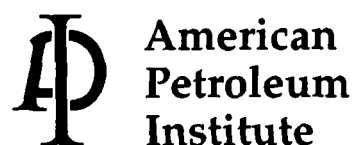


Impact Assessment of New Data On the Validity of American Petroleum Institute Marine Transfer Operation Emission Factors

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Reaffirmed 2001





One of the most significant long-term trends affecting the future vitality of the petroleum industry is the public's concerns about the environment. Recognizing this trend, API member companies have developed a positive, forward looking strategy called STEP: Strategies for Today's Environmental Partnership. This program aims to address public concerns by improving industry's environmental, health and safety performance; documenting performance improvements; and communicating them to the public. The foundation of STEP is the API Environmental Mission and Guiding Environmental Principles. API standards, by promoting the use of sound engineering and operational practices, are an important means of implementing API's STEP program.

API ENVIRONMENTAL MISSION AND GUIDING ENVIRONMENTAL PRINCIPLES

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. The members recognize the importance of efficiently meeting society's needs and our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to these principles:

- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emissions and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

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FOREWORD

Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations (API Publication 2514A) presents correlations and emission factors for estimating total hydrocarbon emissions and evaporative cargo losses from marine vessel loading and ballasting operations of crude oil tankers.

The test programs from which the marine emissions data base was developed were designed to determine the total hydrocarbon emissions from a vessel's cargo tanks during gasoline and crude oil loading and during cargo tank ballasting after the discharge of crude oil. In general, the measurement procedures and data analysis techniques used in API 2514A follow those developed as part of the Western Oil and Gas Association Marine Measurement Program. The tests were conducted during all seasons of the year and in many regions of the country, usually during routine operations.

The data base for crude oil loading emissions consists of emission measurements from 16 separate vessel operations, each of which represents averages of from 1 to 11 different compartments. The entire data base represents the measured emissions from 67 vessel compartments. These data were separated into three categories, as a function of prior cargo and ballast voyage compartment treatment. The emission data from each separate operation were separately analyzed to determine arrival, generated, and total emission factors.

The data base for crude oil ballasting emissions consists of emission measurements from 54 individual vessel compartments. These data were separated into two categories, as a function of the true cargo ullage in the compartment prior to dockside discharge. The emission data from each compartment were analyzed separately to determine total emission factors.

The correlations and factors for estimating emissions are applicable to product and crude oil tankers currently calling at U.S. ports. However, these correlations and factors should not be used for estimating emissions from very large crude carriers (VLCCs) or for vessels that employ crude oil washing. The publication does not address crude oil loading into barges, gasoline tanker ballasting, or in-transit losses since emission data were not available for these operations.

API commissioned CH2M Hill to assess the validity and application of the marine vessel loading and ballasting emission factors documented in Publication 2514A. The validity assessment was necessary due to new crude oil loading test data from Valdez, Alaska, which suggests higher crude oil loading emissions for transfer operations than those predicted by API 2514A equations. The Valdez, Alaska testing was conducted by Alyeska Pipeline Service Company and its owner organizations.

CH2M Hill reviewed and critiqued test data bases and emission models obtained through a literature search and performed a direct comparison of emission test data with predictive emission models by API, ARCO and EXXON. The principal focus of the CH2M Hill work was the review of crude oil loading emissions since the new data primarily pertained to this type of operation.

The test data base/emission model critique and emission comparison tasks found that the API crude oil loading emission model appears to adequately predict emissions for tankers ranging in size from 17,000 to 35,000 dead weight tons (dwt) and for tankers being loaded within the lower 48 states (original test data base). Although the model does not appear to apply to crude oil loading of Very Large Crude Carriers (VLCCs – 100,000 to 499,000 dwt) in Valdez, there is no known test data that conflicts with the model's ability to predict crude oil loading emissions from carriers smaller than VLCCs in the lower 48. On average, the API model adequately estimates arrival emissions from crude oil loading operations.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however,

the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any federal, state, or municipal regulation with which this publication may conflict.

Suggested revisions are invited and should be submitted to the director of the Industry Services Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

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Section 1

Executive Summary

CH2M HILL was retained by the American Petroleum Institute (API) to assess the validity and application of the marine vessel loading and ballasting emission factors documented in the API publication entitled "Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations," API Publication 2514A, Second Edition, September 1981, reaffirmed August 1987. This validity assessment was considered necessary in light of new crude oil loading test data from Valdez, Alaska, which suggest higher crude oil loading emissions than that predicted by the API 2514A equations. The testing was conducted by the Alyeska Pipeline Service Company and its owner organizations.

The assessment incorporated the following elements, a comprehensive literature search and phone survey of API member organizations for published and unpublished information on hydrocarbon emissions from marine vessel loading and ballasting operations, a review and critique of the test data bases and emission models obtained from the literature search, and a direct comparison of emission test data with predictive emission models by API, Atlantic Richfield (ARCO), and EXXON.

A review of crude oil loading emissions was the principal focus of the study since most of the new data obtained pertained to this marine vessel operation.

The API crude oil loading equations were primarily based on test data from Ventura County, California. The ARCO model was designed to correlate crude oil loading emissions from the Alyeska (Valdez, Alaska) test data. The EXXON model was designed to correlate crude oil and gasoline loading emissions with test data primarily from Baytown, Texas.

1.1 Major Study Findings

The major findings of the test data base/emission model critique and emission comparison tasks are as follows:

1. The API crude oil loading emission model appears to adequately predict emissions for tankers ranging in size from 17,000 to 35,000 dead weight tons (dwt) and for tankers being loaded within the lower 48 states (the original test data base). The model does not appear to apply to crude oil loading of Very Large Crude Carriers (VLCCs) in Valdez, Alaska. In addition, there are currently no known test data that conflict with the model's ability to predict crude oil loading emissions from tankers in the lower 48 states that are smaller than VLCCs.
2. The API model on average does an good job estimating arrival emissions from crude oil loading operations.

