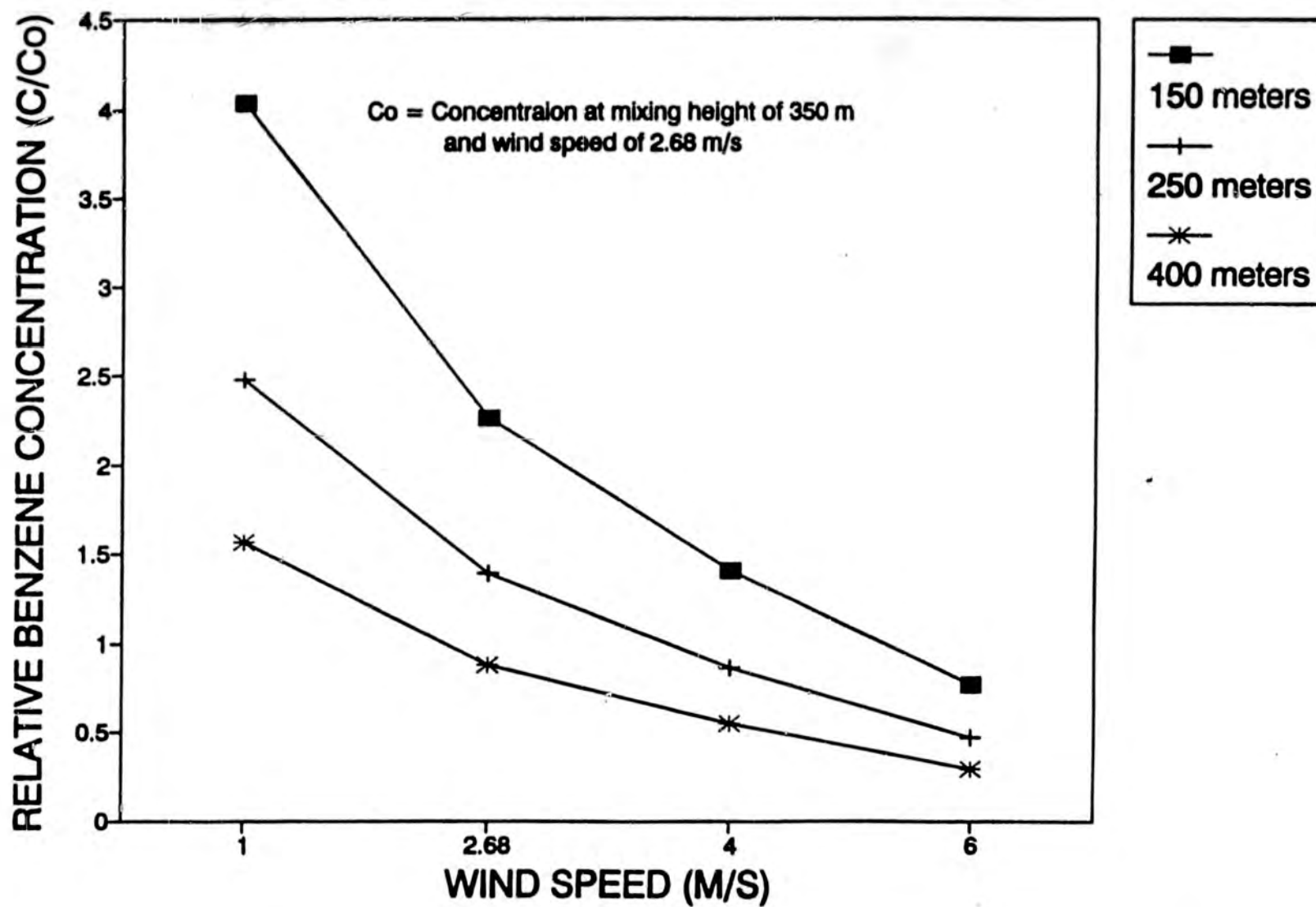


FIGURE 7.4

7.3 Monitored Atmospheric Concentrations at Port Valdez Relative to Urban Regions

It is instructive to compare the monitored concentrations to those reported in urban atmospheres as indicated in Table 7.3. The monitored concentrations at Port Valdez for benzene, toluene, xylenes, and *n*-hexane are within the range of the concentrations reported for Boston and at the lower limits of the concentrations reported for Los Angeles and Denver for benzene and *n*-hexane. Clearly, with respect to the atmospheric concentrations of BETX and *n*-hexane, Port Valdez cannot be considered to be a pristine or rural area (see also Table 3.3).

TABLE 7.3
COMPARISON OF MONITORED CONCENTRATION AT PORT VALDEZ
AND TYPICAL CONCENTRATIONS REPORTED FOR URBAN ATMOSPHERES^(a)

Urban Regions/Monitor Locations, and Year Sampled	Range of Monitored Atmospheric Concentrations (ppb)				
	Benzene	Ethylbenzene	Toluene	Xylenes ^(a)	<i>n</i> -Hexane
Port Valdez, Alaska ⁽¹⁾ , 1991	1.2-7.8	0.19-0.6	1.07-5.78	0.34-1.67	1.11-20.72
Batton Rouge, LA, 1989	0.62-2.98	0.12-1.5	0.61-4.35	0.55-8.61	
Camden, NJ, 1989 ⁽²⁾	0.53-8.24	0.11-2.57	1.10-22.36	0.68-15.25	
Chicago, IL, 1989	0.43-10.59	0.10-3.24	0.54-31.98	0.36-22.35	
Dallas, TX, 1989	0.32-2.07	0.03-0.42	0.26-3.4	0.13-2.77	
Ft. Lauderdale, FL, 1989	0.05-4.18	0.04-1.2	0.08-10.53	0.04-1.2	
Houston, TX, 1989	0.57-7.56	0.02-1.61	0.45-11.36	0.35-6.38	
Miami, FL, 1989	0.05-4.15	0.02-1.38	0.21-12.15	0.14-10.26	
St. Louis, MO, 1989	0.60-27.7	0.18-1.71	1.71-41.69	1.1-50.5	
Washington, DC, 1989	0.58-7.88	0.11-2.52	0.83-18.4	0.58-14.48	
Wichita, KS, 1989	0.35-3.31	0.05-0.85	0.32-5.24	0.20-4.86	
San Francisco, CA, 1986 ⁽³⁾	0.8-5.2				
Batton Rouge, LA, 1985					0.64-6.6
Boston, MA, 1985					0.35-1.88
Cleveland, OH, 1985					0.58-4.78
El Paso, TX, 1985					0.91-7.23
Kansas City, MO, 1985					0.51-3.41
Lake Charles, LA, 1985					0.55-5.71
Las Vegas, NV, 1985					0.5-3.8

Urban Regions/Monitor Locations, and Year Sampled	Range of Monitored Atmospheric Concentrations (ppb)				
	Benzene	Ethylbenzene	Toluene	Xylenes ^(a)	n-Hexane
Port Valdez, Alaska ⁽¹⁾ , 1991	1.2-7.8	0.19-0.6	1.07-5.78	0.34-1.67	1.11-20.72
Philadelphia, PA, 1985					0.67-9.81
Portland, ME, 1985					0.27-4.31
Richmond, VA, 1985					0.51-2.54
St. Louis, MO, 1985					0.72-6.63
Washington, DC, 1985 ⁽²⁾					0.73-2.3
Boston, MA (1981, 1984) ⁽³⁾	1.3		4.7	2	1.1
Chicago, IL (1984-1986) ⁽⁴⁾	3.8-30.3				
San Francisco, CA, 1984 ⁽⁵⁾	0.8-5.2				
Stinson Beach, CA, 1984 ⁽⁵⁾	0.38 ± 0.39 (weighted average)				
Los Angeles, CA, 1984 ⁽⁶⁾	5	2.23			8.06
Los Angeles, CA, 1984 ⁽⁶⁾	1.12	0.69			2.78

(a) Data are from references 2 and 3 unless otherwise indicated.

¹ Range of Average Monitored Concentrations at Port Valdez (Excluding East Gate Monitoring Station), 1991 (see Tables 5.1-5.6).

² All data for sampling date of 1989 are from EPA, 1990, 1989 Urban Air Toxics monitoring Program, EPA OAQPS, Research Triangle Park, NC (EPA-450/4-91-001).

³ All data for sampling date of 1985 are from EPA, 1988, National Ambient Volatile Organic Compounds (VOCs) Database Update, EPA OR&D, Research Triangle Park, NC (EPA/600/3-88-010A).

⁴ Category "Xylenes" in EPA, 1990 data is m/p-xylene. Data also available for o-xylene, but was aggregated with styrene.

⁵ Wester, R.C., H. I. Maibach and L. D. Gruenke, "Benzene Levels in Ambient Air and Breadth of Smokers and non-Smokers in Urban and Pristine Environments", J.Toxicol.Environ.Health, 18, 567-573 (1986).

⁶ EPA, "June-September, 6-9 a.m., Ambient Air Benzene Concentrations in 39 U.S. Cities, 1984-1986". Research Triangle Park, NC, EPA/600/D-87/160 (1987).

⁷ Finlayson-Pitts, B. J. and J. N. Pitts, Jr., "Atmospheric Chemistry: Fundamentals and Experimental Techniques", John Wiley and Sons, New York (1986), Pages 350-351.

⁸ Wallace, L., E. Pellizzari, L. Sheldon, T. Harwell, C. Sparacino, and H. Zelon, "Total Exposure Assessment Methodology (TEAM) Study: Direct Measurement of Personal Exposure through Air and Water for 600 Residents of Several U.S. Cities", in Pollutants in a Multimedia Environment, Cohen, Y. (Editor), Plenum Press, New York (1986); (8a) Average of 48 samples for February 1984; (8b) Average of 48 samples for May 1984.

7.4 Accumulation of BETX and *n*-Hexane in the Soil, Water, Sediment and Suspended Solids Compartments

7.4.1 Overview

The concentrations of BETX and *n*-hexane in the soil, water, sediment, and suspended solids compartments, as determined based on the monitoring data (see section 6.4.4) and the SMCM model, are given in Tables 7.4 and 7.5. Table 7.4 presents the calculated concentrations that would occur for basin-wide concentrations that are taken to be equivalent to the average of the monitoring data for three sites (Old Valdez, High School, and Spit), while Table 7.5 provides the concentrations in the media in the vicinity of the East Gate monitoring site.

The results given in Tables 7.4 and 7.5 are also illustrated in Figures 7.5 and 7.6. The concentration at the East Gate location are higher in all media. This result is expected due to the higher concentrations in the East Gate site relative to the other monitoring sites.

TABLE 7.4
Multimedia Concentrations
Based on Atmospheric Concentrations
Monitored at Port Valdez (Excluding East Gate)

Chemical	Air (ppb)	Water (ng/l)	Soil (ng/kg)	Sediment (ng/kg)	Suspended Solids (ng/kg)
Benzene	1.5	0.901	3.78	0.131	0.181
Ethylbenzene	0.27	0.093	1.39	0.025	0.0823
Toluene	1.26	0.831	10.1	0.246	0.997
Xylenes	0.66	0.663	14.5	0.33	2.0
<i>n</i> -Hexane	1.98	0.0157	2.26	0.0366	0.329

TABLE 7.5
Multimedia Concentrations
Based on Atmospheric Concentrations
Monitored at the East Gate Site at Port Valdez^(a)

Chemical	Air (ppb)	Water (ng/l)	Soil (ng/kg)	Sediment (ng/kg)	Suspended Solids (ng/kg)
Benzene	3.2	1.92	8.06	0.280	0.385
Ethylbenzene	0.36	0.125	1.86	0.033	0.11
Toluene	2.5	1.65	20.1	0.49	1.98
Xylenes	0.81	0.814	17.8	0.405	2.46
<i>n</i> -Hexane	6.58	0.522	7.5	0.122	1.09

^(a) Estimates using basin-average concentrations equivalent to the concentration levels monitored at the East Gate site.

CONCENTRATION IN WATER COMPARTMENT
(MODEL RESULTS)
(Excluding Eastgate)

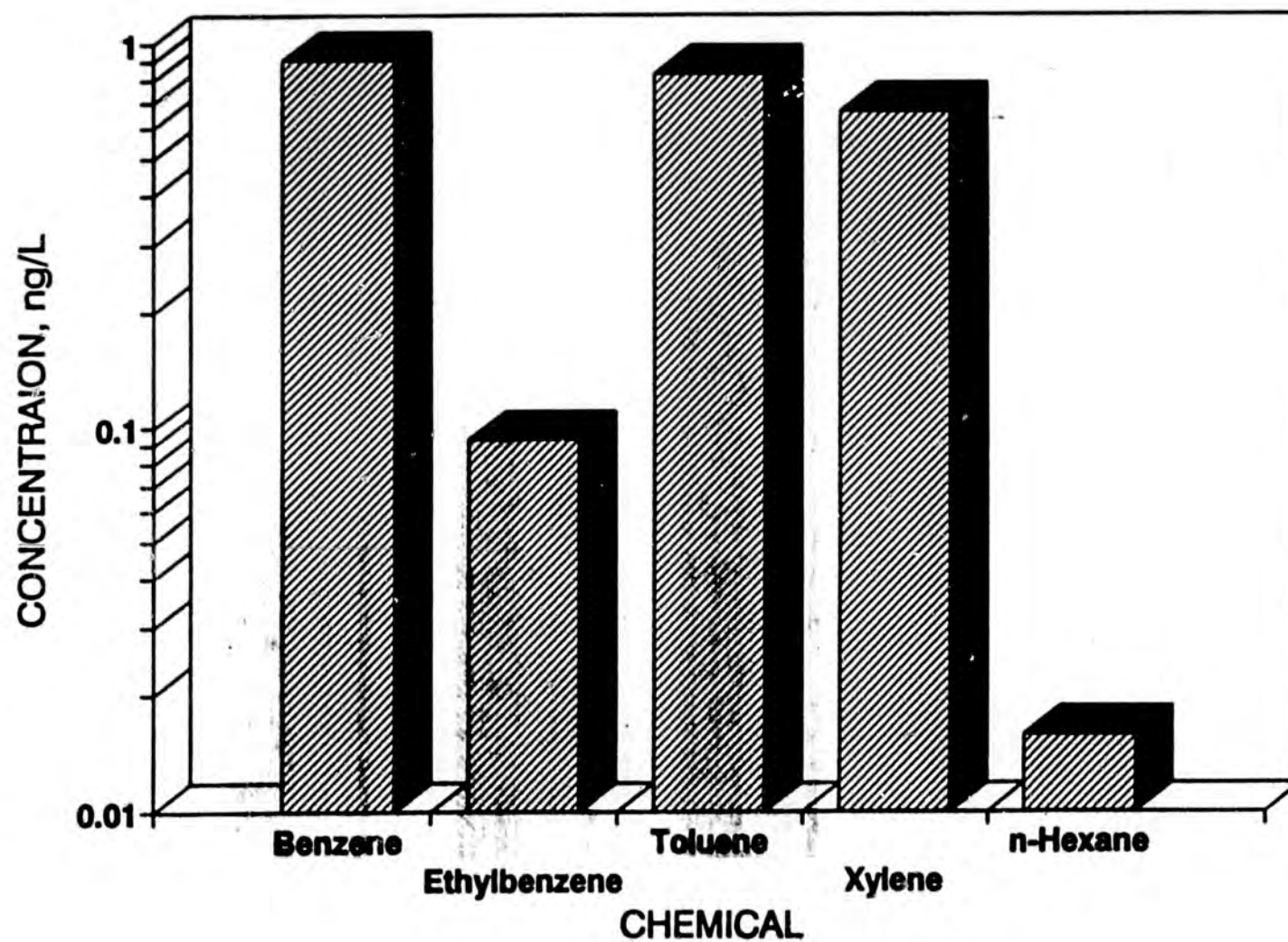


FIGURE 7.5

COMPARTMENTAL CONCENTRATIONS
(MODEL RESULTS)
(Excluding Eastgate)

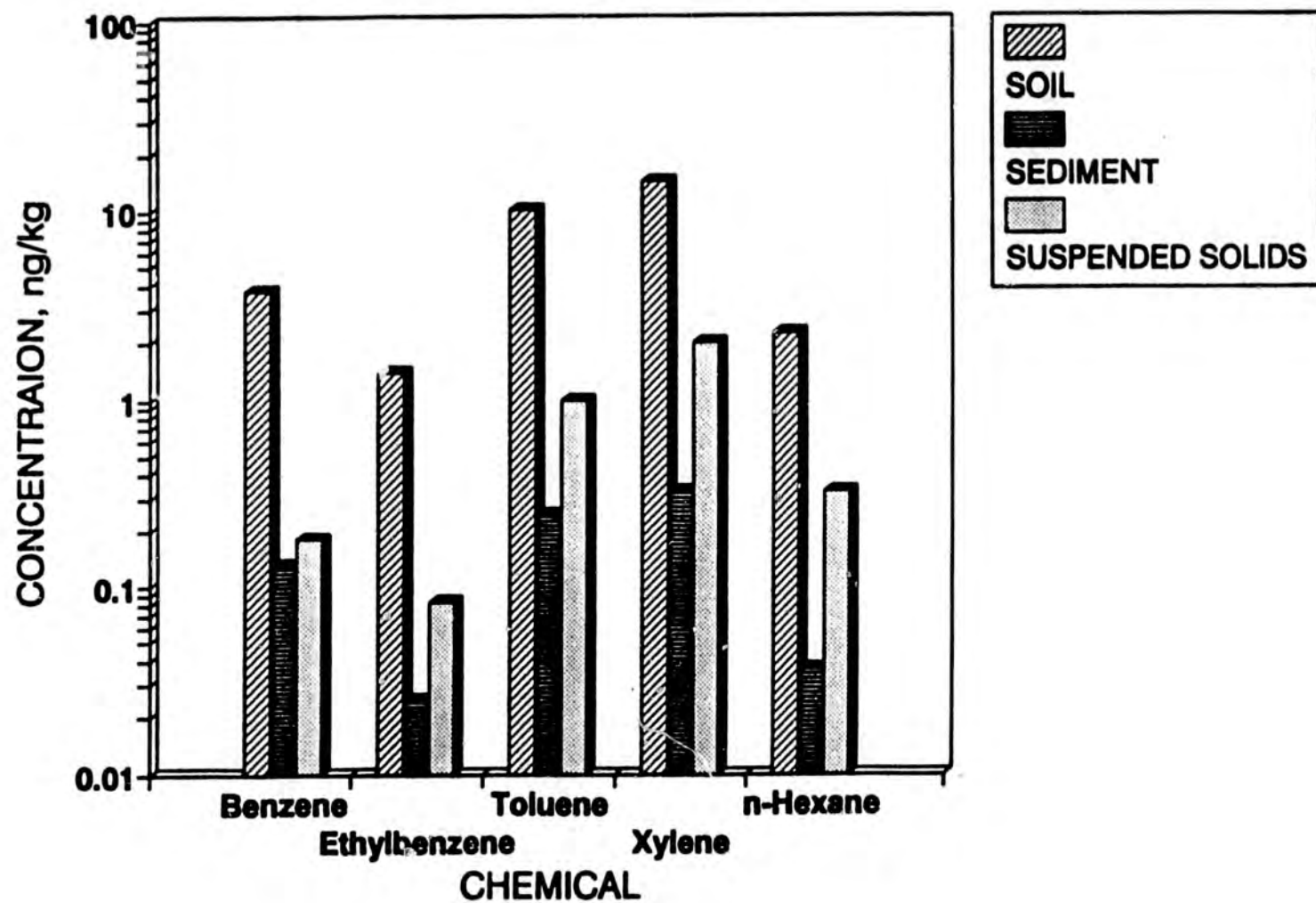


FIGURE 7.6

7.4.2 Soil Compartment

The predicted concentrations of ethylbenzene, *n*-hexane, and benzene in the soil environment, for the base case simulations were in the range of about 1.4 ng/kg to 3.8 ng/kg. Higher concentrations of 10.1 ng/kg and 14.5 ng/kg were calculated for toluene and xylenes, respectively, based on the concentrations monitored at the East Gate site. The above concentrations are low relative to typical concentration observed for soils (see Table 3.3). As evident from Table 7.6 the soil concentrations are in the ng/kg range even for a soil organic carbon content of 4%. Even a ten fold increase in the organic content of the soil to 40% would only results in an increase in xylenes and benzene accumulation in the soil to concentrations of about 0.85 $\mu\text{g/kg}$ and 33 $\mu\text{g/kg}$, respectively. These concentrations are extremely low and monitoring data for typical soils in urban areas, at these expected comparable concentration levels, have not been found for comparison.

