

ALASKA LEGISLATURE SPECIAL COMMITTEE/SUBJECT FILE 8672

2030 SCOMM 78: SENATE SPEC. COMM. ON OIL & GAS, 1991-1992

48

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.

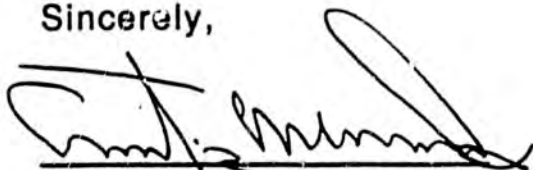
Regardless of the mechanism developed by the Department for recovery of the program costs, it is critically important to the fulfillment of the purpose of this appropriation that the study be performed without any perception of bias. Therefore, in forwarding this responsibility to the Department it is 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.

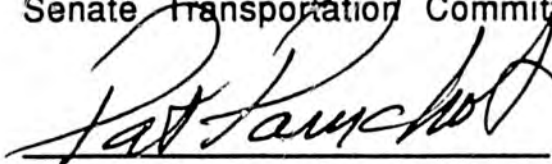
We look forward to working with you on development and implementation of this very important program and appreciate your recent efforts to step up oversight and investigation of tanker practices and operations.

Page 3
BWT Monitoring Program

Sincerely,



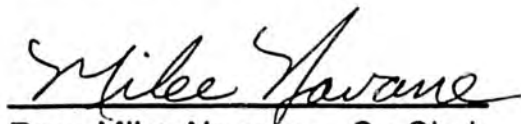
Senator Curt Menard, Chair
Senate Transportation Committee



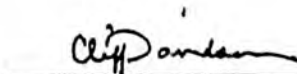
Senator Pat Pourchot, Co-Chair
Senate Finance Committee



Senator Bettye Fahrenkamp, Chair
Legislative Council



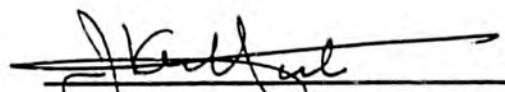
Rep. Mike Navarre, Co-Chair
House Committee on Finance



Rep. Cliff Davidson, Chair
House Committee on Resources



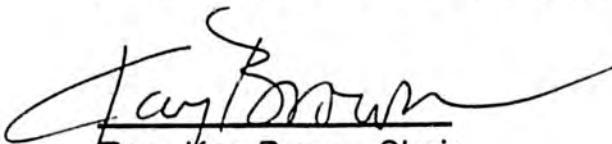
Senator Sam Cotten, Chair
Senate Oil & Gas Committee



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

THIS REPORT WAS PREPARED FOR THE REGIONAL CITIZENS' ADVISORY COUNCIL BY AN INDEPENDENT CONTRACTOR, AND THE STATEMENTS AND CONCLUSIONS HEREIN MAY NOT REPRESENT THE RCAC'S OFFICIAL VIEWS OR POLICIES.

If you have any questions concerning this document please contact Joe Bridgman at the Regional Citizens' Advisory Council, Royal Center, 310 Egan St., Rm 210, Valdez, Alaska. Telephone number (907) 835-5957.

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CORRECTION

**THIS DOCUMENT
HAS BEEN REPHOTOGRAPHED
TO ASSURE LEGIBILITY**

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March 14, 1992

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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.