3. The API model on average underpredicts generated emissions from crude oil loading operations (especially emissions from Valdez, Alaska).
4. The API model does a good job estimating total crude oil loading emissions from the API test data base; however, the model underestimates emissions from the Alyeska test data base.
5. The API and ARCO models do a good job of correlating total crude oil loading emissions to their respective test data bases.
6. The ARCO model overpredicts arrival emissions and underpredicts generated emissions from crude oil loading operations at Valdez, Alaska (Alyeska test data base).
7. The ARCO model does a good job of estimating arrival emissions from the API crude oil loading emission test data base; however, the model overestimates generated emissions from the API test data base.
8. The ARCO model does a good job estimating total crude oil loading emissions from the Alyeska test data base; however, the model overestimates total emissions from the API test data base.
9. Crude oil loading emissions from the Alyeska test data base (on a unit volume loaded basis) were measured on average to be 4 times higher than that measured for the API test data base.
10. The sampling and analytical procedures used in the API and Alyeska crude oil loading emission tests were considered to be of sufficient quality to be used in developing predictive emission models.
11. The API test data base (mainly Ventura County data) contains only a narrow range of tanker sizes (17,000 to 35,000 dead weight tons). In addition, the data base does not include barge loading tests. Barges would be expected to have higher crude oil loading emissions than comparably sized tankers since barges have a larger surface area to compartment volume ratio.

1.2 Validity Assessment

As previously indicated, the API crude oil loading emission model underestimates Alyeska's generated emissions. The following are possible reasons why the API model underestimates these generated emissions. Further study would be needed to confirm these possible reasons.

1. A vapor pressure study is currently being conducted by Alyeska. Preliminary results from the study suggest that the API crude oil vapor pressure nomograph may underestimate the true vapor pressure of Alaskan crude oil.
2. Vapor growth factors of 2 percent were observed during the API (Ventura County) testing; while vapor growth factors of 20 percent were typically observed during the Alyeska (Valdez) testing. Although the reason for these higher vapor growth factors are not known, the test data does indicate that in general the Alyeska tests had larger cargo surface areas, crude loading rates, crude loading temperatures, vessel dead weight tonnages, and temperature differences (between the loaded crude and the compartment vapor) than that indicated for the API tests. The API model does not directly account for these parameters. Incorporating these parameters into the API model may improve the overall validity of the model.

1.3 Recommendations

1.3.1 Crude Oil Loading Emissions

It is recommended that the arrival and generated emission components be recorrelated to include both the original API (WOGA test data from Ventura County, California and the Alyeska test data.) By so doing, the test data base used in the revised API equation would be based on a larger range of tanker sizes (including VLCCs) that are more representative of the fleet population.

It is also recommended that revised parametric equations be developed which predict generated emissions according to two different levels of accuracy. The first equation would be based on TVP (or an equivalent effective volatility measure), vapor growth, and vapor temperature; and essentially follow the form of the existing API equation which is derived from the ideal gas law. The second parametric equation to be developed for the generated emission component would be based on the inclusion of the other parameters listed above that have a significant impact on the generation of emissions.

Lastly, it is recommended that hazardous air pollutants such as benzene be included in the crude oil loading emission estimates. This potentially could entail the inclusion of a table summarizing the percentage of benzene in the hydrocarbon generated as a function of type of crude being loaded.

1.3.2 Gasoline Loading Emissions

As additional test data become available, it is recommended that these data be included in a revised emission factor estimate.

1.3.3 Crude Oil Ballasting Emissions

As part of future updates, it may be useful to recorrelate crude oil ballasting emissions by including parameters for vapor space volume and exposed surface area along with the volume of ballast water, ullage, and TVP already included in the correlation.

Section 2 Introduction

The marine transfer emission factors documented in the American Petroleum Institute (API) publication entitled "Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations, API 2514A" (API, 1987) has been widely accepted by industry and by the Environmental Protection Agency (EPA) as containing accurate equations to calculate emissions from marine transfer operations. However, recent emission testing of crude oil loading operations at Valdez, Alaska, by the Alyeska Pipeline Service Company, together with its owner company organizations, Atlantic Richfield (ARCO), British Petroleum (BP), and EXXON, indicated higher crude oil loading emissions than that predicted by the API equations in API 2514A (Alyeska, 1990).

As a result of this, and a part of the API 2514A reaffirmation process, API retained CH2M HILL to assess the validity of the API 2514A marine vessel loading equations in light of this new Alyeska data and any additional data available in literature and from API members, and to make specific recommendations for improving the validity of API 2514A. Although the evaluation of crude oil loading emissions is the main emphasis of this study, a review and critique of the gasoline loading and crude oil ballasting emission factors and equations in API 2514A was also performed.

This report is divided into five major sections:

1. A summary of the results of a literature search of published information and a telephone survey of unpublished information from API member organizations on marine vessel loading and ballasting emissions (First part of Task 1, Section 3 of the report).
2. A review and critique of the crude oil loading, gasoline loading, and crude oil ballasting emission test data bases and associated emission models (Second part of Task 1, Section 4 of the report).
3. A direct comparison of measured and predicted emissions from marine vessel loading and ballasting operations (Task 2, Section 5 of the report).
4. An assessment of the validity and application of API emission estimates in light of new test data and the reviews summarized in Sections 3 through 5 (Task 3, Section 6 of the report).
5. Specific recommendations on improving the validity and application of API 2514A emission estimates (Task 4, Section 7 of the report).