TABLE 7.6
EFFECT OF ORGANIC CARBON ON THE CONCENTRATION
OF BENZENE IN THE SOIL MATRIX^(a)

Percent Organic Carbon	Concentration
	Concentration for 0.6% Organic Carbon Content
0.1	0.62
1	1.26
4	1.43

^(a) Average concentration calculated for the top ten centimeters of the soil matrix.

7.4.3 Water Compartment

Chemicals that are released to the atmosphere can be transferred to the water column by absorption. The rate of mass transfer from the atmosphere to the water column is a function of the air phase concentration, the Henry's law constant for the chemical, and the wind speed across the water surface (Cohen, 1983, 1985). As indicated in Tables 7.4 and 7.5, the water phase concentrations (calculated for the averaged monitoring data) for BETX and *n*-hexane range from about 0.01 ng/l to 1.9 ng/l. These concentrations are within or below the range of concentrations reported for pristine regions.

Direct discharge of hydrocarbons to the water column is possible via the BWT diffuser (see section 4.4). Figure 7.7 illustrates the change in the water concentrations for benzene (relative to the base case simulation, i.e., no diffuser discharge) as a function of the discharge of benzene through the diffuser. Real-time data for discharge concentrations in the diffuser effluent were not available, however, the estimates provided in Table 4.9 indicate that the discharge rate for benzene is probably in the range of less than 0.4 tons/year to about 8 tons/year. The above results provide a basin-wide average value. In reality, however, dispersion studies in Port Valdez revealed that the ballast effluent is "trapped as a plume under a pycnocline between 50 and 70 m depth (Redburn, 1988). Thus, the actual local concentrations near the diffuser region are likely to be significantly higher than the concentrations predicted in the current study. The study of Yearsley (1987) suggests that BETX concentrations as high as 2.7 $\mu\text{g/l}$ can be reached at the mixing zone boundary of the diffuser discharge during conditions of maximum stratification.

Over the water temperature range of 2°C to 8°C the water phase concentration for benzene was found to increase by about 17 percent. Thus, for Port Valdez it is not expected that the water temperature will significantly affect the water phase concentration. The air temperature has a more significant impact on the rate of transfer of hydrocarbons from the air phase to the water phase and the effect of the air temperature was taken into account in the model simulations. It is worth noting that the accumulation of hydrocarbons in fish will be proportional to the water concentration as indicated by the BCF values (see section 6.3.1). Thus, the concentration of the study chemicals in biota relative to the base case follows the same trend as the concentration in the water compartment.

7.4.4 Sediment and Suspended Solids

The accumulation of airborne hydrocarbons in the sediment is via diffusion from the water column to the sediment. Similarly hydrocarbons absorbed from the atmosphere by the water column are adsorbed by solid hydrosols suspended in the water column. The concentrations of BETX and *n*-hexane in the sediment ranged from 0.025 ng/kg to 0.49 ng/kg and the concentrations in the suspended solids phase range from 0.08 ng/kg to 2.46 ng/kg for the suspended solids (see Tables 7.4 and 7.5). The concentration in the water, sediment, suspended solids and biota can also increase as the result of discharge through the diffuser pipe from the BWT facility as illustrated in Figure 7.8. It should be noted that as the case of the soil compartment the concentration of BETX and *n*-hexane in the sediment is expected to increase relative to the base case of 0.4 % organic content in the sediment matrix. For all of the conditions studied, the calculated concentrations in the sediment and suspended solids were found to be below or within the concentration range reported for pristine regions (see Table 3.3). Thus, it can be concluded that airborne volatile hydrocarbons such as BETX and *n*-hexane do not significantly accumulate in the sediment and in suspended solids.

EFFECT OF WIND SPEED AND MIXING HEIGHT ON BENZENE WATER CONCENTRATION

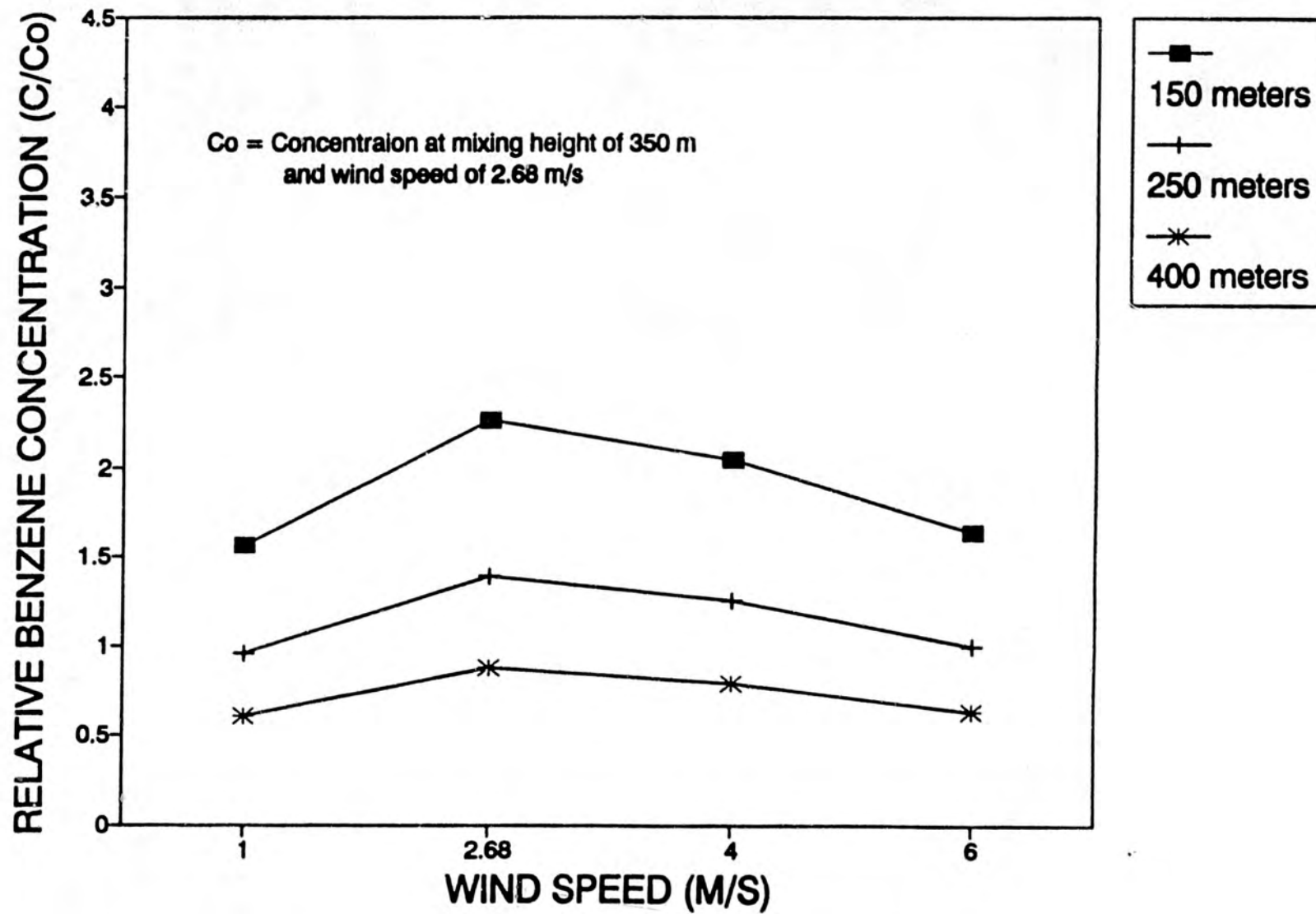


FIGURE 7.7

EFFECT OF DIFFUSER DISCHARGE OF BENZENE ON COMPARTMENTAL CONCENTRATIONS

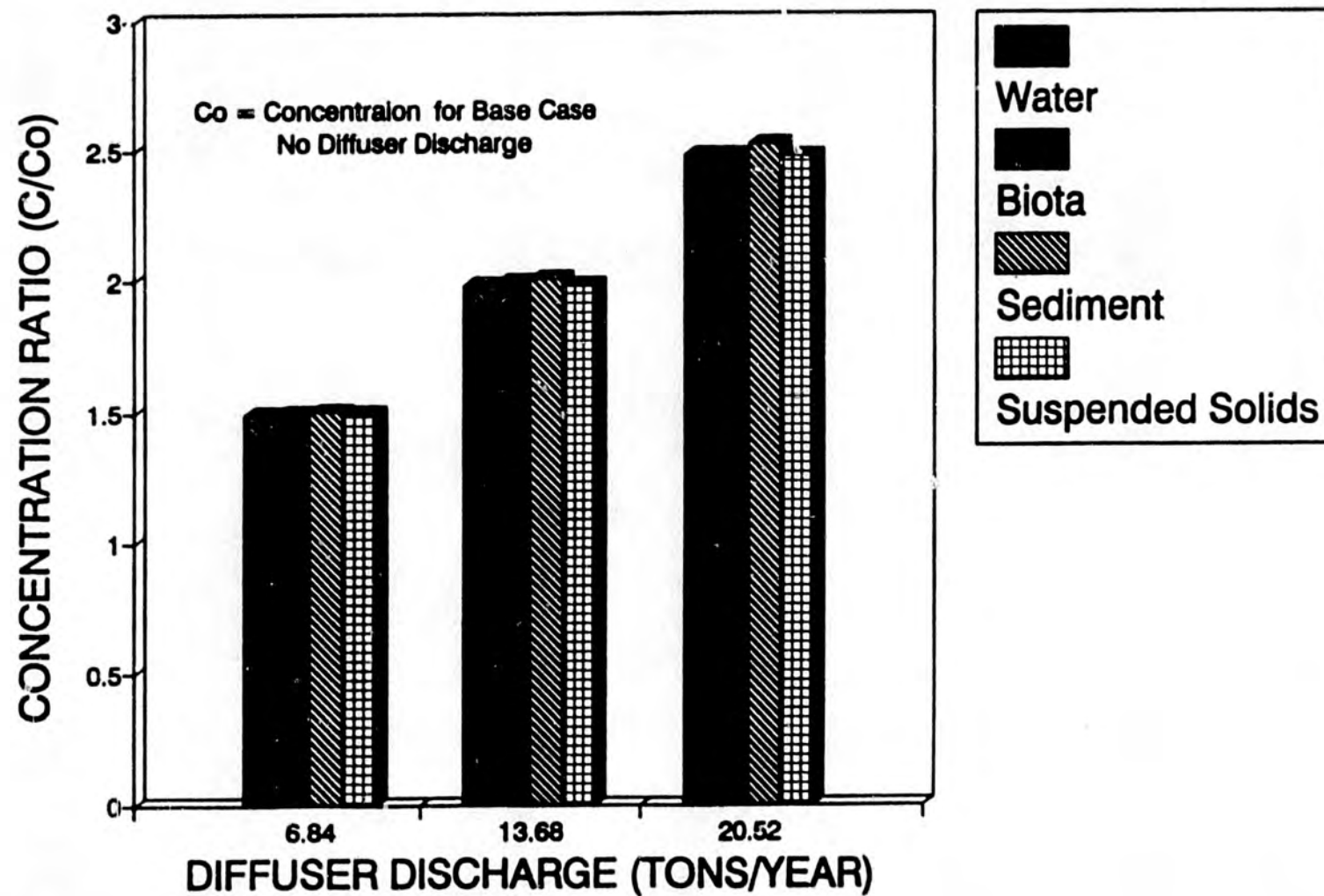


FIGURE 7.8

7.5 Distribution of BETX and *n*-Hexane in the Port Valdez Environment

The hydrocarbons emitted to the environment follow a variety of pathways among the different environmental media. Figures 7.9 -7.13 illustrate the amount of the chemical retained in each of the environmental compartments expressed as a percentage of the total amount present in the Port Valdez environment. The above information is also displayed in Tables 7.7 and 7.8. *n*-Hexane is the most volatile chemical of the group studied and correspondingly about 99.9% of the total *n*-hexane in the environment is present in the air phase compared to 95% for xylenes which has the lowest Henry's law constant for the group of chemicals studied. The percentage of benzene, ethylbenzene, toluene, and xylenes which partitions to the water compartment varies from about 1.7% to 4.8%. In contrast only about 0.05% of *n*-hexane partitions to the water compartment. For BETX and *n*-hexane the percentage of the chemical partitioned to the sediment, suspended solids, soil and the biota compartments is negligible compared with the amount present in the air and water compartment.

TABLE 7.7
PERCENT DISTRIBUTION OF THE STUDY CHEMICALS
IN THE PORT VALDEZ ENVIRONMENT ^(a)

	Air	Water	Soil	Sediment	Suspended Solids (in Water)	Biota
Benzene	96.02	3.92	0.064	3×10^{-4}	5.9×10^{-6}	6.9×10^{-6}
Ethylbenzene	98.25	1.7	0.048	2.4×10^{-4}	1.1×10^{-6}	1.3×10^{-5}
Toluene	96.27	3.65	0.083	5.5×10^{-4}	3.3×10^{-5}	2.0×10^{-5}
Xylenes	95.05	4.78	0.16	1.1×10^{-3}	1.1×10^{-4}	2.1×10^{-4}
<i>n</i> -Hexane	99.92	0.049	0.035	4.6×10^{-5}	7.7×10^{-6}	1.5×10^{-5}

TABLE 7.8
ACCUMULATION OF THE STUDY CHEMICALS
IN THE PORT VALDEZ ENVIRONMENT

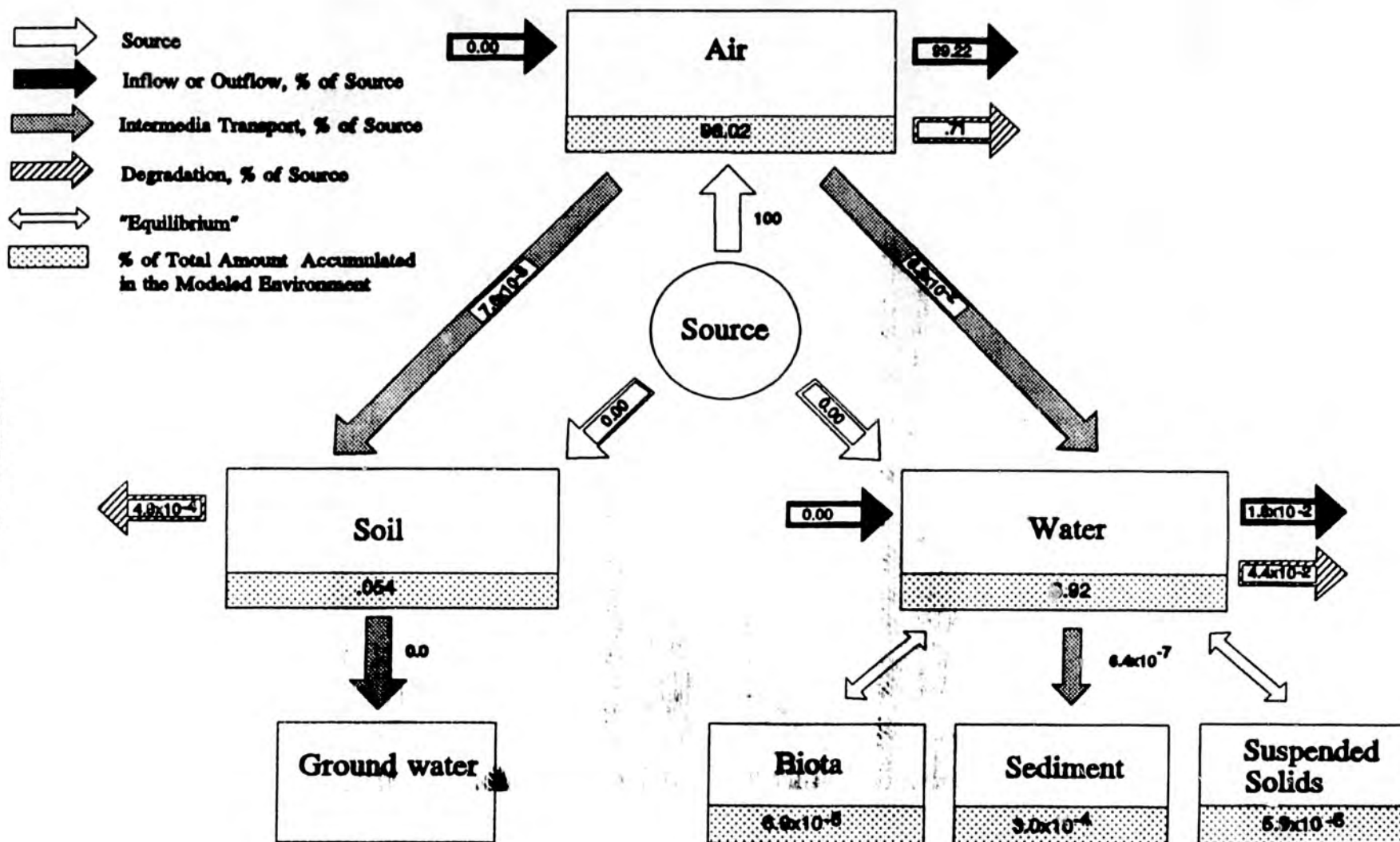
	Total Mass Present in the Full-Port Region (Kg)	Total Mass Present in the Half-Port Region (Kg)
Benzene	329.13	178.1
Ethylbenzene	78.03	42.6
Toluene	326.98	177
Xylenes	198.2	107
<i>n</i> -hexane	455.94	249

^(a) This table presents the total mass of the chemical present in the multimedia environment.