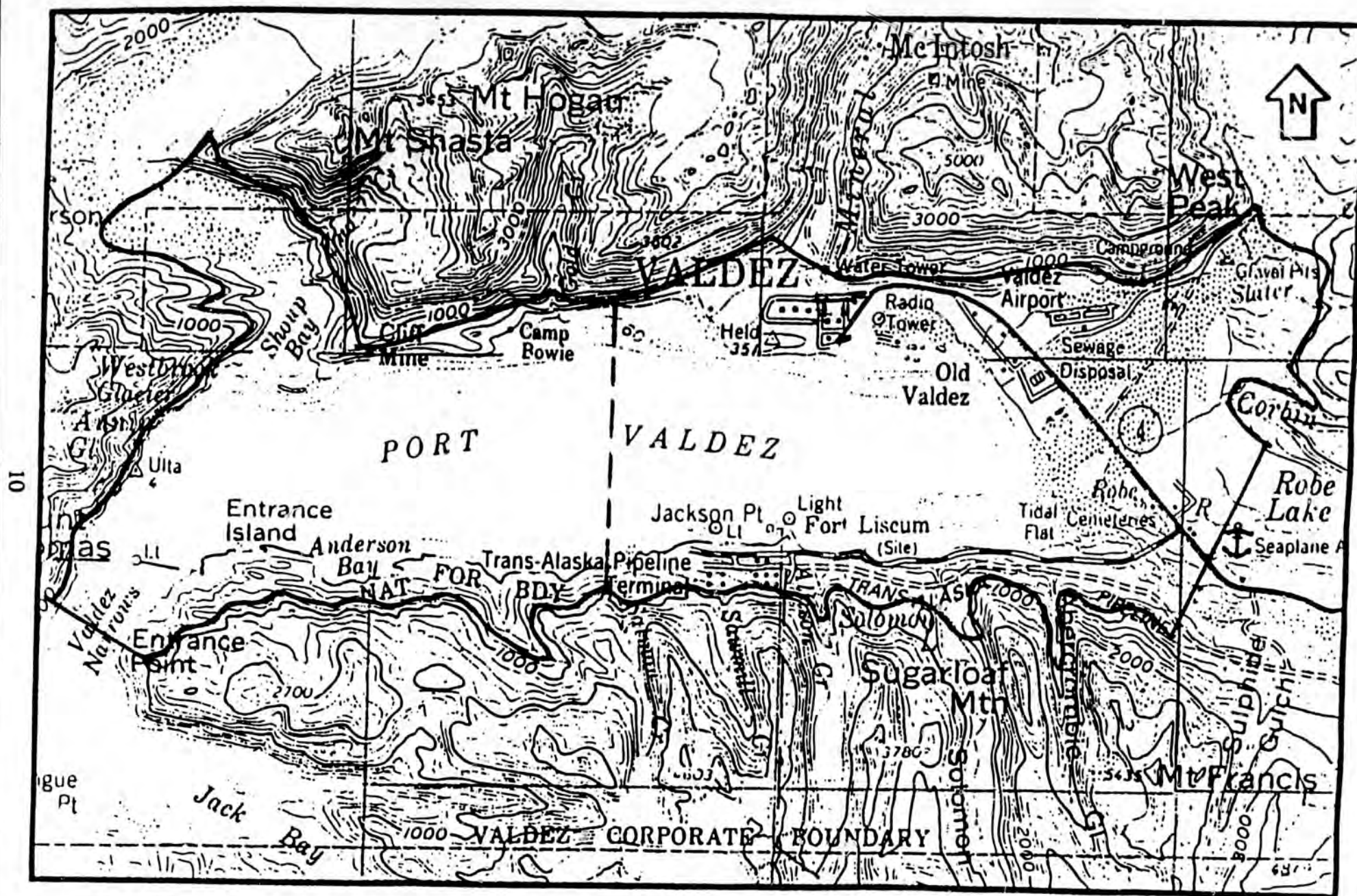


FIGURE 1.1 - Port Valdez and Approximate Borderz of the Study Area (The area to the East of the vertical Dotted line is defined as the Half-Port study area)