Section 3

Literature Search and Survey

CH2M HILL completed a review of the available published literature on marine vessel loading and ballasting emissions, and contacted representatives from EXXON, UNOCAL, Shell, Amoco, Mobil, Chevron, Alyeska, BP, and ARCO to inquire about recent unpublished information on crude oil loading, gasoline ballasting, and gasoline loading emissions and associated predictive emission models that were developed. These representatives were also asked their opinion as to the overall strength and weakness of the API emission equations.

In addition to the API member organizations, source emission testing personnel at local air pollution control districts in Los Angeles, Santa Barbara, and the San Francisco Bay area were contacted in an effort to obtain additional loading and ballasting emission data.

The data and information obtained in the literature search and telephone survey were useful in the qualitative evaluation of marine vessel emissions. The literature search also indicated that the following predictive models would be useful in assessing the validity of the API predictive models:

1. The ARCO PLANO mechanistic model for estimating crude oil loading emissions from Valdez, Alaska (summarized in the Alyeska report)
2. The BP model for estimating crude oil loading emissions from Valdez, Alaska (also summarized in the Alyeska report)
3. A gasoline/crude oil loading emission model developed by EXXON (EXXON, 1976)

With the exception of the Alyeska data and the data used to develop the API 2514A emission factors, there were not other available test data of sufficient content to use in the API emission factor validation process. The test data base used to correlate the EXXON model (mainly EXXON data from Baytown, Texas) were essentially the same as that used to develop the API gasoline loading emission factors.

The literature search reference documents and API member survey comments did, however, provide good information on the mechanisms and parameters involved in generating hydrocarbon emissions during loading and ballasting operations. These references and the results of the phone survey were helpful in reviewing and critiquing the test data bases and associated emission models (Section 4 of this report), and in determining the validity of the API emission models (Section 6 of this report).

Refer to this study's documentation file for the titles of the literature search references that were used in the emission evaluation and for copies of the most substantive phone survey results.

Section 4

Review of Marine Vessel Emission Data Bases/Models

The following is a review and critique of the test data bases and emission models obtained during the literature search task of the study. The API test data bases and associated emission models, as well as other data bases and models of sufficient content to assist in the API validation process, were evaluated here.

4.1 API 2514A, Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations

API 2514A presents correlations and emission factors for use in estimating hydrocarbon emissions from marine vessel transfer operations (API, 1987). The first edition of the publication was published in 1976 and made use of data available at that time for estimating emissions from gasoline loading into tankers and barges. The second edition of the document, published in 1981, and reaffirmed in 1987, used significantly greater quantities of data and added correlations and factors for loading and ballasting of crude oil cargoes. In the document, gasoline loading and crude loading and ballasting operations are separated so the following review will consider each of these activities in turn. All of the data generated for emission estimates for marine vessel loading have been based on measured hydrocarbon concentrations in the vented gases.

4.1.1 Review of Sampling/Analytical Procedures Used for the API Test Data Bases

The emission measurements used to develop the API test data base followed procedures outlined in the Western Oil and Gas Association (WOGA) Marine Measurement Program (May 1977). This measurement program is summarized in Appendix C of the WOGA Report entitled "Hydrocarbon Emissions During Marine Loading of Crude Oils, Ventura County, California," August 1977 (WOGA, 1977). In general, emission measurements were made within MSA Model 53 Gascope with the sampling probe inserted into the ullage trunk. Free ullage measurements were made using metering tape or manual gauging.

Periodic grab samples were taken throughout the loading or ballasting cycles. The vapor molecular weight and vapor composition of these samples were determined using gas chromatography or nondispersive infrared techniques. The results of these analyses were used to develop vapor molecular weight and percent hydrocarbon profiles as a function of ullage. These profiles were in turn used to calculate arrival generated and total emission factors.

The data quality assurance/quality control (QA/QC) practices employed during the WOGA emission measurement program appear to be adequate to produce reliable emission results.

4.1.2 Gasoline Loading

4.1.2.1 Test Data Base Description and Evaluation

The data base used to develop gasoline loading factors included tests during the loading of 100 ships and barges. One hundred twenty two individual compartments were loaded. The ships tested ranged in size from approximately 39,000 dwt to 76,000 dwt. The barges were much smaller (less than 10,000 dwt). The vessel fleet at the time of the test program was a mixture of sizes with approximately 36 percent larger than the tested size range. Gasoline loading emission factors were developed by averaging hydrocarbon concentrations measured during the loading operations. The data treatment incorporated six distinctions or categories of factors, accounting for vessel draft (shallow draft vessels such as barges were found to emit different quantities of hydrocarbons than deeper draft vessels such as ocean-going barges and tankers), volatility of prior cargoes (loading vessels that had carried volatile cargoes on the previous voyage resulted in increased emissions), and compartment operations conducted after discharge of the prior cargo (ballasting, gas-freeing, or cleaning). The measurements made included hydrocarbon concentrations in the compartment upon arrival and concentrations at several stages of filling. The total emissions from a loading operation are then calculated as the sum of the arrival and the generated contribution. Loading operations were described as normal during the test program.

4.1.2.2 Variables Identified as Effecting Emissions

The testing and analysis of data showed that the following parameters have the greatest impact on hydrocarbon emissions from gasoline loading:

- Hydrocarbon content of arriving cargo compartments
 - Prior cargo
 - Compartment treatment during ballast voyage
- Vessel draft
 - Compartment depth

Arrival Hydrocarbon Content. The vapors contained in the empty cargo compartment upon arrival for loading will be displaced by the product loaded. The concentrations depend on the volatility of the cargo previously carried in the compartment and on the degree to which the compartment has been cleaned. The concentrations will be

reduced if the compartment was used for ballasting because ballasting can clean the compartment and displace residual vapors.