An illustration of the transfers of the study chemicals among the various compartments is also provided in Figures 7.9-7.13 for the half-port region (see section 6.4.2). In these figures the transfer rates between any two compartments, the rate of degradation, and the convective transport away from the half-port region are given in terms of the percentage of the annual emission rate from the marine terminal. It is interesting to note that the percent of the chemical degraded in the atmosphere ranges from about 0.7% to 30%. Also, the rate at which the study chemicals are convected away from the Valdez Port area range from about 63% to 99% (assuming an average wind speed of 2.68 m/s). In order to obtain the transfer rates for the full-port region, the transfer rates between compartments as given in Figures 7.9-7.13 (given in terms of percentages of the total emission rate) should be multiplied by a factor of 2.56 for exchange between the atmosphere and the water compartment, and also for exchange between the water and suspended solids, sediment, or biota compartments. The transfer rates between the atmosphere and the soil compartment for the full-port region are larger by a factor of 1.27 than for the half-port region. The rate of degradation in the atmosphere for the full port region is a factor of 1.82 larger than for the half-port region and the rate of degradation for the soil and water compartments are larger by factors of 1.27 and 2.56, respectively, than the results for the half-port region. The mass of BETX and n-hexane present in the Port Valdez environment is illustrated in Figure 7.14. It is worth noting that since these chemicals are volatile their presence in the environment is directly proportional to their respective concentrations in the atmospheric compartment. The bulk of the chemicals that are emitted to the atmosphere are either degraded in the atmosphere or they are convected by wind away from the Port Valdez region.

The various compartments with the exception of the sediment and soil reach equilibrium or "steady state" rapidly while the concentrations in the sediment compartments continue to increase at a slow rate. Figure 7.15 illustrate the rise in the concentrations of benzene in the Port Valdez area, assuming an initially pristine area. The concentrations increase rapidly to their "annual average" value except for the sediment and soil compartments in which the migration of the hydrocarbons is diffusion controlled. Finally, it is noted that precipitation scavenging is not a sufficient process for the removal of BETX and n-hexane. Precipitation scavenging, however, is expected to be an important process of input of airborne particle-bound contaminants (e.g., Benzo(a)Pyrene) and highly water soluble chemicals (e.g., SO₂) to the soil and water compartment.

Multimedia Fluxes and Partitioning of Benzene in Valdez, Alaska



Total Amount Accumulated in the Modeled Environment = 178.1 kg

Total Source = 50.77 kg/hour

FIGURE 7.9

Multimedia Fluxes and Partitioning of Ethylbenzene in Valdez, Alaska

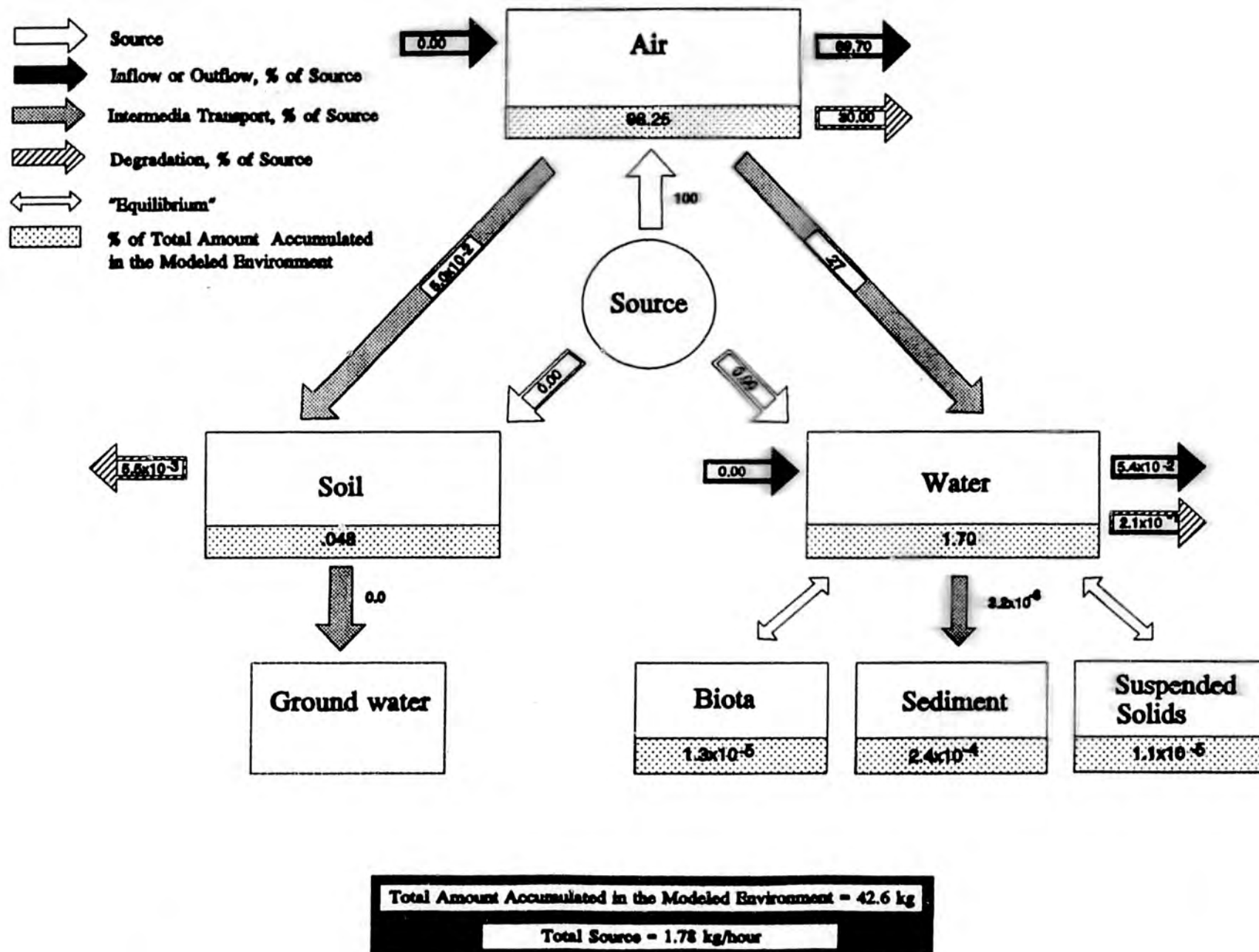
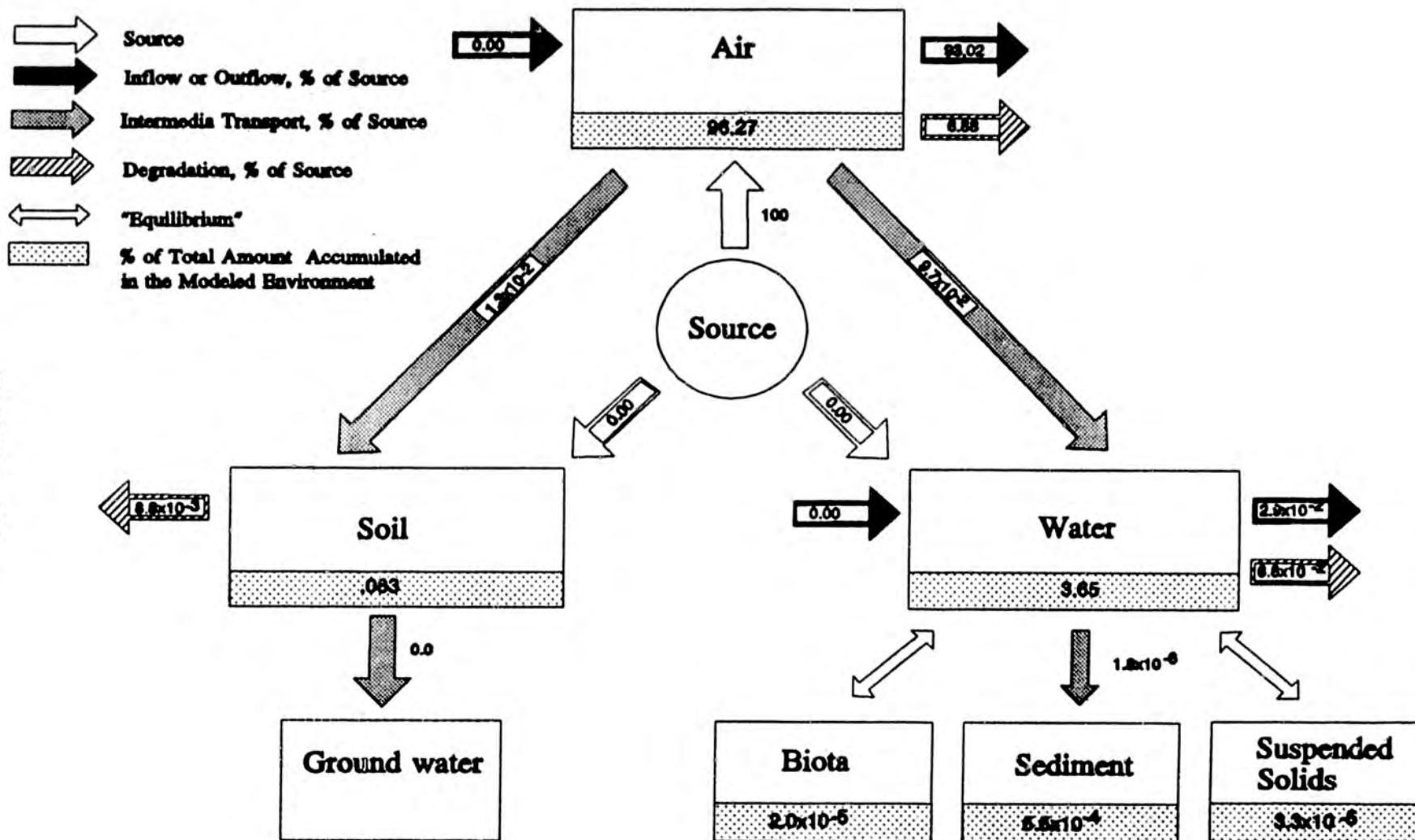