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

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

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

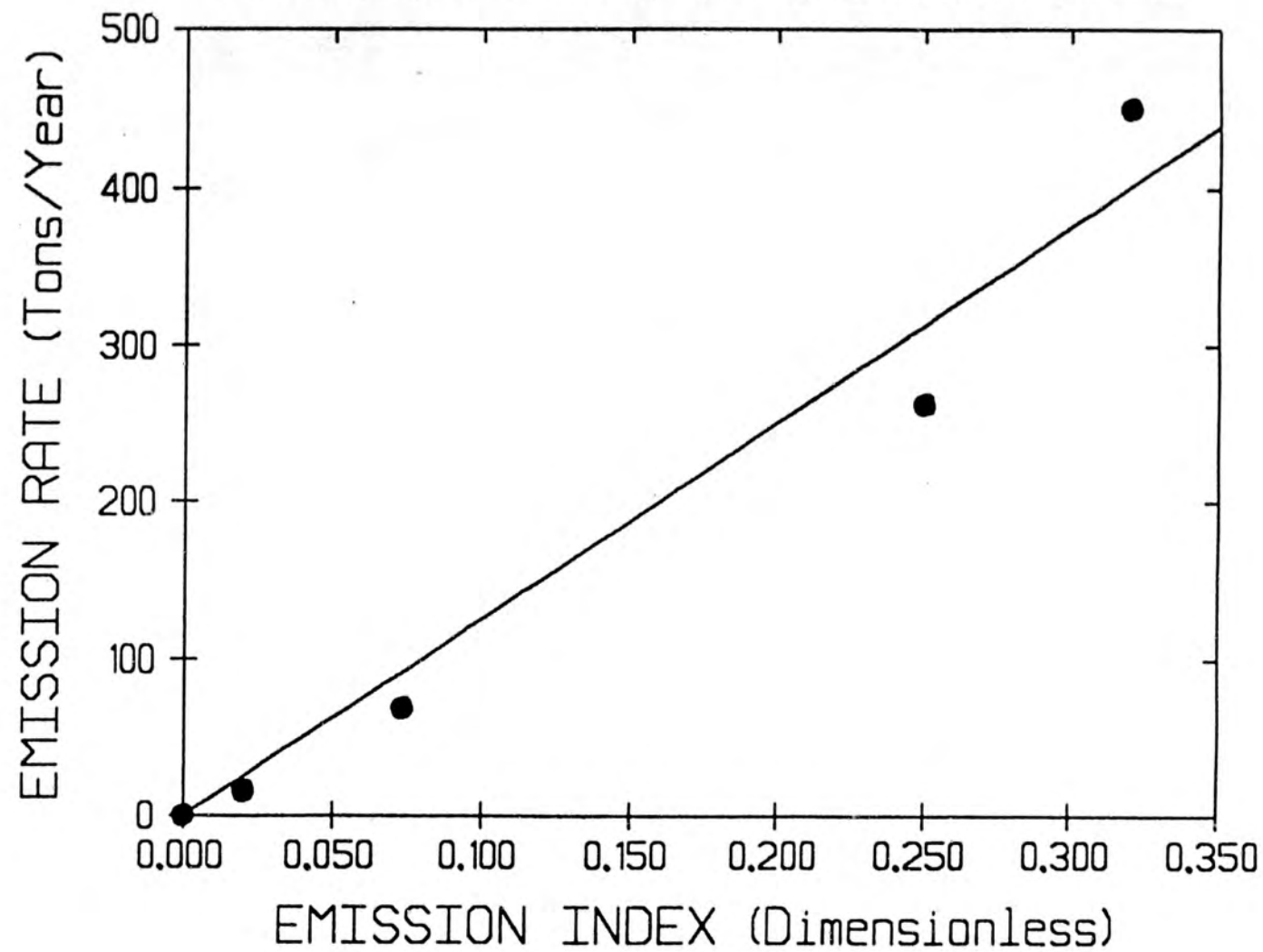


FIGURE 3.1

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
n-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/C_w ; C_b - concentration in biota, C_w - 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)