Vessel Draft. Vessel draft was noted as strongly affecting emissions with a significant increase for shallow draft barges compared to ocean going barges and tankers. This may be due to increased surface area for evaporation for a similar volume loaded into a shallow draft compartment.

Other Data Recorded During Testing. The following data were recorded during each of the testing events:

- Date and vessel name
- Identification number, capacity, and depth of compartments loaded
- Ambient, emitted vapor, and cargo/ballast water temperatures
- Loading rate
- Identification, volume, and Reid Vapor Pressure (RVP) of loaded cargo

These data were not specifically incorporated into the factors presented in API 2514A although an attempt was made to develop a correlation for gasoline loading using some of the parameters.

Assessment of Gasoline Loading Factors. The averaging of measured values that was conducted to develop the gasoline loading factors in API 2514A should result in reasonable estimates for average emissions from large numbers of loaded compartments. The 90 percent confidence intervals for each of the factor categories show that as the number of loaded compartments increases, the factors more reliably estimate the total emissions. For single compartment loadings, the 90 percent confidence interval can range by an order of magnitude, suggesting shortcomings in using these factors for limited loading events. Correlations of emissions to compartment specifics (cargo surface area, compartment depth, and type of loading and loading rate), and to the specifics of the cargo (true vapor pressure [TVP], temperature) might improve these emission estimating tools.

4.1.3 Crude Oil Loading Emissions

API Publication 2514A presents three different emission estimating techniques for crude oil loading operations. The techniques, varying based on the information known about the crude and loading operation, are increasingly exact with increasing information on the crude and loading operation. If no specific information is available for instance, information in the publication recommends use of an overall factor of 1 pound hydrocarbons emitted per 1,000 gallons crude loaded. This factor is the most general and least reliable of the estimating techniques. If information on the prior cargo and compartment treatment during the ballast voyage are known, a more accurate estimate of emissions is possible. If the crude oil vapor pressure is also known, as well as information on the crude vapor pressure and the ballast voyage compartment

treatment, then the most accurate emission estimating techniques is possible. The latter model is considered the most reliable of the techniques and is the focus of the following discussion.

4.1.3.1 Test Data Base Description and Evaluation

The API 2514A data base for crude oil loading consisted of emission measurements from 67 tanker compartments. The data were a collection of emission measurements obtained during 16 tanker operations in which each operation included loading of from 1 to 11 different compartments. The tanker testing was conducted in Ventura County for WOGA (WOGA, 1977). Chevron was the author of the WOGA testing report.

API test data were collected from tankers that ranged in size from 17,000 dwt to 35,000 dwt. During the period of testing, approximately 54 percent of the vessels in the fleet were larger than the tested sizes. In addition, no barges or crude oil washed compartments were included in the model correlations. As indicated, the API crude oil loading test data base includes only a limited tanker size range. This potentially introduces error if the API model is used for tankers outside the size range. The data collected included measured hydrocarbon concentrations upon arrival and periodically throughout the loading event.

Other Data Collected During Testing. The following parameters were recorded during a compartment loading event:

- Date and vessel name
- Identification number, capacity, and compartment depth
- Ambient, emitted vapor, and cargo/ballast water temperatures
- Compartment condition upon arrival (ballast voyage treatment and prior cargo)
- Loading rate
- Identification, volume, and RVP of loaded crude
- Specific gravity and viscosity of crude oil

4.1.3.2 Description of the API 2514A Predictive Equation

The API predictive equation was developed from a theoretical analysis of the loading operation. Total emissions were first characterized using the ideal gas law, and then terms were separated to account for an emission because of hydrocarbons in the compartment upon arrival (E_a), and for an emission term for the hydrocarbons

generated by evaporation during loading. The separation of terms in the API development is of questionable validity for the following reason:

As per the API analysis:

$$E_{\text{total}} (E_t) = (C/100) * 184 * (MV * G/T)$$

where C = the average hydrocarbon concentration for the entire compartment loading event (volume %)

M = the average vapor molecular weight for the entire compartment loading event

G = vapor growth factor

T = vapor temperature (degrees Rankine)

To separate the total loss into a term for the arrival condition and one due to the generated vapor, the portion of the total volume occupied by the generated vapor blanket must be estimated or known. Then, assuming that the compartment is loaded completely and that the vapor space contains a uniform concentration upon arrival, the following equation can be used:

$$E_t = 1.84/T * [(V_a/V_t) * C_a * M_a + (V_g/V_t) * C_g * M_g]$$

where the subscripts t, a, and g refer to total, arrival, and generated respectively, and the other terms are as before.

V_a/V_t will be close to unity because the arrival vapor is assumed uniformly distributed in the compartment that is to be loaded.

V_g/V_t has been determined to be significantly less than unity in other studies, because the generated hydrocarbon blanket occupies a fairly limited volume near the surface of the liquid being loaded.

The separation of terms employed in the API work is as follows:

$$E_t = 1.84 * (C * M) * G/T = 1.84 * (C_a * M_a + C_g * M_g) * G/T$$

In effect, this counts the displaced volume twice, first calculating an emission due to the total volume at the arrival concentration, and then an emission due to the total volume at the generated concentration. The development continues from this separation of terms to a correlation of data for the generated term and producing an emission correlation that fits within the ranges of vessel and crude oil parameters encountered during the measurement program. The following discussion describes the correlation of

the emission model with test data. The correlation is based on the theoretical equation with this separation of terms included.