FIGURE 7.10

Multimedia Fluxes and Partitioning of Toluene in Valdez, Alaska

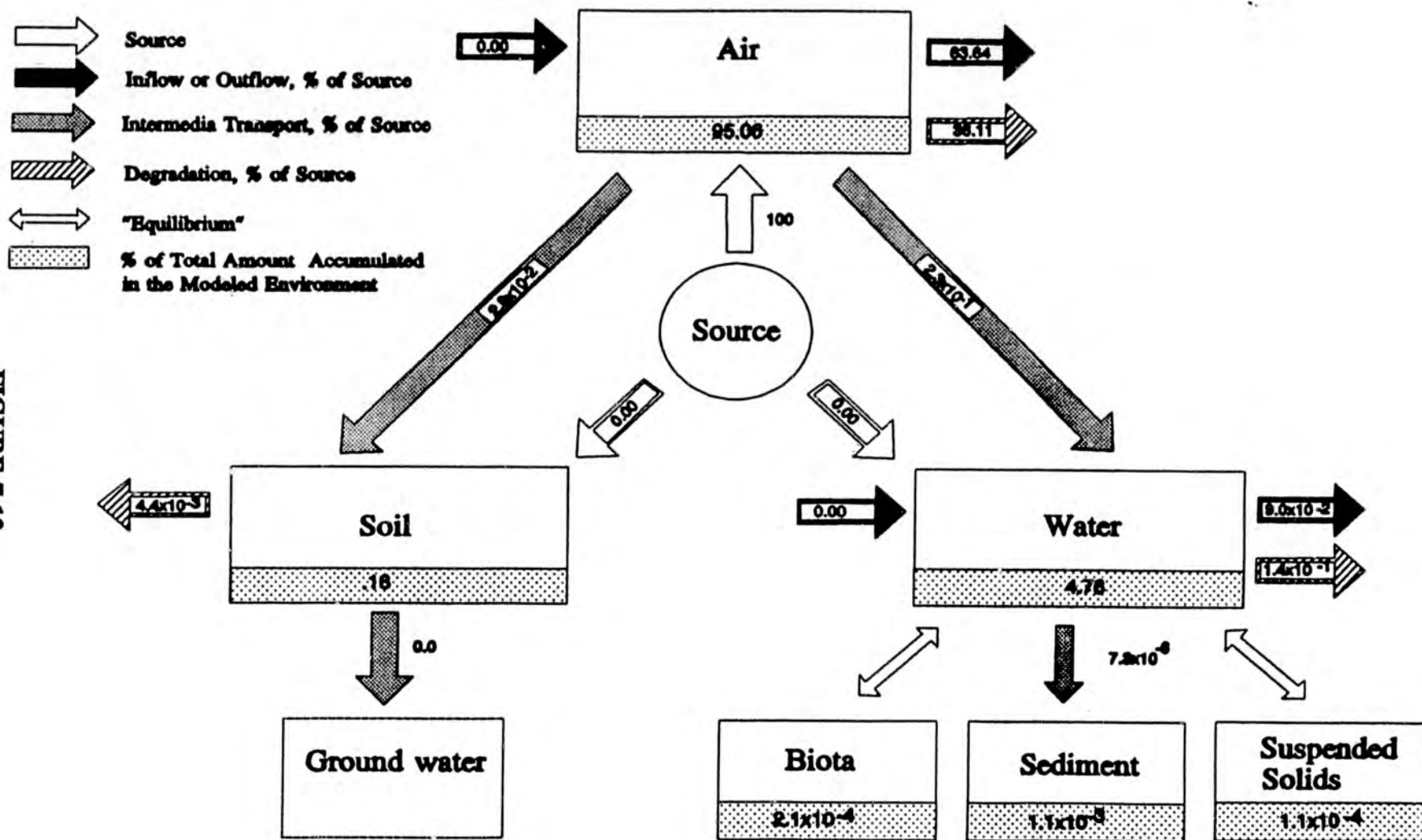


Total Amount Accumulated in the Modeled Environment = 177 kg

Total Source = 29.3 kg/hour

FIGURE 7.11

Multimedia Fluxes and Partitioning of Mixed Xylenes in Valdez, Alaska



Total Amount Accumulated in the Modeled Environment = 107 kg

Total Source = 7.65 kg/hour

FIGURE 7.12

Multimedia Fluxes and Partitioning of n-Hexane in Valdez, Alaska

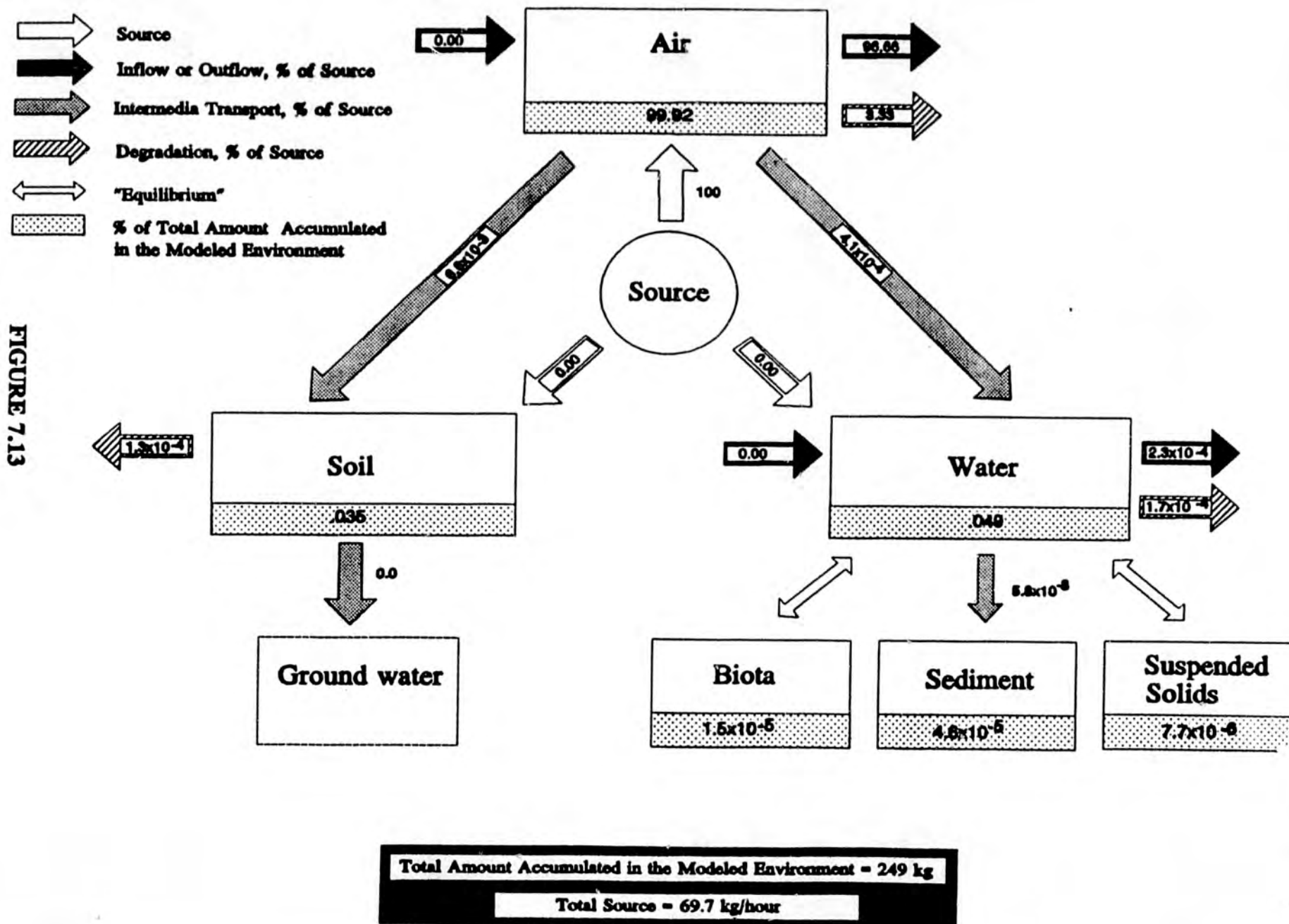


FIGURE 7.13

ACCUMULATION OF BETX AND n-HEXANE
IN PORT VALDEZ

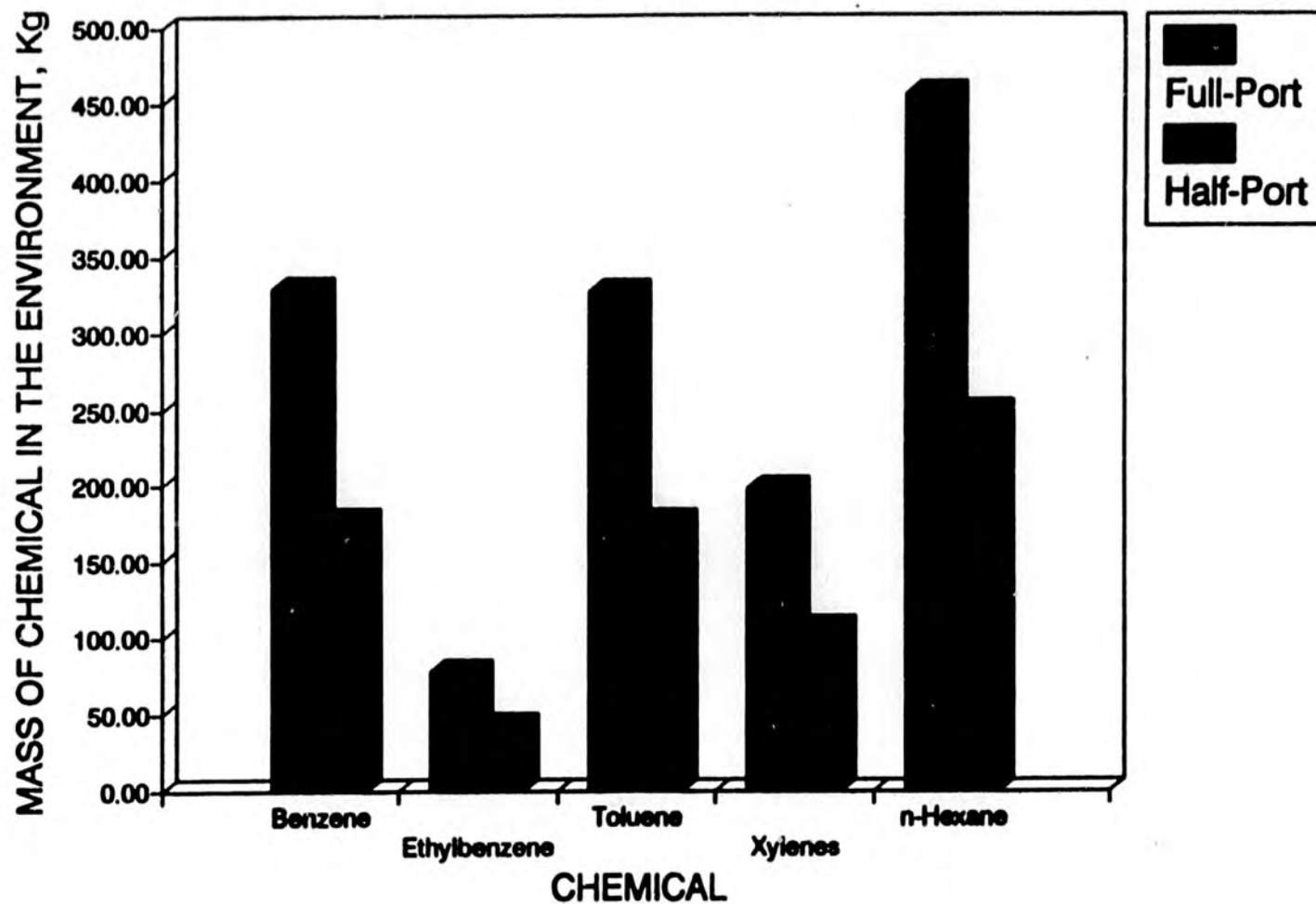


FIGURE 7.14

BENZENE CONCENTRATIONS IN PORT VALDEZ
(Based On Reported Atmospheric Data)

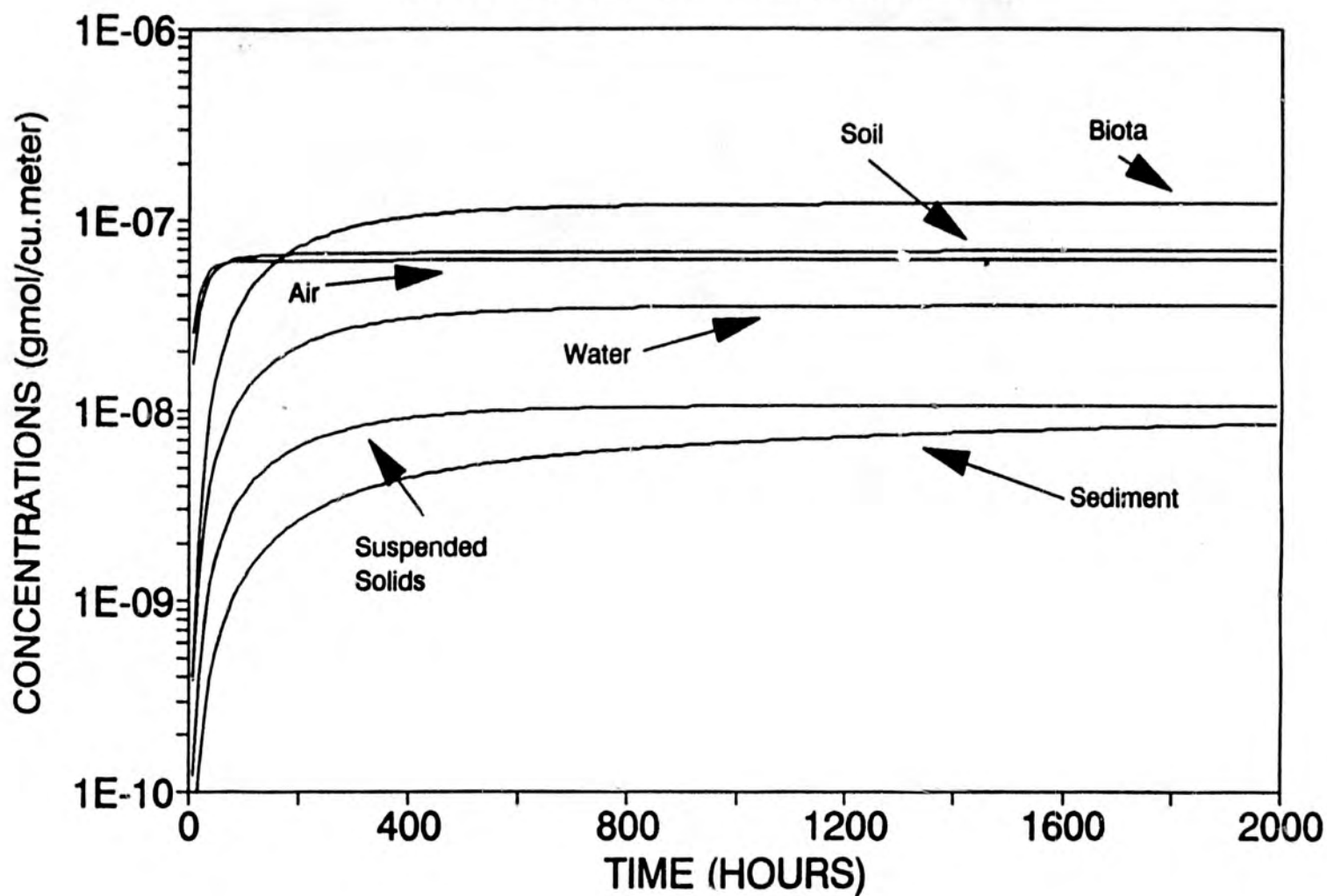


FIGURE 7.15

8. SCREENING-LEVEL EXPOSURE ANALYSIS

8.1 Overview

The assessment of health risk requires the determination of exposure from multiple pathways (Ott, 1985; Liou, 1990; NRC, 1987, 1991; Cohen, 1989). As an illustration, the exposure of the human receptor to chemical pollutants via multiple pathways is shown in Figure 8.1. The major exposure pathways pertinent to human health risk assessment of toxic air pollutants include:

- Inhalation of released contaminants
- Inadvertent and intentional ingestion of crops contaminated by deposition and/or translocation of pollutants
- Ingestion of contaminated soil or soil containing adsorbed pollutants
- Ingestion of fish and other aquatic species contaminated by pollutants present in surface water
- Dermal absorption due to contact with contaminated air, soil and water
- Infant exposure to contaminants in mother's milk
- Drinking water exposure (surface or groundwater)
- Ingestion of dairy products (e.g., ingestion of cow's milk affected by consumption of contaminated feedstock)
- Ingestion of meat and other animal products from game and domestic livestock

The movement of chemicals throughout the food chain may be particularly important to the overall assessment of the exposure of the human receptor to pollutants that tend to bioaccumulate. The determination of exposure of human and ecological receptors to chemical pollutants requires knowledge of pollutant concentrations in all media through which significant exposure can occur. Exposure, in turn, is a function of contaminant concentrations in various environmental media that affect both the receptor directly, as well as various components of the food chain.

EXPOSURE PATHWAYS

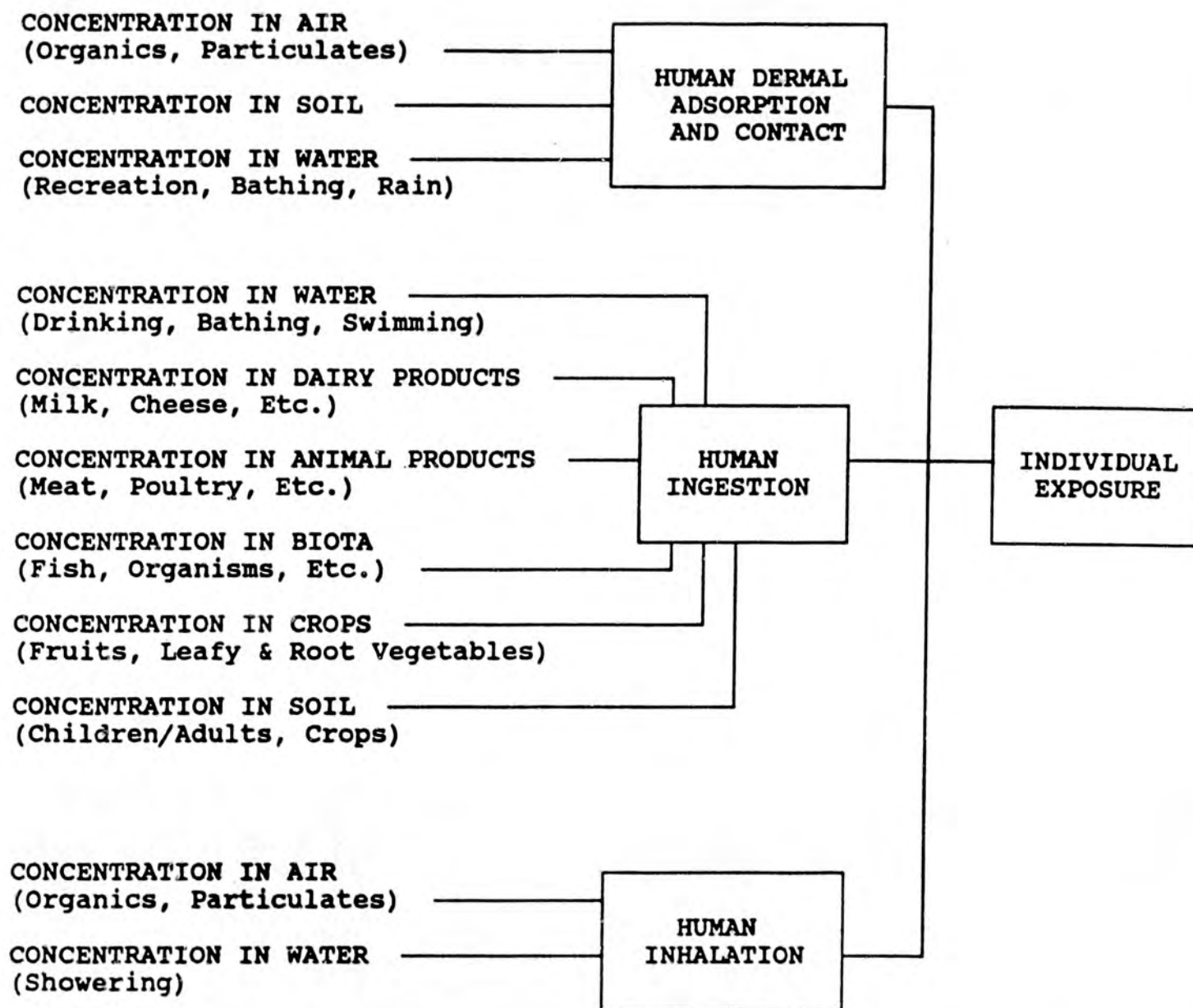


FIGURE 8.1

8.2 General Description of the Modeling Approach

Exposure assessment can be carried out by either direct exposure monitoring, modeling, or combined modeling and monitoring (Wallace, 1987, 1989; NAS, 1991; Liroy, 1990; Sexton and Ryan, 1988; Winer, et al., 1989; Thomas et al., 1989). In this study an approximate exposure assessment for chronic exposures was carried out using the multimedia concentrations determined for the Port Valdez area (see section 7) and the multimedia total dose (MTD) model (Chetty, 1991). The major pathways of the MTD model are illustrated in Figure 8.1. Some of the major features of the MTD model are:

- Dynamic (i.e., time dependent) analysis of dose and dose rate
- Time and age dependent human physiological and anatomical parameters (e.g., receptor's mass, inhalation rate)
- Theoretical model for absorption/desorption via the lungs
- Sub-models for dermal absorption
- Dynamic sub-models to predict pollutant accumulation in the food chain (e.g., vegetation, fish, beef)
- Inclusion of agent metabolism within the human body

The MTD model is more comprehensive than the standard EPA approach to estimating contaminant intake. However, in the present approach the model was run in a mode compatible with the EPA methodology (EPA, 1986a-1986d, 1988a). Chetty (1991) demonstrated that the MTD model can be used to duplicate the EPA guidelines for exposure assessment and other similar models (e.g., McKone and Kastenber, 1986; McKone and Ryan, 1989; McKone and Layton, 1986; McKone and Daniels, 1990) by neglecting metabolism within the human body and other elimination pathways (e.g., urination). The significance of including metabolism through pharmacokinetics models was recently illustrated for benzene by Hattemer-Frey and Travis (1990) and Travis et al. (1990). In this study, however, a conservative estimate of the dose rate (mg/kg/day) was obtained following the recommended EPA approach. It is recognized that such an approach is likely to overestimate the actual exposure and thus the calculated risk. However, this screening-level approach can be used to provide a ranking of expected environmental problems among the various chemicals of concern. Also, it is often the case in risk management that a conservative estimate of risk is utilized in order to provide a safety margin designed to protect the public.

A conservative estimate of dose rate is given by the following equation (Chetty, 1991)

$$\frac{dD}{dt} = \sum_{l=1}^{N_p} \sum_{z=1}^X L_{lz}(t) C_{lz} f_{lz} W_{lz} + \sum_{l=1}^{N_v} \sum_{z=1}^X N_{lz} A_{lz} f_{lz} \quad (8.1)$$

In the current application of the MTD model the first term on the right hand side of Eq. 8.1 represents contaminant intake due to inhalation and ingestion while the second term represents intake due to dermal absorption. The total mass of agent uptake by the receptor is designated by D (μg), f_l is the fraction of time during which exposure occurs for each pathway (dimensionless), and W_l is the absorption or agent uptake factor for pathway l (dimensionless), X is the total number of macro/micro-environments, L_k is the extent of contact of receptor with a given medium designated by the subscript i (e.g. air, water, soil, etc.) via a specific exposure pathway (e.g., inhalation, etc.) (m^3/day , or g/day), and C_k is the concentration ($\mu\text{g}/\text{m}^3$, or $\mu\text{g}/\text{g}$) of the chemical in environmental media i (soil, water, food, etc.) in contact with the receptor. N_k is the flux ($\mu\text{g}/(\text{day})(\text{m}^2)$) of the chemical agent across an exchange boundary (as in dermal absorption), N_v is the total number of exposure pathways where agent exchange is by interfacial transport, A_k is the surface area of the exchange boundary involved in the interfacial transport of agent into the body (m^2), z designates the macro or microenvironment where exposure occurs, and l designates the exposure pathway where agent exchange is by interfacial transport in the absence of a control volume, i.e., soil on exposed skin. It is important to note that Eq. (8.1) leads to a conservative estimate of dose since it neglects agent outflow from the receptor, and production and/or degradation/metabolism of the agent within the receptor.