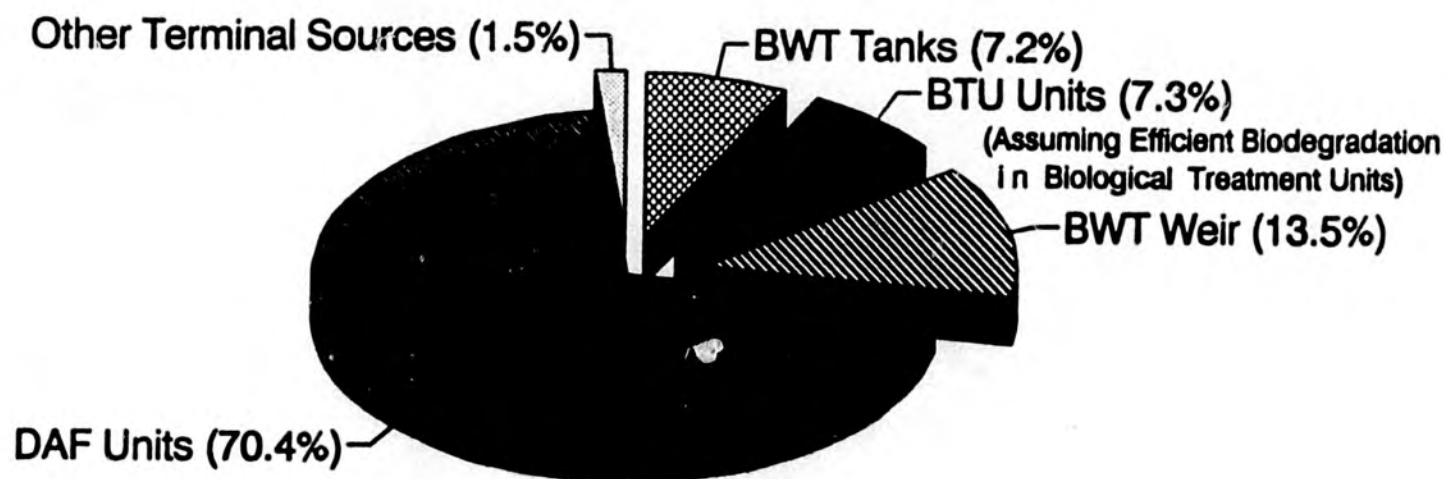


FIGURE 4.1a

SUMMARY OF MARINE TERMINAL EMISSIONS AT PORT VALDEZ

(Excluding Tanker Loading Emissions)

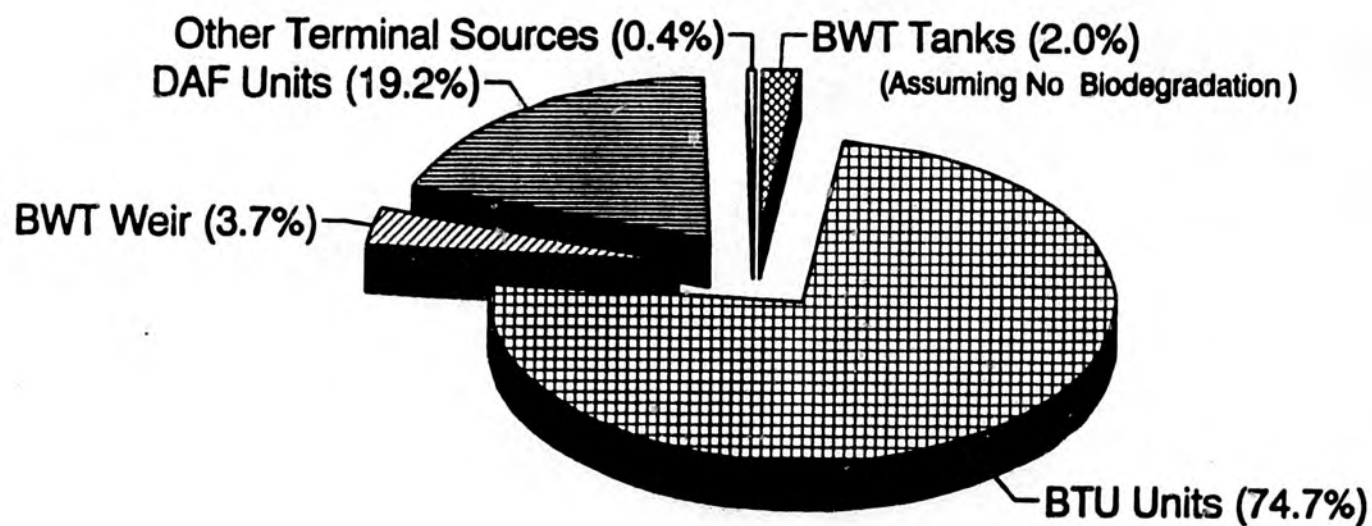


FIGURE 4.1b

SUMMARY OF EMISSION INVENTORY AT PORT VALDEZ

(Including Tanker Loading Emissions)