The API equation contains two parts, E_a for emissions due to hydrocarbons in the compartment upon arrival and E_g for emissions associated with hydrocarbon vapor generated by evaporation during loading. The total emissions for a loading event are the sum of the two parts, or:

$$E_t = E_a + E_g$$

(each factor in pounds hydrocarbons emitted per 1,000 gallons crude loaded).

E_a , the arrival factor, was not a correlation of data but instead averages of the emissions measured for the types of compartment arrival conditions.

E_g , the generated vapor contribution to the total emissions, is defined as follows:

$$E_g = 1.84 [0.44 (TVP) - 0.42] [(M)(G)/T]$$

where:

TVP = true vapor pressure of the crude oil loaded

M = average vapor molecular weight (lb/lbmol)

G = vapor growth factor

T = average vapor temperature (R)

The terms $[0.44(TVP) - 0.42]$ are the concentration in volume percent of the generated vapor. This correlation results from regression and residual analysis of the data with respect to TVP. The equation for E_g was developed using this concentration and the ideal gas law.

The term G, the vapor growth factor, is introduced to account for the increase in vapor volume, beyond the volume of the loaded crude, due to the generation of hydrocarbons by evaporation during loading. It is defined as follows:

$$G = \{ (V_v - V_l) / V_l \} + 1$$

where:

V_v = total vented vapor volume, cubic feet at standard temperature and pressure (STP)

V_l = volume of liquid loaded, cubic feet at STP

The total vented vapor volume was calculated using molar and component material balances on the compartment. These calculations incorporated ullage and cargo surface area as a means to calculate the vapor space volume at the start and end of a

loading event. The data base was evaluated to determine an average vapor growth factor. For crude oil loading, this was determined to be 2 percent ($G = 1.02$), which is recommended for all crude oil loading calculations.

4.1.3.3 Evaluation of API 2514A Predictive Equation for Crude Oil Loading

The API model was developed to be used for large populations of vessels and numerous loading events. As the numbers of compartments evaluated increases, the model should increase in reliability. The model uses averaged values for the contribution of the compartment's arrival vapor space hydrocarbon concentration to the total emissions. The arrival component then relies heavily on the mixture of prior compartment activities and compartment configurations that API incorporated into the data base. Vessel size and prior cargo compartment treatment, for both of which the API document provides limiting ranges, are critical to the use of such averages. For instance, use of the API correlations for VLCCs or crude-oil washed compartments would rely on an average developed from a data base that did not contain these situations. Beyond the limits of the disclaimer, the API data base was developed in warm-climate regions. The differences between crude temperatures and ambient or compartment wall temperatures may be smaller than cold weather terminals experience. Convective heat transfer in the vapor space would enhance transport of cargo from the liquid surface to the overhead space being displaced during loading. The API equation is based on a dependence of emissions on true vapor pressure. True vapor pressure, as a measure of a crude's tendency to evaporate, is a reasonable variable to base those emissions upon. If the nomograph used to determine TVP from reported Reid vapor pressures underestimates the actual TVP (as is suggested by Alyeska personnel [Alyeska, 1992]), then the API correlation would correspondingly underestimate emissions. The API correlation does not incorporate factors for the surface area of the cargo, nor does it include specific loading rate or time correlation. Turbulence at the liquid surface, and the total surface exposed, as well as the time available for mass transfer, all seem important in this emission scenario.

4.1.4 Crude Oil Ballasting Emissions

The API 2514A document contains three estimating techniques for hydrocarbon emissions from crude oil carrier ballasting operations. The techniques increase in accuracy as more information is provided about the operation. The least accurate is the typical overall emission factor of 1.4 pounds emitted per 1,000 gallons ballast water added. If compartment ullage prior to discharge of the cargo is known as well as volume of water added to compartments previously containing oil, the document provides refined emission factors for two categories of these operations. The categories are separated by the extent that the compartment used for ballasting was filled with crude prior to discharge. The most accurate emission estimate can be achieved using the correlation provided for emissions to true vapor pressure and true ullage of the crude oil discharged prior to ballasting. The following discussion focuses on this predictive correlation.

4.1.4.1 Crude Oil Ballasting Data Base Description and Evaluation

The correlation for ballasting operation emissions was developed from hydrocarbon concentration measurements on 54 individual vessel compartments. The vessels tested ranged in size from 42,000 dwt to 121,000 dwt. The fleet was comprised of approximately 79 percent vessels smaller than or equal to 121,000 dwt and 21 percent larger than this size during the period of the testing. The data were separated into two categories based on the true cargo ullage prior to discharge. The hydrocarbon measurements were performed periodically during the ballasting operation.

4.1.4.2 Variables Identified as Effecting Emissions

The measurement and evaluation of concentrations during ballasting operations concluded that the following parameters impact the quantities of hydrocarbons emitted by these operations:

- TVP of the crude oil discharged
- Arrival cargo true ullage
- Volume of ballast water added to the compartment

True Vapor Pressure of the Crude Oil Discharged. During the cargo carrying voyage, the vapor space in the compartment will become saturated with vapor in quasi-equilibrium with the cargo. Upon discharge, the compartment walls are covered with a layer of the same crude oil. This layer evaporates into the vapor space emptied during off-loading. One measure of the tendency of the crude to evaporate into the empty vapor space is its true vapor pressure.

Arrival Cargo True Ullage. The concentration of the vapor vented during a ballasting operation will depend on the volume saturated with vapor during the cargo-carrying voyage, and the surface area of the walls coated with cargo prior to introduction of ballast water. The true ullage of the cargo prior to discharge is a measure of both parameters, assuming a reasonably constant compartment configuration.