Equation 8.1 specifies the time rate of change of the total mass of agent in the body during a specific time period. Frequently however, the agent dose rate for the receptor per kg of receptor body mass is desired (i.e., specific dose rate). If one expresses the dose rate as

$$\frac{dD}{dt} = \alpha \quad (8.2)$$

in which α represents the left hand side of Eq. 8.1. If one defines the specific dose as

$$D_s = \frac{D}{M_m} \quad \text{for } m=1,2 \quad (8.3)$$

where D_s is the specific dose (μg of agent/kg of receptor), and M_m is the mass of receptor (kg), then the specific dose rate, $\dot{D}_s$, can be expressed as

$$\begin{aligned}\dot{D}_m &= \frac{dD_m}{dt} = \frac{d(D/M_m)}{dt} = \frac{1}{M_m} \frac{dD}{dt} + D \frac{dM_m^{-1}}{dt} \\ &= \frac{\alpha}{M_m} - \frac{D}{M_m^2} \frac{dM_m}{dt} \quad \text{for } m = 1, 2\end{aligned} \quad (8.4)$$

Equation 8.4 indicates that the specific dose rate is a function of the change of mass of the receptor. The dose rate is also reported to vary with time as other characteristics of the receptor change with time (e.g., inhalation rate, dietary intake).

Frequently, in health risk analysis, knowledge of the average specific dose rate is needed, in order to determine the corresponding health risk. The time averaged specific dose rate can be obtained by integrating Eq. 8.4 with respect to t and dividing by the time period $(t_f - t_o)$,

$$\bar{D}_m = \frac{1}{t_f - t_o} \int_{t_o}^{t_f} \left[\frac{d\dot{D}_m}{dt} \right] dt = \frac{1}{t_f - t_o} \int_{t_o}^{t_f} \left[\frac{\alpha}{M_m} - \frac{D}{M_m^2} \frac{dM_m}{dt} \right] dt \quad (8.5)$$

Thus, Eq. 8.5 specifies that the average specific dose rate is a function of the receptor's growth rate (i.e., the rate of change in body mass).

The prediction of the average dose and average dose rate, via Eq. 8.1 require a knowledge of the various model parameters. It is beyond the scope of this report to review the various exposure parameters that are used in standard exposure assessment and the interested reader is referred elsewhere (EPA, 1986a-1986d, 1984; CAPCOA, 1990; Vaughan, 1984; Liroy, 1990; Travis and Arms, 1988; McKone, 1986, 1990; Chetty, 1991; and references therein). In the MTD approach as described by Eqs. 8.1-8.5 the specific dose, and average specific dose rate are calculated as a function of the age of the receptor.

8.3 Estimation of Health Risks

Once the dose rate from the various pathways is determined, health risk analysis can be carried out given the appropriate dose-response information. In general, however, one should recognize that the response can be a function of incidence, intensity and severity (Hartung, 1986). The incidence variable is a measure of the fraction (or percentage) of the studied population that exhibits a given response (e.g., presence of tumors). The intensity of the response is a graded or continuous measurement of changes in the individual such as change in growth rate or blood pressure. The severity of responses is a subjective measure which reflects the levels of public concern. For example, one may assign a high severity scale value to birth defects and a relatively lower rating to insomnia or occasional mild headaches. Generally, we expect that the percent incidence will increase with increasing dose rate and that such increase

will be more pronounced as the duration of exposure increases. Toxic chemicals can lead to a variety of health effects including cancer, genetic damage in reproductive cells, affect offsprings in the fetal development stage, or cause a multitude of non-cancer effects. Specific information regarding the study chemicals can be found in the Toxicological Profiles published by the ATSDR and also in the IRIS database.

A simple and often a conservative approach for determining the risk associated with exposure to chemical carcinogens is based on the one-hit model (Bailar, 1988). This model is a standard model used in screening-level risk assessment and it is generally believed to be a conservative model of cancer health risk. Accordingly, the risk of developing cancer is determined from the following relation:

$$R_{ij} = 1 - e^{-(a + q_{ij}D_{ij})} \quad (8.6)$$

where R_{ij} is the health risk for exposure to chemical carcinogen i for exposure pathway j (dimensionless), D_{ij} is the average daily dose rate of chemical carcinogen i (mg/kg.day), and q_{ij} is the cancer potency factor for chemical carcinogen i [(mg/kg.day)⁻¹] via intake pathway j , and a represents the background cancer risk. Since the health risk above background is generally of interest Eq. 8.7 is often used with a set to zero. The cancer potency factors (q_{ij}) which are recommended by the USEPA have been published by the EPA⁸ and they are also available through the computerized IRIS data base. At low specific dose rates eq. 8.6 can be simplified to yield

$$R_{ij} = q_{ij}D_{ij} \quad (8.7)$$

In contrast to carcinogens, the probabilistic risk associated with non-carcinogens is difficult to quantify. However, the regulatory approach to establishing guidelines such as with the reference dose (RfD) method have been discussed in the toxicology literature. The reference dose is the average life-time daily dose below which adverse health effects are not expected. A hazard index can be calculated as the ratio of the specific dose rate to the RfD value. Thus, a hazard index below unity indicates that the environmental concentrations are at the acceptable levels.

The above approaches represent approximate screening-level estimates that lead to conservative life-time estimates of health risks. Risk analysis is complex and it is subject to many uncertainties and varying degrees of interpretation (Glickman et al., 1990). Nevertheless, the simple screening-level approach described above serves as a first order analysis to identify potential environmental problems.

⁸ EPA, Health Effects Assessment Summary Tables, OERR-9200.6-303 (91-1), NTIS #PB91-921199.

8.4 Results and Discussion of Exposure Analysis

8.4.1 Summary of Results

Two scenarios were analyzed in which the human dose rates and resulting risks and the accumulation of the study chemicals in aquatic biota and vegetation were evaluated based on the multimedia concentrations given in Table 7.4. In the first scenario, ingestion values of contaminated food for a reference individual were based on statistical information on the population of the continental United States (EPA, 1984). In the second scenario ingestion rates of contaminated food were used based on a statistical information specifically determined for coastal areas (EPA, 1989). The consumption of fish and shell fish are given in Table 8.1. It was assumed, in both scenarios, that the Valdez population is at the upper 95% and that 90% of its consumption of seafood is from the bay area. Such an approximation believed to provide an upper limit estimate of the contribution of fish ingestion to the overall dose rate. As part of the exposure analysis the accumulation of BETX and *n*-hexane in biota and vegetable were estimated as and the results are given in Table 8.4.

TABLE 8.1
INGESTION RATE VALUES FOR A REFERENCE INDIVIDUAL

Reference Individual Age (yrs)	Ingestion Rate for a Reference Individual in the U.S.		Ingestion Rate for a Reference Individual in Coastal Areas	
	Fin Fish (g/day)	Shell Fish (g/day)	Fin Fish (g/day)	Shell Fish (g/day)
Under 1	0.6	0.5	0.6	0.5
1 to 4	7.0	0.3	7.0	0.3
5 to 9	10.3	1.1	14.9	1.6
10 to 14	12.5	0.9	24.2	2.6
15 to 19	14.0	2.0	24.2	2.6
20 to 24	17.2	3.0	32.7	5.6
25 to 29	20.6	3.5	32.7	5.6
30 to 39	16.2	3.8	34.7	5.8
40 to 59	18.3	3.9	41.8	8.9
60 and over	17.2	2.4	48.6	6.8

The results of the two simulations are given in Tables 8.2-8.3 and Figure 8.2. Table 8.2 provides the overall lifetime average specific dose rate, the lifetime average specific dose rate due to inhalation, the lifetime average specific dose rate due to ingestion, and the lifetime average specific dose rate due to dermal absorption based on the average monitored concentrations (see Table 7.4). The lifetime average specific dose rates are the average dose rates calculated up to the length of a reference individual's lifetime, which was set to seventy years. The overall lifetime average specific dose rates in the tables accounts for the uptake of the chemical from the major exposure pathways (excluding indoor exposure). Indoor exposure to hydrocarbons can be significant indoors and it is well documented that significant exposure to benzene can occur due to both active and passive cigarette smoking (Webster, 1986; ATSDR, Toxicological Profile for Benzene, 1991).

TABLE 8.2
LIFETIME AVERAGE SPECIFIC DOSE RATES
FOR MULTIMEDIA CONCENTRATIONS
BASED ON THE AVERAGED MONITORED AIR CONCENTRATIONS

Chemical	Overall (mg/kg/day)	Inhalation (mg/kg/day)	Ingestion (mg/kg/day)	Dermal Absorption (mg/kg/day)
Ingestion Intake Values Based on a Reference Individual in the U.S. (USEPA, 1984)				
Benzene	2.10E-03	2.10E-03	9.66E-07	9.61E-10
Ethylbenzene	3.08E-04	3.08E-04	1.51E-07	1.48E-10
<i>n</i> -Hexane	4.69E-03	4.69E-03	2.45E-06	2.18E-09
Toluene	1.88E-03	1.88E-03	9.03E-07	8.84E-10
Xylenes	6.90E-04	6.90E-04	3.69E-07	3.33E-10
Ingestion Intake Values Based on a Reference Individual in Coastal Areas (USEPA, 1989)				
Benzene	2.10E-03	2.10E-03	1.03E-06	9.61E-10
Ethylbenzene	3.08E-04	3.08E-04	2.47E-07	1.48E-10
<i>n</i> -Hexane	4.70E-03	4.69E-03	8.22E-06	2.18E-09
Toluene	1.88E-03	1.88E-03	1.29E-06	8.84E-10
Xylenes	6.91E-04	6.90E-04	1.03E-06	3.33E-10

LIFETIME AVERAGE SPECIFIC DOSE RATE
(Based on Reported Concentration Data)

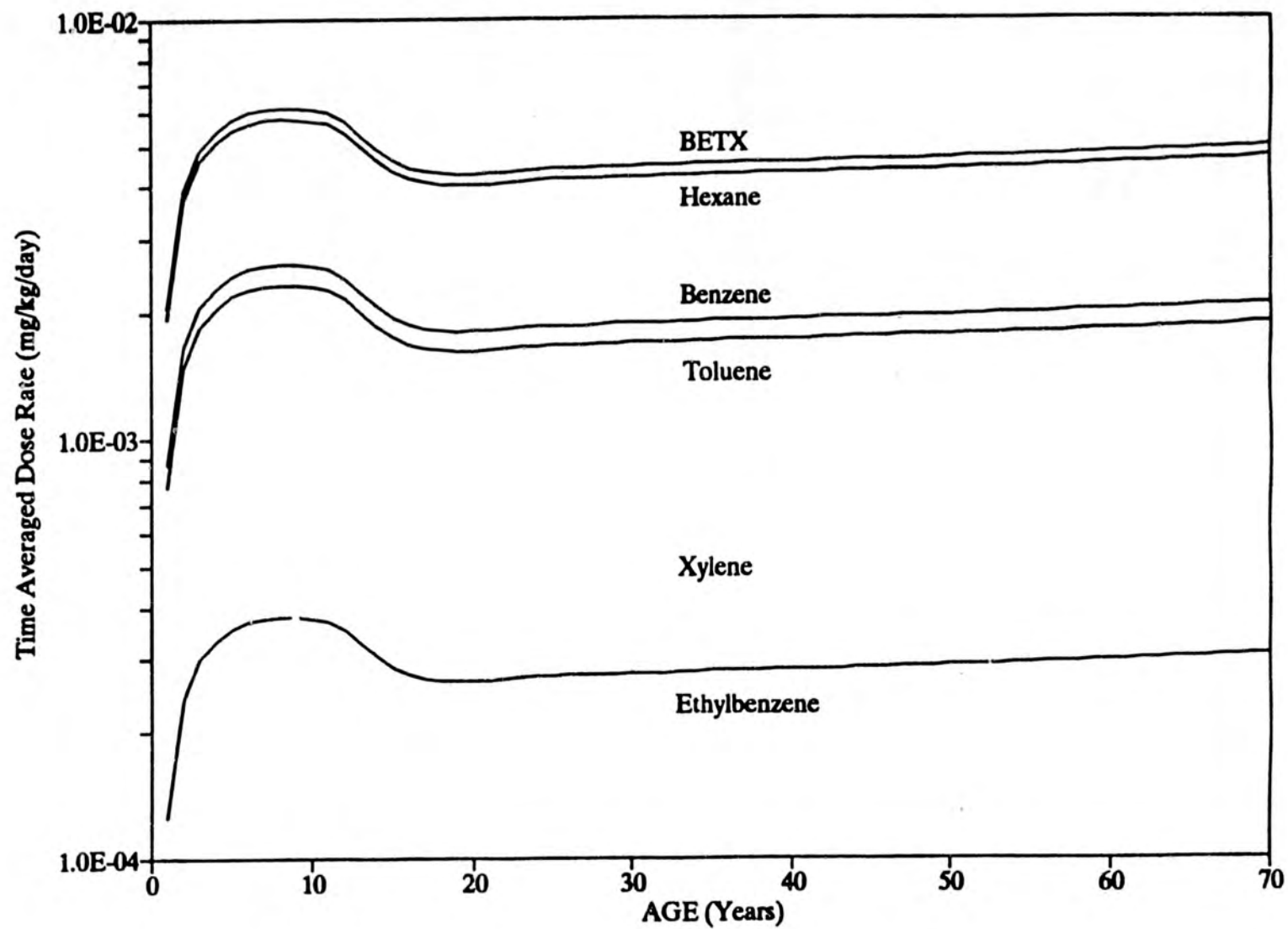


FIGURE 8.2

The overall specific dose rates for the individual chemicals and the cumulative average specific dose rate for BETX as a function of the age of the reference individual are depicted in Figure 8.2. For example, the average dose rate of the chemical corresponding to twenty years in the figures indicates the overall lifetime average specific dose rate if an individual lived in the region from birth to an age of twenty years. The specific average dose rate increases rapidly in the early years as the receptors' rate of change of mass and rate of inhalation increases rapidly. Past the age of about eight years the specific dose rate decreases towards the nearly constant value which is reached at the age of about eighteen years. Thus, for an individual born and raised at Port Valdez, the average dose rate equal in value to the lifetime-average specific dose rate is reached at the age of about eighteen years. The results in Figure 8.2 present only one possibility, one can carry out the analysis for different scenarios in order to obtain the dose rate for individuals who have moved to or away from Port Valdez at different stages of their life.

The toxicological information used for determining the hazard indices or carcinogenic risk for the study chemicals are shown in Table 8.3 along with the corresponding values of the hazard index and incremental lifetime cancer risk for the above case studies. Finally the level of accumulation (in units of $\mu\text{g/kg}$) of the five study chemicals in fish and vegetation are given in Table 8.3. These results are demonstrative of expected level of accumulation of BETX and *n*-hexane in biological receptors.

8.4.2 Inhalation Pathway

The inhalation pathway is the dominant mode of human to BETX and *n*-hexane. It is obvious from Tables 8.2-8.3 that the inhalation dose rate is directly proportional to the atmospheric concentration of the inhaled chemical

The five study chemicals have available toxicological information (see Table 8.3) that can be used to estimate the potential health risks. Only benzene is considered to be a carcinogen with a potency factor of $.029 (\text{mg/kg/d})^{-1}$ for inhalation uptake. For the other four chemicals the dose rates must be compared to the reference dose (RfD). With the above factors (see Table 3.1 and 8.3) the upper estimate of the risk from exposure at the average air concentrations is estimated to be 6.09×10^{-5} . These risk estimates correspond to a life-time cancer risk due to exposure to benzene 1 person in 16,420. Given the approximate nature of this conservative analysis it is more appropriate to report this risk rounded to a risk of 1 person in 20,000.

Comparison of the other four study chemicals shows that the inhalation pathway represents the major contribution to the hazard index. Again, the air concentration has the major influence on the contaminant intake via inhalation and hence the resulting value of the hazard index. The highest hazard index of 0.024 was calculated for *n*-hexane, which also had the highest estimated air concentration. Thus, the exposure *n*-hexane is approximately 2.4% of the

reference dose (RfD). For ethylbenzene, toluene, and xylenes the hazard indices were found to be in the range of 10^{-3} - 10^{-5} ; It appears that, from the viewpoint of human health, the concentrations of these chemicals in the Port Valdez atmosphere are within the acceptable levels. The above results are approximate basin-average values and they do not reflect actual or site-specific health risks. A more detailed analysis, has been conducted by Alyeska, to account for activity-time patterns for the targeted population through personal exposure monitoring (Yocom et al., 1991). This study is currently under review by the Valdez Air Study Review Committee, recently formed by the Regional Citizens' Advisory Council.

8.4.3 Ingestion and Dermal Absorption Pathways

Contaminant intake via the ingestion pathway was found to be significantly less than the inhalation pathway. The chemical concentration in the water compartment has the major influence on the accumulation of the study chemicals in fish with uptake by plants being most influenced by the air phase concentration. The comparison between the ingestion values based on a reference individual in the United States and from coastal area reveals that the increased consumption of local biota has a negligible influence on the overall lifetime average specific dose rate. However, the increase in consumption of local fish does significantly affect contaminant intake via ingestion.

Contaminant intake via the dermal absorption pathway is also insignificant when compared to the inhalation and ingestion pathways. The contribution of dermal absorption to the lifetime average specific dose rate is approximately six orders of magnitude less than that of inhalation and three to four orders of magnitude less than the contribution of ingestion. The main factor influencing the amount of chemical dermally absorbed is the magnitude of the air concentrations; as the atmospheric concentration increases, for a given chemical, contaminant intake by the human receptor due to dermal absorption is also expected to increase.

8.4.4 Accumulation of the Study Chemicals in Biota and Vegetation

The accumulation of the chemicals in aquatic fauna (biota) are given in Table 8.4. The results for fin fish are based on the model of Thomann (1989) which describes the uptake of the chemical accounting for growth of the fish and excretion of the chemical. From Table 8.4 it is clear that *n*-hexane displays the highest degree of bioaccumulation followed toluene, benzene, xylenes, and ethylbenzene, respectively. The major parameters affecting the predicted concentration in fin fish are the water concentrations and the octanol-water coefficient. It is worth noting that even though benzene displays a higher environmental concentration in water than toluene, the predictions for bioaccumulation of toluene are slightly higher; this trend is consistent with the higher BCF value for toluene.