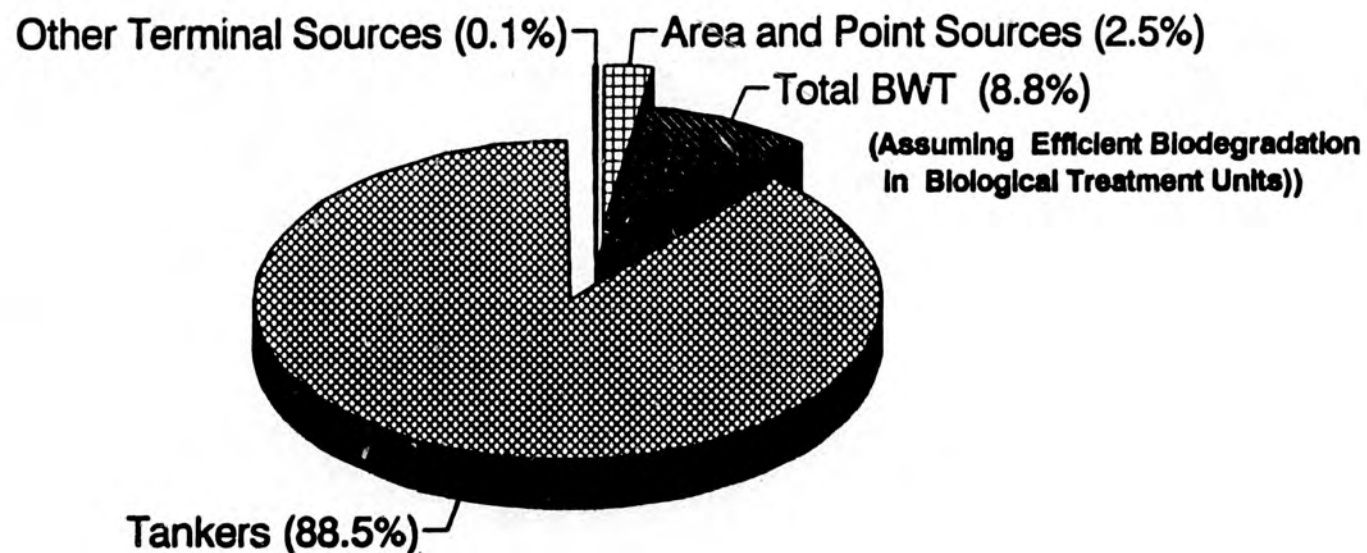


FIGURE 4.2a

SUMMARY OF EMISSION INVENTORY AT PORT VALDEZ

(Including Tanker Loading Emissions)

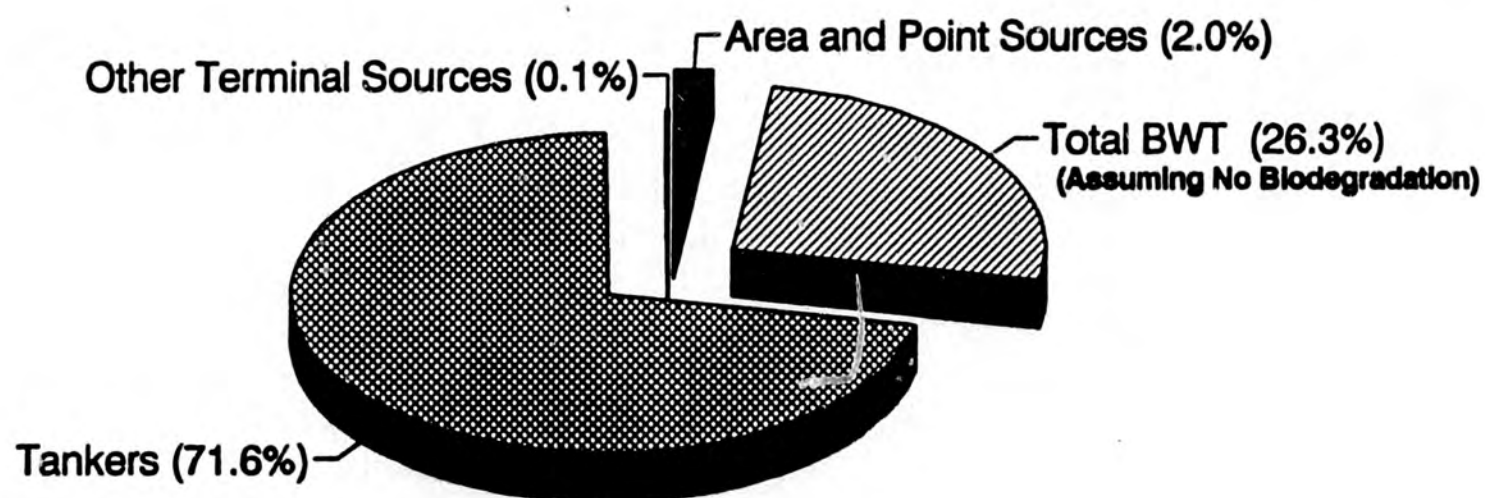


FIGURE 4.2b

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.