Volume of Ballast Water Added. The ballast water added displaces the hydrocarbon-rich vapor space. It is reasonable to expect a directly proportional correlation.

Other data recorded during testing included:

- Date and vessel name
- Identification number, capacity, and compartment depth
- Ambient, emitted vapor, and cargo/ballast water temperatures
- True ullage before dockside discharge of cargo

- Unloading and ballasting rates; time between unloading and start of ballasting operations
- Identification, RVP, specific gravity, and viscosity of discharged crude oil; volume of ballast water loaded

4.1.4.3 Description and Evaluation of Ballasting Correlation

Regression and residual analysis of the hydrocarbon concentrations measured during ballasting operations led to the following correlation of emissions to the true vapor pressure of the discharged crude and the true ullage prior to discharge:

$$E_b = 0.31 + 0.20(TVP) + 0.01(U_a)(TVP)$$

where:

E_b = Total ballasting emission factor (lb/1,000 gal water loaded)

TVP = True vapor pressure of discharged crude oil (psia)

U_a = True ullage prior to dockside discharge (ft)

The correlation contains terms that attempt to account for the mass transfer potential and for the space available for the transfer to occur, true vapor pressure, and ullage respectively. To extend this relationship to other vessel size ranges, correlation of the emissions to vapor space volume or exposed surface area might be more universally applicable.

4.2 Valdez Tanker Loading—Alyeska Report

The Alyeska Report (1990), is the most recently developed document that quantifies hydrocarbon emissions from crude oil loading of marine vessels. This report documents the approximately 80 tests that were conducted over a 9-month period. The testing was conducted at the Valdez Marine Terminal. The purpose of the testing and evaluation is:

- To quantify the hydrocarbon vapor emissions associated with tanker loading at the Valdez Marine Terminal in Valdez, Alaska.
- To identify the parameters affecting the quantity of hydrocarbon emissions.

The Trans-Alaska Pipeline System accepts crude oil from various sources on the North Slope of Alaska for transport to the Valdez Terminal. The Terminal has facilities for

holding and loading the oil into tankers. Oil arriving at the Terminal may be loaded directly from the pipeline into tankers or held temporarily in storage tanks for later loading. The vapors in the tanker's compartments are displaced as crude oil fills the compartments.

ARCO and BP performed separate evaluations of the test data obtained during the study. The objective was to correlate a model that would enable emission losses to be calculated directly from loading data and ship configuration data. The results of this effort were two mechanistic models that predict emissions from crude oil loading operations.

4.2.1 Test Data Base Description and Evaluation

The Alyeska emission factor test data used to develop the correlation included data from crude oil tankers only, no gasoline loading data were obtained. Therefore, Alyeska data are not considered applicable for comparison with the API 2514A gasoline loading equation.

The Alyeska testing program commenced in February 1990, and 80 tests were conducted on 20 tankers. All tankers were bottom loaded in basically the same manner. Twenty tankers were outfitted for testing, 11 different groups of tankers were actually tested because 4 of the groups had several tankers identical in construction.

The weight of the tankers ranged from 75 Mdw to 265 Mdw, and the volume of cargo ranged from 490 MBbl to 1,800 MBbl. Two different types of cargo vent systems were used; 90 percent of the tankers were equipped with a vent header and mast riser, and 10 percent were equipped with individual compartment vents.

4.2.1.1 Variables Identified as Effecting Emissions

The testing and evaluation determined that the following parameters impact the quantities of hydrocarbon emissions from crude oil loading operations:

- Hydrocarbon content of arriving tanker vapor
- Crude oil temperature/tanker temperature
- Volume of crude oil loaded
- Tanker size/configuration
 - Area of the liquid surface in the tank
- Natural Gas Liquid Content of Crude
 - Reid vapor pressure
- Loading Time
- Extent of tanker capacity filled

Arrival Hydrocarbon Content. The tanker contains hydrocarbon vapors in the empty compartment when it arrives in port. The quantity of the vapors depend upon the level of cleaning or ballasting, following discharge of the previous cargo. The arrival vapors are a significant factor in loading emissions because these vapors are displaced from the tanker during loading.

Crude Oil Temperature/Tanker Temperature. During the crude oil loading (the temperature was recorded periodically) the crude temperature ranged from 61°F to 115°F. The temperature varied as a function of the time spent in tankage. The vapor, ambient air, and seawater temperatures were recorded but apparently used only to establish a range of conditions.

Crude Volume Loaded. The volume of crude oil loaded is the fundamental source of vapor emissions. The physical process of crude transfer is the displacement mechanism for causing vapor to be emitted from the tankers. The volume of crude loaded is directly proportional to hydrocarbon emissions.

Tanker Size and Configurations. Although not as well understood as other factors, tanker configuration affects hydrocarbon emissions. The surface area available for evaporation is considered to be a factor in hydrocarbon emissions.

Crude Oil Composition. The hydrocarbon emissions from tankers are a function of the crude oil volatility, which is a function of composition and temperature. At Alyeska, natural gas liquid (NGL) is added to the crude oil in the production fields. Varying the NGL content of the crude is the only way to adjust the composition. For a 3-week period, the NGL was not added to the crude in the field. This was the field that produced 75 percent of the crude. Test results indicated that varying the NGL content of the crude only had a minor impact on emissions.

Loading Time. It was observed during the testing that a longer load time increases emissions, but the effects were small compared to the other factors.

Extent of Tanker Capacity Filled. A few of the tankers were filled to 85 percent capacity, but most were filled to greater than 90 percent of capacity. Test results indicated that the effect of incompletely filled tankers was minor.