TABLE 8.3

**TOXICOLOGY INFORMATION AND THE HAZARD POTENTIAL
FOR PREDICTED OVERALL LIFETIME AVERAGE SPECIFIC DOSE RATES**

Chemical	Inhalation Reference Dose ^a (mg/kg/day)	Oral Reference Dose ^a (mg/kg/day)	Potency Factor Inhalation ^a (mg/kg/day) ⁻¹	Potency Factors Oral ^a (mg/kg/day) ⁻¹	Hazard Index (HI) or Cancer Risk (CR)
					Average Air Concentration
Ingestion Intake Values Based on a Reference Individual in the U.S. (USEPA, 1984)					
Benzene	---	---	2.9E-2	2.9E-2	6.09E-05 (CR)
Ethylbenzene	1.0	1.0	---	---	3.08E-04 (HI)
n-Hexane	2.0E-01	6E-2	---	---	2.35E-02 (HI)
Toluene	2.0	2.0E-1	---	---	9.44E-04 (HI)
Xylenes	3.0E-01	2.0	---	---	2.30E-03 (HI)
Ingestion Intake Values Based on a Reference Individual in Coastal Areas (USEPA, 1989)					
Benzene	---	---	2.9E-2	2.9E-2	6.09E-05 (CR)
Ethylbenzene	1.0	1.0	---	---	3.08E-04 (HI)
n-Hexane	2.0E-01	6E-2	---	---	2.36E-02 (HI)
Toluene	2.0	2.0E-1	---	---	9.46E-04 (HI)
Xylenes	3.0E-01	2.0	---	---	2.30E-03 (HI)

The shell fish concentrations were predicted from the experimental data for accumulation of the chemical by both water and food uptake (Southworth et al., 1978). The correlation was based on the octanol-water coefficient of the chemical and the concentrations predicted for these organisms are dependent on the magnitude of the water concentrations and the octanol-water partition coefficient.

The predicted chemical concentrations in leafy vegetables and root vegetables grown in the study area are given in Table 8.4. The predicted concentrations were estimated from the predicted soil concentrations and octanol-water coefficient (Briggs et al., 1982; Chetty, 1991; and references therein). Benzene displays the highest accumulation in leafy vegetables followed by toluene, *n*-hexane, xylenes, and ethylbenzene. For root vegetables, *n*-hexane exhibits the highest accumulation followed by toluene, benzene, xylenes, and ethylbenzene. The above order of accumulation is expected consistent with the higher soil and air concentrations and bioconcentration factors for the chemicals exhibiting greater bioaccumulation.

Although the accumulation of BETX and *n*-hexane (originating from the marine terminal) in biota and vegetation appears to be at low level, data on toxicological and ecological impacts at such low concentration levels are unavailable. Obviously more work is needed to establish the effect of chronic exposure of aquatic organisms and plants exposed to low contaminant concentration levels.

TABLE 8.4
ACCUMULATION OF STUDY CHEMICALS
IN BIOTA AND VEGETATION PREDICTED BY THE MTD MODEL

Chemical	Fin Fish ($\mu\text{g/kg}$)	Shell Fish ($\mu\text{g/kg}$)	Leafy Vegetables ($\mu\text{g/kg}$)	Root Vegetables ($\mu\text{g/kg}$)
Predictions Based on Average Air Concentrations				
Benzene	1.38E-01	4.56E-03	3.69E-03	3.91E-09
Ethylbenzene	2.21E-01	4.09E-03	1.31E-04	5.56E-09
<i>n</i> -Hexane	1.33E+01	1.76E-01	2.13E-03	1.22E-06
Toluene	8.80E-01	2.02E-02	2.82E-03	2.69E-08
Xylenes	1.52E-00	2.79E-02	2.27E-03	9.96E-08

9. CONCLUSIONS

Based on the basin-wide analysis conducted in this study the following conclusions can be stated:

1. The concentrations of BETX and *n*-hexane monitored by Alyeska at Port Valdez are typical of the concentration levels observed in other urban areas. The concentrations at Port Valdez, on the average, are typical of the average or the low end of the concentration range observed in urban atmospheres. Peak concentrations higher by up to one to two orders of magnitude relative to the average concentrations have been measured. Clearly, with respect to the atmospheric concentrations of BETX and *n*-hexane, Port Valdez cannot be considered to be either a pristine or a rural area.
2. Human exposure to ethylbenzene, toluene, xylenes, and *n*-hexane leads to a lifetime average contaminant intake rate ranging from about 3.1×10^{-4} mg/kg/day to 1.8×10^{-3} mg/kg/day. The dose rates, for the above non-carcinogens, are significantly below the EPA reference dose (RfD) at which adverse health effects may occur. However, it must be noted that higher average daily intake, by a factor ranging from 2 to 10, can result from occupational exposure near and at the terminal as suggested by the higher concentrations of BETX and *n*-hexane reported from the East Gate monitoring station.
3. Human exposure to benzene leads to a lifetime average benzene intake rate estimated to be about 2.1×10^{-3} mg/kg/day. At this exposure level a conservative analysis of human health risk due to exposure to benzene, based on a basin-wide average concentration revealed that the expected lifetime cancer health risk is about 1 in 20,000. The risk to terminal workers may be greater since their daily dose of benzene, due to occupational exposure, may be significantly higher relative to non-terminal workers. It is important to note, however, that the daily dose of benzene for cigarette smokers (and those exposed to benzene through passive smoking) may be significantly higher compared to the dose received due to exposure to ambient levels of benzene. Obviously, a detailed analysis of exposure is required in order to assess the detailed health risks from all sources (see section 10).
4. The estimation of BETX emissions from the BWT facility indicates that the biological treatment units may be a major source of BETX emissions if they are not as efficient in biodegrading BETX as claimed by Alyeska.

5. Accumulation of BETX and *n*-hexane in biota is in the range of 0.14 $\mu\text{g/kg}$ to 13.3 $\mu\text{g/kg}$. It is not known if such low levels of accumulation in fish can lead to adverse effects (on fish and other aquatic organisms) as the result of chronic exposure.
6. Accumulation of BETX and *n*-hexane in vegetation is in the range of 1.3×10^{-4} $\mu\text{g/kg}$ to 3.7×10^{-3} $\mu\text{g/kg}$. No documented adverse effects on vegetation due to low concentrations of BETX or *n*-hexane have been documented in the literature. Adverse effects can occur when hydrocarbon emissions also affect ozone formation. However, this is not believed to be the case at Port Valdez.
7. The monitored concentrations reported by Alyeska and upon which part of the analysis in this study was based represent an incomplete set. For the 8/90 - 9/91 sampling period the average percentage of data not reported ranged from about 39.8% to 48.6%. Thus, presently there is an undetermined degree of uncertainty in the adequacy of the monitored data for obtaining meaningful average concentrations.

10. RECOMMENDATIONS

1. There is a need to establish the level of confidence in the Alyeska ambient air monitoring data for specific hydrocarbons (e.g., BETX and *n*-hexane) in order to determine the appropriate error bounds on the reported monitoring data. As part of the above task, the correlation between the reported data, missing data, and the tanker loading activity logs must be established.
2. There is a need to reconcile the estimated emissions with the monitoring data in order to determine the contribution of the terminal operations to the ambient levels of hydrocarbons in the Port Valdez area. This task will require that appropriate air dispersion models are used using the rich meteorological data base accumulated for Port Valdez and the available emission estimates.
3. There is a need to conduct a careful review of the tanker loading emission study in order to establish the uncertainty in the emission estimates reported by Alyeska. Such information is crucial if these emission estimates are to be used by Alyeska to establish the contribution of emissions from the terminal to the exposure of the residents of Valdez to petroleum hydrocarbons.

4. There is a need to establish the effectiveness of the biological treatment units (BTU) in the BWT facility. Convincing evidence should be presented that the BTU are indeed biodegrading BETX at the rate implied by Alyeska. If biotreatment is not as effective as it is claimed to be then the BTU can contribute significantly to the air emissions from the BWT facility.
5. Realistic exposure assessment that encompasses the actual exposed population including Alyeska employees should be conducted. In fact, a detailed personal exposure monitoring study was undertaken by Alyeska and a review of this study was recently undertaken by the Valdez Air Study Review (VASR) Committee convened by the Regional Citizens' Advisory Council (RCAC). It is hoped that the Alyeska study will provide the additional information required to assess the potential human health risks associated with the operation of the marine terminal at Port Valdez.
6. Although polyaromatic hydrocarbons of crude oil origin have been identified in the Port Valdez sediment their sources have not been clearly identified. Since polyaromatic hydrocarbons tend to bioaccumulate, it is essential that their origin and potential impact on the marine environment is clarified.
7. There is a need for a systematic program focused on the evaluation of ecological risks to the Port Valdez marine environment as the result of chronic exposures to low concentrations of hydrocarbons (both VOCs and polycyclic hydrocarbons).

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APPENDIX A

OVERVIEW OF THE SMCM MODEL

A.1 Model Equations

The SMCM model consist of both uniform compartments and non-uniform compartments. The chemical mass balance equation for each type of compartment are given below along with a brief description of the parameter estimation methods used in the SMCM model.

A.1.1 Uniform Compartments

The material balance equations for the uniform well-mixed compartments in the SMCM model (air, water, biota and suspended solids) are given by

$$\frac{d(V_i C_i)}{dt} = \sum_{j=1}^N A_{ij} K_{oi} C_j - C_i + \sum_{j=1}^N \Omega_{ij} + \sum_{j=1}^N (Q_{ji} C_j - Q_{ij} C_i) + R_i + S_i \quad i=1, \dots, N-J, \quad i \neq j \quad (1)$$

with the initial conditions

$$C_i = C_i(0) \quad \text{at } t = 0 \quad (2)$$

where V_i is the volume of compartment i (m^3), C_i is the concentration of the species of interest in compartment i ($gmol/m^3$), N is the total number of compartments, J is the total number of non-uniform compartments, A_{ij} is the interfacial area between compartments i and j (m^2), K_{oi} is the i^{th} side overall mass transfer coefficient between compartments i and j (m/hr), C_j^* is the pollutant concentration in compartment i which would be in equilibrium with compartment j and it can be expressed as $C_j^* = C_j H_j$ (refer to Eq. 19), R_i is the production or degradation rate of chemical ($gmol/hr$), S_i is the source strength ($gmol/hr$), Q_{ij} and Q_{ji} are the volumetric flow rate (m^3/hr) from compartment i to compartment j , and compartment j to compartment i , respectively. The term on the left hand side represents the rate of accumulation of chemical in compartment i . The first term on the right hand side of Eq. 1 represents the rate of the chemical mass entering or exiting compartment i by interfacial mass transfer. The second term, $\sum_{j=1}^N \Omega_{ij}$ accounts for additional intermedia transport processes between compartments i and j such as dry deposition of particle-bound organics and rain scavenging. The third term accounts for the net convective flow of the chemical into compartment i . The volumetric flow rate associated with the air compartment and its surrounding environment is evaluated based on the concept of air recirculation, accounting for non-ideal mixing. The fourth term represents the production/degradation by chemical reaction. Although this term is modeled in this work as a

pseudo first order process, the inclusion of more complex kinetic expressions can be incorporated without a loss of generality. Finally, the last term is the net input into the compartment from source emissions.

The loss of pollutant mass in the air compartment resulting from rain scavenging can be incorporated via the second term of Eq. 1, e.g.,

$$\Omega_{aw} + \Omega_a = -R^*(A_{aw} + A_{as}) \lambda_g^* C_a H_{wa} \quad (3)$$

where the subscripts a, w, and s represent the air, water and soil compartments, respectively; R^* is the precipitation rate (e.g., mm/hr); A_{as} and A_{aw} are the air/soil and air/water interfacial areas, respectively; C_a is the pollutant concentration in the air compartment, and H_{wa} is the dimensionless chemical water/air partition coefficient (i.e., $H_{wa} = C_w/C_a$, at equilibrium). λ_g^* is a dimensionless gaseous rain scavenging ratio; it describes the efficiency by which rain drops can remove contaminants from the air, and varies between 0 and 1 for chemicals which are nonreactive in the aqueous phase. Contaminants entering to the water compartment due to rainfall are also incorporated by using the second term of Eq. 1, e.g.,

$$\Omega_{aw} = R^* A_{aw} \lambda_g^* C_a H_{wa} + f_{ro} (R_o) L_{ro} H_{as} \lambda_g^* C_a H_{wa} \quad (4)$$

The terms on the right hand side of Eq. (4) account for the amount of pollutant added to the water compartment by wet deposition and surface runoff, respectively. R_o is the runoff rate (m/hr), f_{ro} is the fraction of runoff which will reach surface waters, L_{ro} is the length perpendicular (m) to the direction of runoff flow, and H_{as} is the height of the sheet of runoff water (m).

A.1.2 Non-uniform Compartments

The soil and sediment are treated as non-uniform compartments in the SMCM model. The pollutant transport processes in these compartments are dominated by molecular diffusion which leads to significant concentration gradients in these compartments.

Pollutant transport in the three-phase (air, water, and solids) soil matrix can be approximated, assuming the soil phases to be in local equilibrium (Cohen and Ryan, 1990), by a one-dimensional diffusion equation with convection and chemical reaction.

$$\frac{\partial C_m}{\partial t} = \frac{\partial}{\partial z} \left(D_m \frac{\partial C_m}{\partial z} \right) - V_m \frac{\partial C_m}{\partial z} + R_m + S_m \quad (5)$$

with the initial condition

$$C_m = C_m(0, z) \quad \text{at } t=0 \quad (6)$$

and the flux boundary conditions

$$V_m C_m - D_m \left(\frac{\partial C_m}{\partial z} \right) = R^* \lambda_g^* C_a H_{m,a} + k_{a,m} (C_a - C_m / H_{m,a}) \quad \text{at } z=0 \quad (7)$$

$$-D_m \left(\frac{\partial C_m}{\partial z} \right) = k_{gw,m} (C_m / H_{m,gw} - C_{gw}) \quad \text{at } z=L \quad (8)$$

or

$$\left(\frac{\partial C_m}{\partial z} \right) = 0 \quad \text{at } z=L \quad (9)$$

where the depth from the soil-atmosphere surface is designated by z , C_m is the pollutant concentration in the soil matrix, and V_m is the effective water infiltration rate in the soil matrix (m/hr) (Jury et al., 1983) as defined below.

$$C_m = (1 - \epsilon_m - \epsilon_{rw}) C_p + \epsilon_{rw} C_{rw} + \epsilon_m C_a \quad (10)$$

$$V_m = \frac{V_w}{H_{m,rw}} \quad (11)$$

in which C_p , C_{rw} and C_a are the concentrations in the soil-solids, soil-water, and soil-air phases, respectively, ϵ_m , ϵ_{rw} are the volume fractions of the soil-air and soil-water, respectively, and V_w is the interstitial velocity of water in the soil matrix (m/hr) which is determined from a detailed submodel for water infiltration and evaporation. $H_{m,a}$ and $H_{m,rw}$ are the soil matrix/soil-air and the soil matrix/soil-water partition coefficients, respectively (defined in Eqns. 21 and 22). D_m is the effective diffusion coefficient (m^2/hr) that can be estimated as discussed later in the paper. $k_{a,m}$ is the air-side mass transfer coefficient at the soil/atmosphere interface, and $k_{gw,m}$ is the water-side mass transfer coefficient at the soil/groundwater interface. R_m is the rate of production or degradation per unit volume of soil matrix ($gmol/hr.m^3$), and S_m is the source strength of pollutant per unit volume of soil matrix ($gmol/hr.m^3$). This source strength can in principle be a function of time and position. However, the above approach for the soil matrix with a buried chemical layer may be unreasonable. Therefore, for the case of buried chemical simulation, an alternative approach is applied as described in the following paragraph. Through the use of the boundary conditions (Eqns. 7-9), it is recognized that the uniform compartments and non-uniform compartments are not necessarily in dynamic equilibrium at the boundaries, and

thus more appropriate flux boundary conditions are applied at the top and bottom boundaries of the soil compartment (Eqns. 7-9). Specifically, the deposition of water-borne pollutant, the infiltration of rain water, and the interfacial mass transfer constrained by equilibrium are incorporated to the top flux boundary condition (Eq. 7). Furthermore, two different flux boundary conditions are provided in the SMCM model for the bottom boundary. One accounts for the chemical transport to groundwater (Eq. 8); although groundwater is not treated as a compartment in the current work, a flux condition at the bottom boundary of the soil compartment is incorporated to account for chemical transport to groundwater. It is worth noting that, as a first approximation, the pollutant concentration in the bulk groundwater (i.e., C_{gw} in Eq. 8) is simply assumed to be zero, i.e. equivalent to assuming an initially uncontaminated groundwater. A modification of the above approach can be made by incorporating a simple groundwater model into the SMCM approach to account for the time variations of C_{gw} . The other flux condition (Eq. 9) allows the setting of the flux of the chemical through the bottom of the compartment to be zero. This is valid so long as the concentration front has not reached the bottom boundary at $z = L$, or if the bottom boundary is indeed impermeable to the solute.

The material balance of pollutant transport in the sediment compartment is also treated by a one-dimensional diffusion equation similar to Eq. 5. In the current screening approach, convection due to water infiltration into the sediment compartment is neglected, and the sediment matrix is assumed to be a two-phase system (water and solids). The flux boundary conditions for the sediment compartment are

$$-D_{sed} \left(\frac{\partial C_{sed}}{\partial z} \right) = K_{w,sed} (C_w - C_{sed} / H_{sed,sdw}) \quad \text{at } z=0 \quad (12)$$

$$\left(\frac{\partial C_{sed}}{\partial z} \right) = 0 \quad \text{at } z=L \quad (13)$$

where C_{sed} is the pollutant concentration in the sediment matrix as defined below

$$C_{sed} = (1 - \epsilon_{sdw}) C_{sdp} + \epsilon_{sdw} C_{sdw} \quad (14)$$

in which C_{sdp} and C_{sdw} are the pollutant concentrations in the sediment-solids and sediment-water phases, respectively. The volume fraction of water in the sediment is denoted by ϵ_{sdw} , and $K_{w,sed}$ is the water-side mass transfer coefficient at the water/sediment interface. D_{sed} is the effective diffusion coefficient in the sediment, and it can be estimated as discussed later in the paper. Finally, $H_{sed,sdw}$ is the sediment matrix/sediment-water partition coefficient as defined in Eq. (20).

A.2 Parameter Estimation Methods

In the SMC model, various theoretical and empirical parameter estimation methods are used (as shown in Table A.1) such that the required input data are substantially reduced, and the temperature variations of diffusivities, partition coefficients and mass transfer coefficients are taken into account. Also, the temperature dependence of the reaction rate constants can be incorporated via user input for parameters in the Arrhenius-type equation for the rate constants. The estimations of major model parameters such as partition coefficients, mass transfer coefficients, diffusion coefficients, transport parameters associated with rainfall, and meteorological parameters are briefly described in sections 2.1 -2.5.