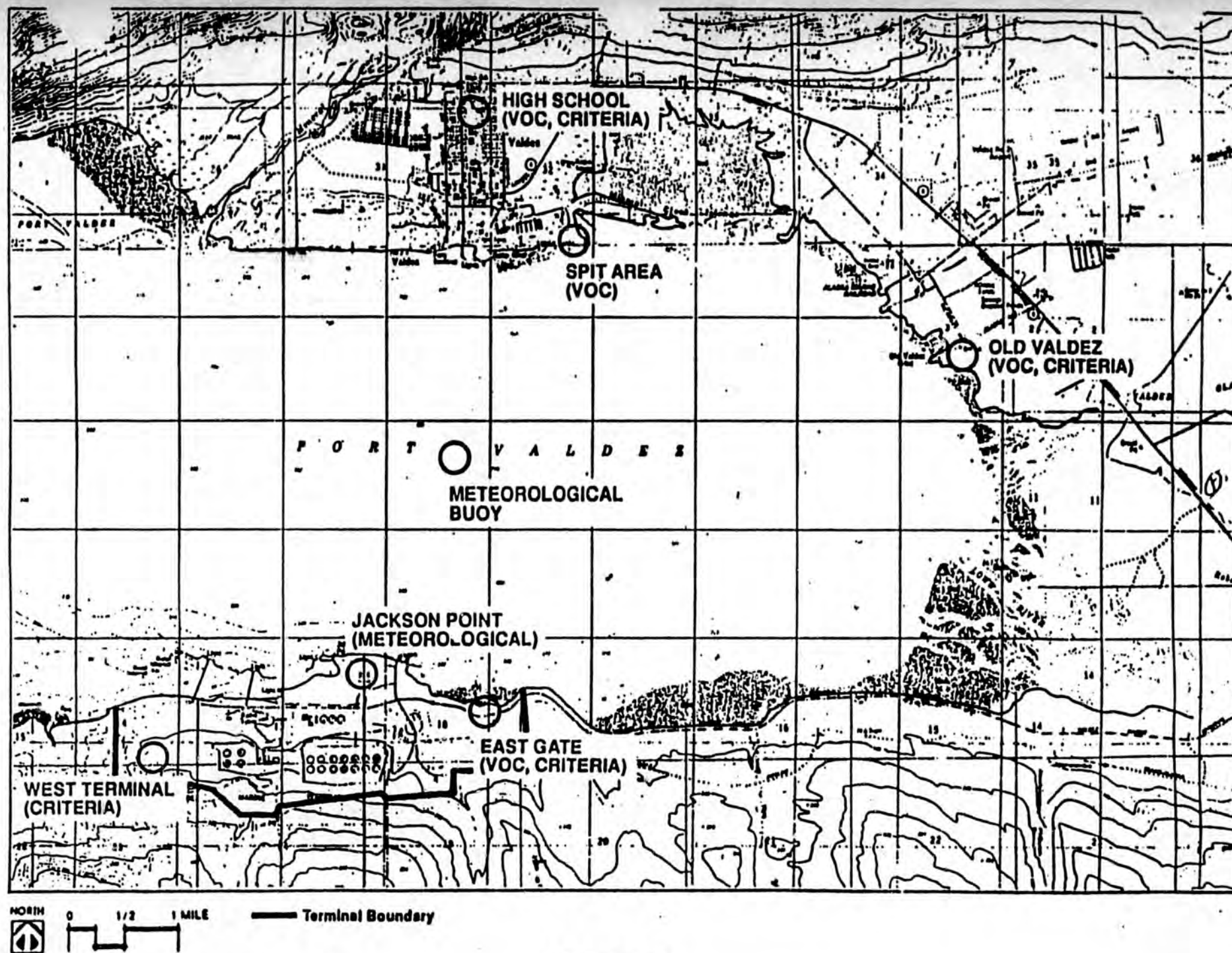


FIGURE 5.1

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).