Other Data Recorded During Testing. The following data were recorded during each of the testing events:

- I.G. manifold pressure
- Barometer pressure
- Oil API gravity
- Vapor space temperature profile
- Compartment profile, percent hydrocarbon
- Oil loading rate
- Crude oil sample
- Sample temperature
- Compartment ullage readings
- Seawater temperature
- Ambient temperature
- Tanker history and other relevant data

The data collected were not necessarily incorporated into the equations, but used to establish a range of loading parameters in which the equations are valid.

Alyeska Vessels Compared to US Fleet Population. Tank vessels include both tankers that are self-propelled and barges, which are not. The difference between tankers and barges is tank configuration; tankers are deeper and have less surface area, while barges are shallow and have greater surface area. Aside from some oceangoing barges, barges usually travel the inland waterways of the United States. The tankers, other than those used for petroleum importation, are used mainly in coastal traffic, since almost no petroleum is exported.

Tankers in active trade in the United States range in size from less than 1,000 dwt to 406,000 dwt. Data obtained from the U.S. Coast Guard, at the end of 1986, show 152 U.S.-flag tankers of more than 20,000 dwt trading in U.S. water, as well as 990 foreign-

flag tankers of more than 20,000 dwt. In 1986, there were only 81 U.S.-flag tankers of less than 20,000 dwt.

In 1986, 3,968 barges in the U.S. were certified to carry subchapter D cargoes (flammable liquids, including crude oil and gasoline). Inland barges generally transport between 10,000 barrels and 40,000 barrels of cargo.

The tankers used in the Alyeska emission study ranged in size from 75,000 dwt to 265,000 dwt. Since over 65 percent of the U.S. flag tankers are larger than 20,000 dwt, the tankers used in the Alyeska testing should be considered representative of the overall U.S. fleet tanker population. However, it should be noted that barges were not included in the Alyeska testing program.

4.2.1.1 Review of Sampling/Analytical Procedures Used by Alyeska

This section summarizes the evaluation of sample collection procedures and analytical methodologies for the purpose of evaluating vapor emissions during tanker loading at the Valdez Terminal. The methods used for the Alyeska study were consistent with those recommended in API publication 2514A and also are currently the best available technologies for the collection and analysis of these types of samples.

Sample Collection. The procedures used for vapor sample collection for the Alyeska study are consistent with those recommended by WOGA and documented in API 2514A. The specific procedures used were optimized for the specific sampling conditions of this study. Most notable, precautions were taken to prevent the inclusion of entrained liquids and residual air in the samples, and field measurements of hydrocarbon content in the tanks were made to optimize sample collection.

Analysis. The Alyeska document describes the general analytical protocol used for the analysis of samples collected and gives rationale supporting the selection of these methods. In general, the procedures described were used to quantify vapor samples for nonhydrocarbon and hydrocarbon constituents to C₁₀. The method used is based on ASTM Procedure D1945 with modifications to enhance the quantification of the C₆₊ constituents. The procedures described are consistent with the guidelines found in API publication 2514A second edition, September 1981, reaffirmed August 1987 (API, 1987).

Publication 2514A describes the methods for determining the hydrocarbon emissions associated with marine vessel transfer operations. Appendixes 3 and 4 to API 2514A provide guidelines for selecting analytical procedures to be used for analyzing vapor samples collected for estimating emissions from the loading and ballasting of marine tankers. The guidelines describe several acceptable approaches and recommend the most preferred. The Valdez study used an analytical protocol that was consistent with the recommended guidelines.

The Alyeska document indicated that aromatic constituents were analyzed by EPA Method 5020, which uses a photo ionization detector with an injection by syringe. It is stated that this method has a relative error of 10 percent because of the injection method. Because of this error, the benzene values were computed from the C_6 values, because the error associated with C_6 analysis was only 3 percent. It was also assumed that the composition of the crude was stable. This method is acceptable, however, it is desirable to have an independent means to verify a result. The analysis of aromatics by Method 5020 compared to the results obtained by ratio calculations would have been an ideal verification. The error associated with Method 5020 could have been reduced by using an injection loop instead of syringe.

The overall QA/QC practices used by Alyeska to estimate emissions appear to be adequate to produce reliable emission results. The practices also appear to be consistent with API methodologies.

4.2.2 Description of ARCO Mechanistic Model

Based on the testing results at the Valdez Terminal, the ARCO Plano Research Center developed a computer simulation program to help understand the factors that influence emissions. The computer simulation provides the most complete understanding of the hydrocarbon vaporization process. However, a simpler mathematical method for correlating tanker emissions was developed so that it can be easily applied to actual loading events. This equation accurately predicts the measured emissions from the Alyeska testing because it is an empirical equation of the test data.

The form of the mathematical equation was developed based on the computer simulations. The actual measured data were used to correlate the exponents of the mathematical equation. The equation giving the best fit is:

$$\text{Ton HC} = X1 * \text{Factor} * T^{X2} (A * \text{Time})^{X3} (\text{Vol oil} / \text{Vol tanker})^{X4} \text{ppbHC}^{1.25} (1 - y_{\text{HC}} / y_{\text{HCsat}})^{0.43} + 448 * \text{Vol oil} * y_{\text{HC}}$$

where:

Ton HC = tons of hydrocarbons emitted

Factor = empirical factor, which depends on tanker class

T = temperature, F

A = area for evaporation, ft^2

Time = time to load the tanker, minutes

Vol oil = volume of oil loaded, MMBbls

Vol tanker = volume of inert gas space in oil cargo tanks upon arrival, MMBbls

ppb HC = pounds of HC evaporated per barrel of oil (flash calc)

yHC = mole fraction of hydrocarbon vapors in inert gas upon arrival

yHCsat = equilibrium mole fraction of hydrocarbon in inert gas (flash calc)

The above equation is divided into two terms. The first term or generated emission component accounts for the hydrocarbon emissions generated during oil loading. The second term or arrival component ($448 \cdot \text{Vol oil} \cdot y_{\text{HC}}$) accounts for the hydrocarbon vapor initially contained in the compartment, which is displaced during loading.