A.2.1 Partition Coefficients

The partition coefficients, H_i , which appear in the model equations are defined using the fugacity approach (Mackay and Paterson, 1981), i.e.,

$$H_i = \frac{C_i}{C_j} = \frac{Z_i}{Z_j} \quad (15)$$

where Z_i is the fugacity capacity (gmols/m³-Pa) of compartment i. Thus, using the fugacity approach, one needs only to calculate the fugacity capacity for each compartment, and all the partition coefficients are defined. The fugacity capacities for the air and water are given by

$$\text{Air} \quad Z_a = \frac{1}{RT} \quad (16)$$

$$\text{Water} \quad Z_w = \frac{1}{H} \quad (17)$$

where H is the Henry's law constant for the solute (Pa.m³/gmol). The partitioning between soil/air, sediment/water, and suspended solids/water partition coefficients can be correlated with the organic carbon content of the solid phase, and the solute octanol/water partition coefficient. For example, the fugacity capacity of the sorbed phase Z_{sp} can be evaluated as

$$Z_{sp} = \frac{K_p \rho_{sp}}{H} \quad (18)$$

where ρ_p is the density of the solid particles (g/cm^3), and K_p is the sorption coefficient with units of $\text{m}^3 \text{ water}/10^6 \text{ g sorbent}$ given by

$$K_p = K_{oc} X_{oc} \quad (19)$$

in which K_{oc} is the organic carbon/water partition coefficient which has units of $\text{ml solution/g organic carbon}$, and X_{oc} is the mass fraction of organic carbon contained in the solid phase (dry weight basis). Various correlations of K_{oc} with the octanol/water partition coefficient (K_{ow}) have been proposed in the literature (Lyman et al., 1990), and K_{ow} has been experimentally determined for many substances (Lyman et al., 1990). These values are well established and should be used whenever possible.

The fugacity capacities of sorbed phases can be calculated given Eqs. 18-19, and the densities and the organic carbon contents of the solid particles in the sediment, soil and suspended solids compartments. Subsequently, the dimensionless sediment matrix/sediment-water partition coefficient ($H_{\text{sedm},\text{sdw}}$) is estimated from a mass balance over the water and solid phases contained in the sediment

$$H_{\text{sedm},\text{sdw}} = C_{\text{sedm}}/C_{\text{sdw}} = (1 - \epsilon_{\text{sdw}}) H_{\text{sdp},\text{sdw}} + \epsilon_{\text{sdw}} \quad (20)$$

where ϵ_{sdw} is the volume fraction of water in the sediment, and $H_{\text{sdp},\text{sdw}}$ is the sediment solid particle/sediment-water partition coefficient evaluated by taking the ratio of Z_p for sediment to Z_w . Similarly, the soil matrix/soil-air partition coefficient ($H_{\text{sm},\text{sa}}$) and soil matrix/soil-water partition coefficients ($H_{\text{sm},\text{sw}}$) can be estimated from a mass balance over the soil-air, soil-solids and soil-water phases. The resulting expressions for $H_{\text{sm},\text{sa}}$ and $H_{\text{sm},\text{sw}}$ are given by

$$H_{\text{sm},\text{sa}} = C_{\text{sm}}/C_{\text{sa}} = (1 - \epsilon_{\text{sw}} - \epsilon_{\text{sa}}) H_{\text{sp},\text{sa}} + \epsilon_{\text{sw}} H_{\text{rw},\text{sa}} + \epsilon_{\text{sa}} \quad (21)$$

$$H_{\text{sm},\text{sw}} = C_{\text{sm}}/C_{\text{sw}} = (1 - \epsilon_{\text{sw}} - \epsilon_{\text{sa}}) H_{\text{sp},\text{sw}} + \epsilon_{\text{sw}} + \frac{\epsilon_{\text{sa}}}{H_{\text{rw},\text{sa}}} \quad (22)$$

where ϵ_{sw} is the volumetric soil water content, ϵ_{sa} is the volumetric soil air content, $H_{\text{sp},\text{sa}}$ is the soil solid particle/soil-air partition coefficient, and $H_{\text{sp},\text{sw}}$ is the soil solid particle/soil-water partition coefficient. Finally, the partitioning between biota and water is estimated by the use of a bioconcentration factor (BCF).

$$\text{BCF} = C_p/C_w \quad (23)$$

where C_b is the pollutant concentration in biota. If BCF data are not available, then an appropriate correlation of BCF with K_{ow} should be utilized (Lyman et al., 1990).

A.2.2 Mass Transfer Coefficients

The overall mass transfer coefficients, K_{oi} , from compartment i to compartment j can be estimated using the two-film resistance theory

$$1/K_{oi} = 1/k_i + H_j/k_j \quad (24)$$

where k_i and k_j are the i^{th} and j^{th} side individual mass transfer coefficients. The estimation of each individual mass transfer coefficient is briefly described below.

The gas-side mass transfer coefficient at the atmosphere-soil interface ($k_{a,m}$) can be determined from the deposition velocity to a fully rough surface for a reference chemical. Accordingly,

$$k_{a,m1} = k_{a,m2} (D_{a1}/D_{a2})^{2/3} \quad (25)$$

where D_a is the molecular diffusivity of the pollutant in air, subscript 1 denotes the pollutant species under study and subscript 2 defines a reference species. It should be noted that Eq. 25 is based on the observation that the gas-side mass transfer coefficient at the atmosphere-soil interface is correlated with the Schmidt number $Sc^{2/3}$ (Fernandez de la Mora and Friedlander, 1982). Experimental data on the gas-side mass transfer coefficient for a variety of chemicals have been reported by Sehmel (1980), and these data can be applied for the reference species in Eq. 29. In addition, the correlation of Brutsaert (1975) can also be used to evaluate the air-side mass transfer coefficient at the atmosphere-soil interface.

The volumetric mass transfer coefficient for water/biota exchange can be estimated from either experimental data (Neely et al., 1974) or an appropriate empirical kinetic model such as the recent model proposed by Barber et al. (1988) for a variety of fish species.. For the biota compartment, it is often more convenient to use a volumetric water/biota mass transfer coefficient, which is preferred since it is difficult to quantify the surface area for water/biota interfacial mass transfer.

In the SMC model, the sediment-water mass transfer coefficient (water side) is determined using the correlation of Thibodeaux and Becker (1982) which expresses the mass transfer coefficient as a function of wind speed, the depth and fetch of the lake. The water/suspended solid mass transfer coefficient (water side) is estimated from the correlation of Rowe et al. (1965). The air-side mass transfer coefficient is evaluated from the set of correlations of Brutsaert (1975), which is recommended for the gas-side mass transfer coefficient

to a smooth or rough water-air interface. Finally, the liquid-side mass transfer coefficient at the water-air interface is determined from the correlation developed by Cohen and Ryan (1985) which is a predictive momentum-mass transfer analogy for the liquid-side mass transfer coefficient.

A.2.3 Diffusion Coefficients

The effective diffusivity of the chemical of interest, D_m , in the soil matrix is calculated by using the method proposed by Jury et al. (1983), which assumes local chemical equilibrium between the soil phases,

$$D_m = \frac{\epsilon_m D_a / \tau_a + \epsilon_{rw} H_{rw,m} D_w / \tau_w}{\epsilon_m + \epsilon_{rw} H_{rw,m} + (1 - \epsilon_m - \epsilon_{rw}) H_{sp,rw}} \quad (26)$$

where ϵ_m is the volumetric soil air content, ϵ_{rw} is the volumetric soil water content, $H_{rw,m}$ is the water/air partition coefficient, $H_{sp,rw}$ is the soil-sorbed phase/soil-water partition coefficient, and D_a and D_w are the air and water molecular diffusivities, respectively. The air and water phase tortuosities, τ_a and τ_w , respectively, can be approximated by using the following empirical correlations (1984),

$$\tau_a = [(\epsilon_m + \epsilon_{rw}) / \epsilon_m]^{2.13} \quad (27)$$

$$\tau_w = [(\epsilon_m + \epsilon_{rw}) / \epsilon_{rw}]^{2.13} \quad (28)$$

The air phase and water phase diffusion coefficients are calculated using the Chapman-Enskog method and the Wilke-Chang correlation (1979), respectively. Finally, the effective diffusivity in the sediment is determined from an equation similar to Eq. 26 with D_m replaced by D_{sm} , and the subscript s in Eqs. 30-32 replaced by sd .

A.2.5 Meteorological Parameters

Temporal variations in weather conditions such as changes in temperature and changes in precipitation are incorporated in the SMCM model. For example, the daily ambient temperature in the region under consideration is approximated from the average monthly ambient temperatures using the method of Jamison (1982). The required input data are thus reduced to 12 monthly values for each year of simulation.

The SMCM model has a rain generation module which can generate rainfall events randomly distributed for each month with specified levels of rainfall intensity, duration and total monthly rainfall throughout the simulation time. The required input data for rainfall simulations are therefore reduced to the amount of total rainfall (mm) for each month and the number of events of a given intensity for each month. In the SMCM approach, since data for a particular year or monthly averages for multiple years can be used, rainfall distributions which are characteristic of the region but with a degree of randomness from year to year, can be handled.

A.3 Source Types and Other Simulation Scenarios

In order to provide for a variety of scenario simulations, four types of uniformly distributed (UD) sources (non-repetitious constant, non-repetitious sinusoidal, constant repetitious, and sinusoidal repetitious) were considered for the air and water compartments, whereas only a non-repetitious constant UD source was applied for the soil and sediment compartments. The non-repetitious constant source is applicable for scenarios where the pollutant is released with a constant source strength, and it allows the source strength to be turned on at any given time and turned off at any time before the end of simulation. The non-repetitious sinusoidal source can be applied for scenarios where chemical emission follows the pattern of sinusoidal variation such as chemicals emitted from industrial plumes. In such a case, the SMCM application would only be appropriate if multiple plumes exist over an area of sufficient size to treat the point sources as distributed sources. The constant repetitious source allows the source strength to be turned on and turned off sequentially. Finally, the sinusoidal repetitious source provides for modeling of diurnal or seasonal variation such as the emissions of pollutants from automobile traffic. In this latter example, the average source strength may represent the average daily pollutant emission rate from traffic, whereas the source amplitude represents the maximum (or minimum) variation from the average source strength.

The SMCM model can also be used to estimate the source strength given spatial-averaged monitored concentrations. The SMCM model can also simulate scenarios without source emissions by setting the source strength to zero. Such scenarios may be of interest in modeling the distribution of pollutants in areas that are initially polluted. For such scenarios, sufficiently high initial concentrations (above background) are required as input for the appropriate SMCM compartments. The SMCM model output include the concentrations in the various compartments as a function of time, the percent of the total mass of the chemical present in each compartment, and the chemical transfer rates from one medium to another. Details of the numerical algorithms of the SMCM model can be found elsewhere (Cohen et al., 1990).

APPENDIX B
EMISSION INDEX AND EMISSION HAZARD INDEX
FOR SELECTED PETROLEUM HYDROCARBONS

Spreadsheet for Prioritizing the Study Chemicals.

status: yes indicates that no RfD has been assigned but ill health effects have been observed

inc missing vapor pressure data

* used very approximate vapor pressure, need to revise if compound is included on list

NOTE: A volatility index of unity indicates that the compound exists as a gas under normal ambient conditions.

The values listed for the volatility index, emission index, and the emission hazard index are approximate values.

The indices should be used only for ranking petroleum hydrocarbons with respect to air emissions.

Formula	Status	Compound	Concentration mg/L	MW, g/mol	Volatility Index	Emission Index	Emission Hazard Index = Emission Index times		Potency Factor, kg-day/mg high	RfD, mg/kg/day low
							High PF	Inv Low RfD		
	inc	(2-Methylbutyl)benzene	183.4							
C H4		Methane	75.3	16	1.0E+00	8.36E-02				
C2 H6		Ethane	432.3	30	1.0E+00	4.80E-01				
C3 H8		Propane	2474.9	44	1.0E+00	2.75E+00				
C4 H10		n-Butane	3395.3	58	1.0E+00	3.77E+00				
C4 H10		isobutane	3123.3	58	1.0E+00	3.47E+00				
C5 H10		Cyclopentane	1293.1	70	3.9E-01	5.67E-01				
C5 H12		isopentane (2-Methylbutane)	7232.9	72	7.9E-01	6.34E+00				
C5 H12		n-Pentane	8486.9	72	5.5E-01	5.21E+00				
C6 H6		Benzene	2990.0	78	9.7E-02	3.23E-01	9.38E-03	yes	0.029	APP A
C6 H12		Cyclohexane	4801.5	84	1.1E-01	5.97E-01				
C6 H12		Methylcyclopentane	4304.0	84	1.7E-01	7.93E-01				
C6 H14		Dimethylbutane	1.4	86	3.5E-01	5.27E-04				
C6 H14		n-Hexane	2756.0	86	1.6E-01	4.79E-01		7.99E+00		0.08
C6 H14		2-Methylpentane	37.9	86	2.7E-01	1.15E-02				
C6 H14		3-Methylpentane	13.5	86	2.4E-01	3.65E-03				
C7 H8		Toluene	6395.8	92	3.4E-02	2.43E-01		1.22E+00		0.2
C7 H14		1,1-Dimethylcyclopentane	386.0	98	4.5E-02	1.92E-02				
C7 H14		cis-1,2-Dimethylcyclopentane	6.7	98	4.5E-02	3.35E-04				
C7 H14		trans-1,2-Dimethylcyclopentane	1737.0	98	4.5E-02	6.63E-02				

Formula	Status	Compound	Concentration, mg/L	MW, g/mol	Volatility Index	Emission Index	Emission Hazard Index = Emission Index times			Potency Factor, kg-day/mg high	RfD, mg/kg/day low
							High PF	Inv	Low RfD		
C7 H14		Ethylcyclopentane	791.9	98	4.5E-02	3.94E-02					
C7 H14		Methylcyclohexane	8521.0	98	5.0E-02	4.73E-01					
C7 H16		2,2-Dimethylpentane	0.2	100	7.8E-02	1.95E-05					
C7 H16		n-Heptane	20.1	100	5.3E-02	1.18E-03					
C8 H16		cis-1,2-Dimethylcyclohexane	492.2	112	1.8E-02	8.63E-03					
C8 H16		trans-1,2-Dimethylcyclohexane	1138.7	112	2.4E-02	3.00E-02					
C8 H16		cis-1,3-Dimethylcyclohexane	2354.6	112	2.6E-02	6.88E-02					
C8 H16		trans-1,4-Dimethylcyclohexane	791.3	112	2.8E-02	2.43E-02					
C8 H16		1-Ethyl-1-methylcyclopentane	57.9	112	2.1E-02	1.35E-03					
C8 H16		cis-1-Ethyl-2-methylcyclopentane	86.9	112	2.1E-02	2.03E-03					
C8 H16		trans-1-Ethyl-2-methylcyclopentane	781.7	112	2.1E-02	1.83E-02					
C8 H16		cis-1-Ethyl-3-methylcyclopentane	260.6	112	2.1E-02	6.09E-03					
C8 H16		trans-1-Ethyl-3-methylcyclopentane	270.2	112	2.1E-02	6.32E-03					
C8 H16		Isopropylcyclopentane	125.5	112	2.1E-02	2.93E-03					
C8 H16		n-Propylcyclopentane	2422.2	112	2.1E-02	5.67E-02					
C8 H16		3-Trimethylcyclopentane	0.4	112	2.1E-02	8.87E-06					
C8 H16		4-Trimethylcyclopentane	0.4	112	2.1E-02	8.87E-06					
C8 H16		trans,cis-1,2,3-Trimethylcyclopentane	656.2	112	2.1E-02	1.53E-02					
C8 H16		trans,cis-1,2,4-Trimethylcyclopentane	511.5	112	2.1E-02	1.20E-02					
C8 H18		Methylheptane	1.3	114	4.2E-02	6.02E-05					
C8 H18		n-Octane	3.0	114	1.4E-02	4.78E-05					
C9 H8		Indene	19.3	116	2.0E-03	4.23E-06					
C9 H12		meta-Ethyltoluene	1100.1	120	5.4E-03	6.59E-03					
C9 H12		ortho-Ethyltoluene	1215.9	120	4.6E-03	6.22E-03					
C9 H12		para-Ethyltoluene	617.6	120	5.3E-03	3.61E-03					
C9 H12		Isopropylbenzene	269.5	120	5.7E-03	1.82E-03					
C9 H12		n-Propylbenzene	704.5	120	5.7E-03	4.43E-03					
C9 H12		1,2,3-Trimethylbenzene	984.3	120	2.2E-03	2.45E-03					
C9 H12		1,2,4-Trimethylbenzene	1756.3	120	3.4E-03	6.68E-03					
C9 H12		1,3,5-Trimethylbenzene	1426.2	120	4.6E-03	7.31E-03					
C9 H18		n-Butylcyclopentane	415.0	126	4.7E-03	2.18E-03					
C9 H18		sec-Butylcyclopentane	665.9	126	4.7E-03	3.50E-03					
C9 H18		cis-1-Ethyl-3-methylcyclohexane	658.9	126	4.7E-03	4.52E-03					
C9 H18		trans-1-Ethyl-3-methylcyclohexane	627.3	126	4.7E-03	3.30E-03					