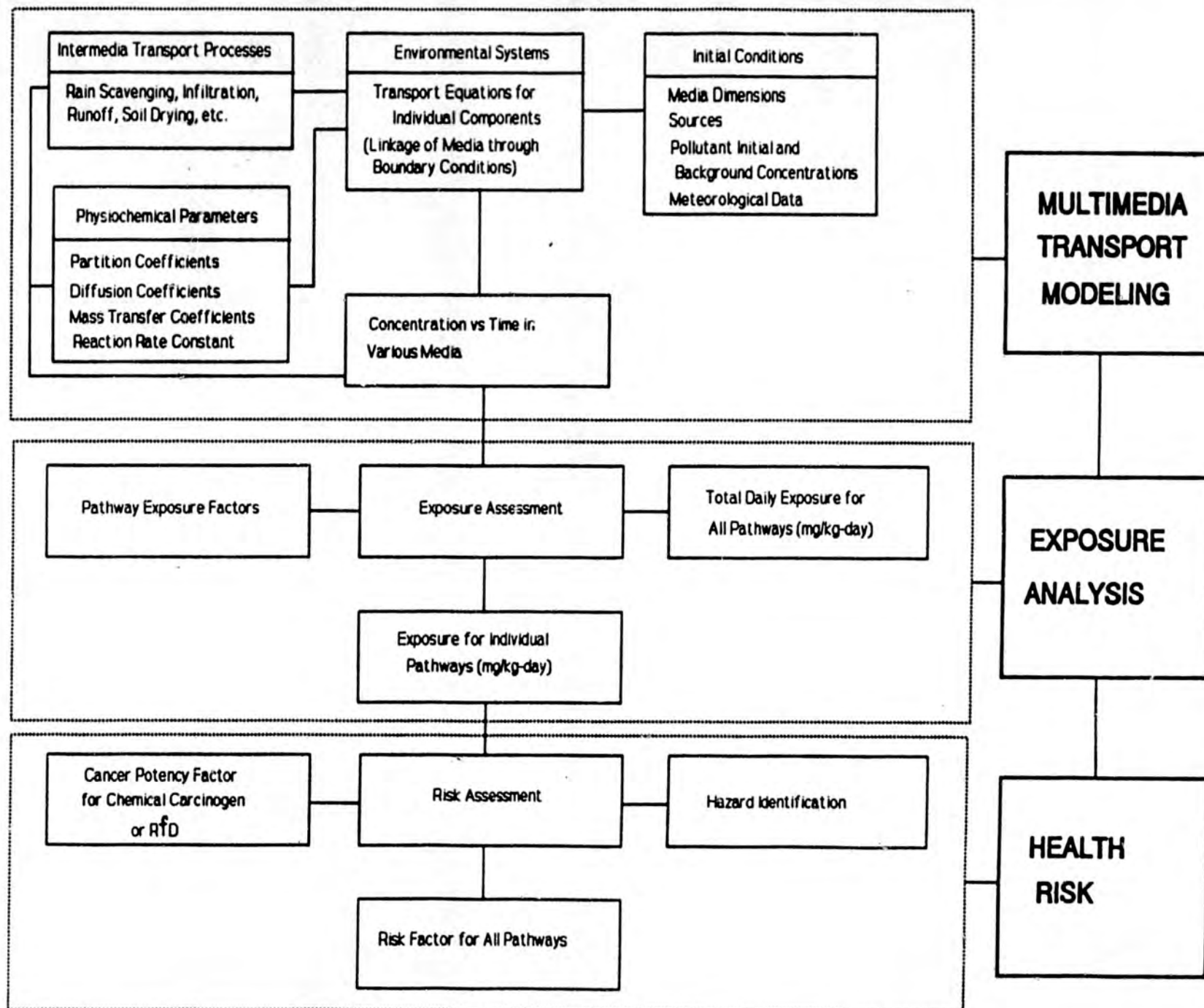
The movement of pollutants across environmental phase boundaries (e.g., air/water, soil/air) is the result of a variety of intermedia transport processes. As an illustration, a list of some of the major intermedia transport processes is given in Table 5.7. Detailed discussions of intermedia transfer 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 SMCM model is not a substitute for detailed dispersion modeling. However, the SMCM model can be coupled with concentration estimates from dispersion models or monitoring data. For example, given air phase concentrations the SMCM model can be used to calculate chemical distribution in the environment and intermedia transfers of released hydrocarbons (Cohen et al., 1990).