The first term X1 is a conversion factor that accounts for all the necessary conversion units.

The empirically developed tanker "factor" accounts for the differences in sizes of tankers. Each tanker is assigned a "factor" based on its weight in dwt. The factors range from 1.060743 for 265,000 dwt tankers down to 0.804015 for 75,000 dwt tankers.

The crude temperature has been handled by a single temperature term that is raised to an empirically determined exponent X2.

The cross sectional area and loading time are handled by their product raised to an empirically determined exponent X3.

The degree to which the gas space is displaced by oil (volume of oil loaded/volume of tanker) is raised to an empirically determined exponent X4.

The effect of crude oil composition is accounted for by including the volatility of the oil as determined with a flash calculation. The flash calculates the pounds of hydrocarbon evaporated per barrel of oil flashed at 85 F and 15.36 psia, which is the average conditions for the tanker loadings. The 1.25 exponent for this term was determined with hypothetical data.

The term $(1 - y_{\text{HC}}/y_{\text{HCsat}})$ accounts for the approach to equilibrium between the vapor and liquid phases in the compartment.

The arrival component ($448 \cdot \text{Vol oil} \cdot y_{\text{HC}}$) is the mass of residual hydrocarbons initially contained in the gas that is displaced by the incoming oil. The coefficient 448 was determined from the ideal gas law.

The ARCO hydrocarbon emissions equation is a correlation from the testing results performed at the Valdez Terminal. The model accurately predicts measured hydrocarbon emissions from the tankers tested. The calculated values compare well to the

measured values, with an average error of 1.54 percent and a average absolute error of 11.64 percent.

The ARCO hydrocarbon emissions model assumed that 11 light hydrocarbon components (C_1 , C_2 , C_3 , $i-C_4$, $n-C_4$, $i-C_5$, $n-C_5$, C_6 , cyclo- C_6 , benzene, and toluene) were vaporizable. The remainder of the black oil was considered to be nonvaporizable. Based on the hydrocarbon emissions equation, a similar equation was developed for benzene. The format is identical to the hydrocarbon equation; however, the coefficients and exponents were recorrelated for benzene emissions. Benzene emissions are approximately 1 percent of the average total hydrocarbon emissions for the entire Alyeska test data base.

4.2.2.1 Comparison to API 2514A

A qualitative comparison of the ARCO model to the crude oil loading equation in API 2514A brings to light the following differences between the two equations:

- The ARCO and API equations both identify two types of emissions; arrival and generation emissions. However, the two terms are calculated by different methods. API's arrival term is defined as a single number based upon the tanker's prior cargo and arrival conditions. The ARCO equation arrival term is calculated using the concentration of the arrival vapor and volume of crude loaded.
- The TVP of the crude is directly used to calculate generated emissions using the API model while crude volatility flash calculations are used to calculate generated emissions from the ARCO model.
- The surface area available for evaporation inside the tanker cargo compartment and loading time are used in the ARCO equation to calculate generated emissions. It is known from equations for diffusion that surface area and time are directly proportional to mass transfer. As a result, surface area and loading times would be expected to influence the generation of emissions. In contrast, the API model incorporates a vapor growth factor term (based on test data) to calculate generated emissions.
- The ARCO equation expresses generated emissions as proportional to the square of the crude temperature. The API equation incorporates the crude temperature as a function TVP. The Alyeska report states that the crude oil temperature has a significant impact on the generation of emissions during crude oil loading.
- During the Alyeska testing, crude was bottom loaded into the tankers. Other methods of crude loading cause more turbulence within the cargo hold, which result in higher emissions. Therefore, the data from the

Alyeska study should be used with caution when applied to other loading methods.

- Several other factors considered in the ARCO equation to estimate generated emissions include: the approach to equilibrium between the vapor and liquid phases, percent of capacity the tanker is filled, and the amount of hydrocarbon that is volatilized per barrel of crude.

The ARCO model predicts hydrocarbon emissions from crude oil loading only. The API 2514A document also contains equations for gasoline loading and crude oil ballasting emissions.

The ARCO equation appears to be more detailed than the API crude oil loading equation. However, the ARCO equation is based only on testing performed at the Valdez Terminal. Developers of the ARCO equation indicated that the ARCO model should not be used to calculate emissions loading operations in any locations other than the Valdez Terminal.

It should also be noted that the API crude oil loading emission model was intentionally designed to be less detailed than that developed by ARCO since the API model is intended to have a much wider application and be most applicable to large emission inventories.

4.2.3 Description of BP Mechanistic Model

Unlike the ARCO equation, the BP mechanistic model is not a simplified mathematical method, but rather a computer simulation program. The computer model was developed from the testing data at the Valdez Terminal. The model was tuned to tanker emission data for the major tanker classes, and used to predict hydrocarbon emissions as a function of the following parameters:

- Area—cargo surface area available for evaporation
- Boundary layer thickness—the distance from the gas/oil interface to where the vapor space is well mixed with hydrocarbon
- Change in vapor space temperature—between initial and final temperatures recorded during the loading
- Crude loading rate
- Molecular weight of vaporizing hydrocarbon—determined in advance from flash calculation