Formula	Status	Compound	Concentration, mg/L	MW, g/mol	Volatility Index	Emission Index	Emission Hazard Index = Emission Index times		Potency Factor, kg-day/mg high	RfD, mg/kg/day low
							High PF	Inv Low RfD		
C9 H18		trans-1-Ethyl-4-methylcyclohexane	530.8	126	4.7E-03	2.79E-03				
C9 H18		isobutylcyclopentane	96.5	126	4.7E-03	5.08E-04				
C9 H18		isopropylcyclopentane	357.1	126	4.7E-03	1.88E-03				
C9 H18		1-Methyl-1-ethylcyclohexane	173.7	126	4.7E-03	9.14E-04				
C9 H18		1-Methyl-3-propylcyclopentane	521.1	126	4.7E-03	2.74E-03				
C9 H18		n-Propylcyclohexane	1235.2	126	4.7E-03	6.50E-03				
C9 H20		n-Nonane	0.7	128	7.4E-03	5.92E-06				
C10 H8		Naphthalene	791.3	128	6.6E-05	5.78E-05	0.00E+00	1.45E-02		0.004
C10 H14		n-Butylbenzene	241.3	134	1.1E-03	2.82E-04				
C10 H14		1,2-Diethylbenzene	115.8	134	9.2E-04	1.19E-04				
C10 H14		1,3-Diethylbenzene	193.0	134	1.2E-03	2.54E-04				
C10 H14		1,2-Dimethyl-3-ethylbenzene	154.4	134	1.1E-03	1.81E-04				
C10 H14		1,2-Dimethyl-4-ethylbenzene	453.6	134	1.2E-03	5.97E-04				
C10 H14		1,3-Dimethyl-2-ethylbenzene	144.8	134	1.1E-03	1.69E-04				
C10 H14		1,3-Dimethyl-4-ethylbenzene	530.8	134	1.2E-03	6.98E-04				
C10 H14		1,3-Dimethyl-5-ethylbenzene	453.6	134	1.2E-03	5.97E-04				
C10 H14		1,4-Dimethyl-2-ethylbenzene	299.2	134	1.2E-03	3.94E-04				
C10 H14		isobutylbenzene	241.3	134	3.0E-03	8.11E-04				
C10 H14		1-Methyl-2-isopropylbenzene	67.6	134	9.2E-04	6.91E-05				
C10 H14		1-Methyl-4-isopropylbenzene	164.1	134	1.3E-03	2.40E-04				
C10 H14		1-Methyl-2-propylbenzene	337.1	134	9.2E-04	9.28E-04				
C10 H14		1-Methyl-3-propylbenzene	897.5	134	1.2E-03	1.18E-03				
C10 H14		1-Methyl-4-propylbenzene	269.5	134	1.3E-03	4.23E-04				
C10 H14		1,2,3,4-Tetramethylbenzene	636.9	134	2.6E-04	1.86E-04				
C10 H14		1,2,3,5-Tetramethylbenzene	366.7	134	2.6E-04	1.07E-04				
C10 H14		1,2,4,5-Tetramethylbenzene	212.3	134	1.3E-04	3.10E-05				
C10 H20		sec-Butylcyclohexane	1022.9	140	6.6E-03	7.48E-03				
C10 H20		tert-Butylcyclohexane	415.0	140	6.6E-03	3.03E-03				
C10 H20		1,3-Dimethyl-2-ethylcyclohexane	675.5	140	6.6E-03	4.94E-03				
C10 H20		1-Ethyl-2,3-dimethylcyclohexane	125.5	140	6.6E-03	9.17E-04				
C10 H20		isobutylcyclohexane	443.9	140	6.6E-03	3.24E-03				
C10 H20		cis-1-Methyl-4-isopropylcyclohexane	202.7	140	6.6E-03	1.48E-03				
C10 H20		trans-1-Methyl-4-isopropylcyclohexane	212.3	140	6.6E-03	1.55E-03				
C10 H20		cis-1-Methyl-3-propylcyclohexane	365.7	140	6.6E-03	2.89E-03				

Formula	Status	Compound	Concentration, mg/L	MW, g/mol	Volatility Index	Emission Index	Emission Hazard index = Emission Index times		Potency Factor, kg-day/mg	RfD, mg/kg/day
							High PF	Inv Low RfD	high	low
C10 H22		Decanes	32436.5	142	2.4E-03	8.54E-02				
C11 H10		1-Methylnaphthalene	878.2	142	3.9E-04	3.85E-04				
C11 H10		2-Methylnaphthalene	1234.5	142	3.9E-04	5.50E-04				
C11 H16		1-Methyl-3-tert-butylbenzene	86.9	148	7.9E-04	7.62E-05				
C11 H16		1-Methyl-4-tert-butylbenzene	57.9	148	6.6E-04	4.23E-05				
C11 H24		Heptadecanes	30173.6	156	5.3E-04	1.76E-02				
C12 H8	inc	Acenaphthylene	9.7	152		0.00E+00		yes		APP A
C12 H8 O	inc	Dibenzofuran	67.6	166		0.00E+00				
C12 H18		1,3,5-Trimethylbenzene (recovered oxide conc)	135.1	162	2.6E-04	3.95E-05				
C12 H24	inc	trans-1-Methyl-2-(4-methylpentenyl)cyclopentane	212.3	166		0.00E+00				
C12 H26		Dodecanes	35678.0	170	2.6E-04	1.94E-02				
C13 H10		Fluorene	86.9	166	1.1E-05	1.82E-06		2.54E-05		0.04
C13 H14		C3 alkyl Naphthalenes	2219.5	170	3.9E-05	9.73E-05				
C13 H26		Tridecanes	42775.6	184	1.1E-04	5.00E-03				
C14 H10		Anthracene	9.7	178	2.6E-06	2.62E-10		9.41E-10		0.3
C14 H10		Phenanthrene	193.0	178	2.6E-06	5.94E-07		yes		APP A
C14 H16	*	C4 alkyl Naphthalene	1081.5	184	3.9E-05	4.86E-05				
C14 H30		Tetradecanes	49566.3	198	2.6E-05	1.45E-03				
C15 H12	*	Methyl phenanthrenes	772.0	192	2.6E-06	2.36E-06				
C15 H32		Pentadecanes	48757.6	212	6.6E-06	3.56E-04				
C16 H10	*	Fluoranthene	9.7	202	2.6E-06	2.82E-08		7.05E-07		0.04
C16 H10	*	Pyrene	9.7	202	2.6E-06	2.82E-08		9.41E-07		0.03
C16 H34		Hexadecanes	39637.1	226	2.6E-06	1.16E-04				
C17 H38		Heptadecanes	52902.3	240	9.2E-07	5.41E-05				
C18 H12	*	Benz[a]anthracene (1,2-Benzanthracene)	9.7	228	2.6E-06	2.82E-10	B2	yes	B2	APP A
C18 H12	*	Chrysene	36.6	228	2.6E-06	1.13E-07	B2	yes	B2	APP A
C18 H38		Octadecanes	58604.2	254	1.3E-06	6.80E-05				
C19 H14	*	Methyl chrysene	36.6	242	2.6E-06	1.13E-07				
C19 H40		Nonadecanes	56302.4	268	3.9E-07	2.86E-05				
C20 H12	*	Benzo[b]fluoranthene (3,4-Benzofluoranthene)	36.6	262	2.6E-06	1.13E-07	B2		B2	
C20 H12	*	Benzo[k]fluoranthene (10,11-Benzofluoranthene)	19.3	262	2.6E-06	5.94E-08	B2	yes	B2	APP A
C20 H12	*	Benzo[j]fluoranthene (11,12-Benzofluoranthene)	48.3	262	2.6E-06	1.41E-07				
C20 H12	*	Benzo[a]pyrene	9.7	252	2.6E-06	2.82E-08	3.24E-07	yes	11.5	APP A
C20 H18	*	7,12-Dimethylbenz[a]anthracene	29.0	266	2.6E-06	8.46E-10	B2	yes	B2	APP A

Formula	Status	Compound	Concentration, mg/L	MW, g/mol	Volatility Index	Emission Index	Emission Hazard Index = Emission Index times		Potency Factor, kg-day/mg high	RfD, mg/kg/day low
							High PF	Inv Low RfD		
C21 H16	ino	3-Methylcholanthrene	29.0	268		0.00E+00	B2	yes	B2	APP A
C22 H12	*	Benzo[ghi]perylene	38.6	276	2.6E-06	1.13E-07		yes		APP A
C22 H12	*	Indeno[1,2,3-cd]pyrene	135.1	277	2.6E-06	3.95E-07	B2	yes	B2	APP A
C22 H14	*	Dibenz[a,h]anthracene (1,2:5,6-Dibenzanthracene)	212.3	278	2.6E-06	6.21E-09	B2	yes	B2	APP A
C22 H14	*	Dibenzo[a,e]pyrene (1,2:4,5-Dibenzopyrene)	96.5	278	2.6E-06	2.82E-07				
C22 H14	*	Dibenzo[a,h]pyrene	96.5	278	2.6E-06	2.82E-07				
C22 H14	*	Dibenzo[a,i]pyrene	96.5	278	2.6E-06	2.82E-07				
C22 H14	*	Dibenzo[a,j]pyrene	96.5	278	2.6E-06	2.82E-07				

Study says Valdez at risk

By Susan Price
Valdez Vanguard

People kept piling in, scrambling for chairs in a council chambers packed wall-to-wall with people a week ago. After a Regional Citizens' Advisory Council board member recited the UCLA professor's extensive academic background, the professor joked:

"You've heard about my life.

Now I'm going to tell you about yours."

Yoram Cohen — whose past includes a doctorate, more than 60 articles, numerous reports, serving on various professional journal editorial boards, developing pollution software that's used in 20 universities, plus writing a textbook — began to talk about airborne hydrocarbons, specifically benzene, in Valdez.

He explained that his six-month project — commissioned by RCAC's Terminal and Environmental Monitoring Committee for \$42,200 — was only an overview of existing literature and data on the airborne chemicals from the Alyeska terminal. He was to outline the pollution issues, estimate the exposure to Valdez residents, identify where the gaps in information are, and recommend what needs to be done.

After a cautious preface, Cohen said a number of things in his Thursday afternoon presentation that kept some people on the edge of their chairs.

He said people in Valdez have a 1-in-20,000 risk of getting cancer in a 70-year life span. He explained how the U.S. Environmental Protection Agency uses 1-in-a-million as an acceptable level.

He explained the chances of obtaining cancer from benzene is highest for babies and young children. The risk tends to level off on a slightly downward slope. He said in his 3/4-inch report the chances for cancer from benzene are greater for

smokers and those that breathe passive smoke.

Cohen explained how when benzene enters the air in Valdez, 99 percent of it leaves Valdez, and that from what's left, 96 percent of goes into the air, 3.9 percent goes into the water and .05 percent goes into the soil.

It's like filling a swimming pool, he said later. A certain amount will keep flowing over. But then a specific amount stays in the pool. Of what's left in the pool, 96 percent of it goes into the air. Cohen said either the swimming pool is very small, or more likely, it's a "very large flow" into the pool.

The professor explained how Valdez compares with other cities. Not Cordova, or Seward, or Anchorage, but places like Los Angeles; Washington, D.C.; Miami; Boston and St. Louis.

He showed graphs to pinpoint the Valdez highs and lows of the BETX chemicals, focusing on benzene. (BETX is comprised of benzene, ethylbenzene, toluene, xylenes and normal-hexane. The latter four are not carcinogens and fall significantly below the level the EPA says adverse health affects may occur.)

Some people said later they found the graphs a bit startling. For benzene, the Valdez high was above the Los Angeles and Miami highs and Boston average, the same as the Washington high and below the St. Louis high.

The Valdez low estimates came in slightly above the Los Angeles low and above the Washington, St. Louis and Miami low. It fell slightly under the Boston average.

The Valdez high for normal-hex-

ane, which is not a carcinogen, came in clear above the numbers for Washington, Los Angeles, St. Louis, Miami and Boston.

The researcher said the main issue is benzene in the air; hydrocarbons in fish and vegetable are minuscule by comparison.

Cohen's report is particularly interesting because Alyeska subcontractors are working on the company's own studies.

One is based on the data collected from four air monitoring stations throughout Valdez to determine the level of benzene and other volatile organic compounds, as well as criteria pollutants (ozone, carbon monoxide, oxides of sulfur and nitrogen and others).

Right now, the VOCs, including benzene, from the terminal aren't

regulated. But the EPA is working to formulate those regulations and should be finished by November, an Alyeska spokeswoman said.

A second health risk study also being done by Alyeska contractors examines Valdez residents' exposure to benzene. It's sometimes called the "vest study" because 60 residents were fitted with vests that had sampling tubes on the lapel to siphon air for two 24-hour periods, one in August 1990 and another last February.

But to make it more interesting, the EPA is in the midst of deciding whether or not Alyeska will need to install a \$200 million hard piping vapor recovery system, which would cut hydrocarbon emissions from tanker loading by at least 95 percent, a TOEM official said.

Hard piping — called "hard" because it's fixed in place and is permanent — captures toxic vapors that normally escape into the atmosphere while tankers take on crude. If the EPA requires it in November, the system would have to be in place within two years. An Alyeska spokeswoman said the company is working on the engineering design work now.

He said if the treatment facility is not biodegrading BETX to the extent Alyeska claims, then it could be a major source of additional emissions.

The next day, an article that appeared in the Anchorage Times quoted Marnie Isaacs, Alyeska's spokeswoman, as saying the report's risk assessment was "unprofessional." That started things rolling.

Valdez called major air polluter

Alaska port blamed for 46% of oil tanker emissions in US

By William P. Coughlin
GLOBE STAFF

The loading of huge tankers with Alaskan crude oil at Valdez may be responsible for 46 percent of all airborne petroleum hydrocarbons emitted at oil tanker terminals nationwide, an Alaskan watchdog committee says.

The group and other studies found air pollution at Valdez close to that in heavily polluted urban areas and much higher than in Boston.

The Valdez citizen group, the Terminal Operations and Environmental Monitoring Committee, was set up under the 1990 Oil Pollution Act to monitor oil transportation and operations of Alyeska Pipeline Service Co.

Alyeska, the oil industry consortium that runs the terminal, has been under congressional scrutiny for reported environmental violations since the 1989 Exxon Valdez spill.

On Friday, the Valdez citizens

panel revealed findings of two American Petroleum Institute-sponsored conclaves in January, along with an independent study on effects of toxic airborne hydrocarbons at Valdez by Yoram Cohen, a member of the National Research Council and a specialist on pollutants.

Joe Bridgeman, the Valdez committee coordinator, said the citizens group also reported that Alyeska unleashes 94.7 million pounds of volatile organic compounds, including 900,000 pounds of carcinogenic benzene, into the air each year.

The group said Alyeska asked the Environmental Protection Agency in August to exempt the tanker terminal from expected federal regulations under the Clean Air Act that would require costly vapor controls at tanker terminals.

The American Petroleum Institute conferees were told by the EPA's David Markwood, an environmental engineer in Durham, N.C., that, "of a nationwide total of 98,000 metric tons," or 202,972,000 pounds, "emitted from all marine oil loading docks each year, Alyeska releases about 48,000 metric tons. That's 46 percent of the total. It's a big number," he said.

Two Alyeska representatives told the Petroleum Institute meeting that the problems are manageable and that a suggested \$125 million vapor control system can be installed, Bridgeman said.

But Bridgeman and Greg Winter, a member of the citizens group who attended the institute sessions, said company officials have said in recent interviews that the emissions pose no health problem.

In his separate study of atmospheric pollutants conducted for the Valdez group, Cohen found that concentrations of certain hydrocarbon toxins released into the air over tiny, isolated Valdez - population, 4,068 - is comparable to that found in urban areas such as Los Angeles.

Cohen said average benzene concentrations at Valdez measure between 1.2 and 7.8 parts per billion, compared with 5 parts per billion in Los Angeles and 1 to 2 in Boston.

Cohen's report also challenged the trustworthiness of industry data. "There is a need to establish confidence in Alyeska's ambient air monitoring data for hydrocarbons," the report said.

"The major statement here," Cohen said in an interview, "is that as far as hydrocarbons are concerned ... it is surprising to find atmospheric levels of chemicals at Valdez are in the range of levels found in numerous urban atmospheres. ... It is not a pristine place."

But, he said, unlike in urban areas, "people at Valdez have an opportunity to control it."

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Peer Review*



Expert says Benzene levels very high

Valdez is comparable with Lower 48 cities

By Pat Lynn

Editor, *The Pioneer*

CITY HALL -- A pollution expert from the University of Los Angeles, California, says the benzene levels in Valdez are comparable and often higher than found in Lower 48 cities, including his hometown of Los Angeles which is notorious for its air pollution.

Dr. Yoram Cohen's study suggests that Valdez residents are subject to high levels of health-threatening pollution, most of it generated from the loading of oil tankers at the Alyeska terminal and from the terminal's ballast water treatment plant.

Much of the study focuses on the annual release of 450 tons of benzene, a cancer-causing agent, that poses a cancer risk of 1-in-

20,000 or five times higher than the 1-in-100,000 viewed as acceptable risk from any single chemical by the U.S. Environmental Protection Agency.

"The conclusion is that concentration of BETX (compounds) are typical of what would find in other rural areas. So the notion is that the Port of Valdez, as far as BETX is concerned, is neither rural area nor pristine," Dr. Cohen told the audience.

"What does it mean to you?" he asked the audience. "It's up to the residents of Valdez to determine whether that is acceptable or unacceptable."

"What does it mean for me in Los Angeles. It means I don't have to go all the way to Valdez to breathe clean air," he told his audience in the City Council Chambers.

Benzene levels in Valdez, he said, are comparable and sometimes exceed those in Los Angeles, Boston, Miami and Washington, D.C.

(See: *Benzene*, page 7)



(Photo by PATTY GINSBERG)

DR. YORAM COHEN gives his benzene report at the RCAC Annual Meeting. City Attorney Bill Walker listens attentively.

Benzene, contd.

(from page 1)

Dr. Cohen's conclusions with respect to terminal pollutants may be difficult for Valdez residents to assess since benzene emissions are among the compounds not regulated by the U.S. Environmental Protection Agency at the terminal in the absence of a health-risk study to determine their impact on Valdez residents.

Dr. Cohen is an Associate Professor in Chemical Engineering at UCLA. He was contracted for \$40,000 to conduct the air quality study in Valdez. His report was released here last Thursday to coincide with the annual meeting of the RCAC -- the Regional Citi-

zens Advisory Committee which provides oversight of Alyeska's operations.

His study is based on existing data largely supplied by Alyeska which is conducting its own air quality study, the results of which are expected by this June. Dr. Cohen did not conduct any independent field tests in Valdez.

Dr. Cohen's conclusions drew a skeptical response from Alyeska spokeswoman Marnie Isaacs. She termed the study "unprofessional" and said Dr. Cohen's claim of a 1-in-20,000 cancer risk factor "an extraordinarily unprofessional statement without the

data."

Alyeska is under pressure from the state Department of Environmental Commission to bring its tanker-loading pollution emissions under control. It's now estimated that as many as 43,000 tons of hydrocarbons are emitted into the air annually from tanker loadings.

One suggestion, albeit a very costly one, is to construct a vapor recovery system that would, in effect, capture the hydrocarbons during tanker loadings and pipe them to Alyeska incinerators for burning.

Alyeska has estimated the cost of a vapor recovery system at \$200 million. Alyeska officials say they have misgivings about such a system not only on the grounds of cost but because they have a high potential for explosion.