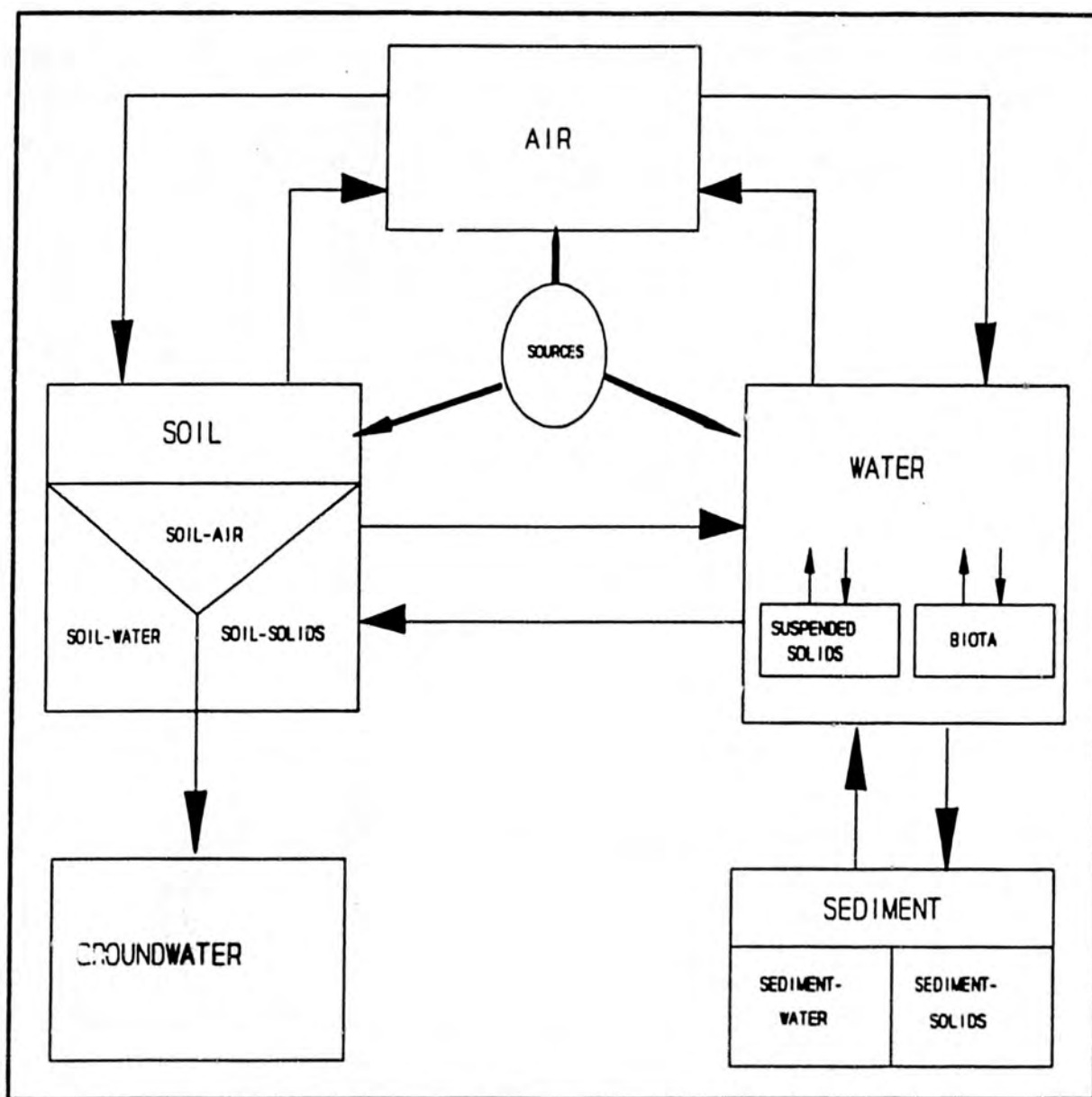


Figure 6.1 - Schematic Representation of the SMCM Model Environment

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_{sw} is defined as

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

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

$$\text{BCF} = C_b/C_w \quad (6.12)$$

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)

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

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).