

Emissions Estimation Technique Manual

for

Aggregated Emissions from Service Stations

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EMISSIONS ESTIMATION TECHNIQUE MANUAL: AGGREGATED EMISSIONS FROM SERVICE STATIONS

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1.0 Introduction

1.1 The NPI

The National Pollutant Inventory (NPI) was established under a National Environment Protection Measure (NEPM) made by the National Environment Protection Council (NEPC) under Commonwealth, State and Territory legislation on 27 February 1998. This Measure is to be implemented progressively through the laws and administrative arrangements of each of these participating jurisdictions (i.e. State and Territory Governments).

The NEPM and an associated Memorandum of Understanding for the NPI, which have been published as a single document by the NEPC, provide more details on the purpose and structure of the NPI, and the arrangements for implementation of the NEPM that have been agreed by the jurisdictions. Users of this Manual should read this publication if they are unfamiliar with the NEPM or the NPI.

1.2 Purpose and Scope of the Manual

The NPI will be developed as an internet database designed to provide information on the types and amounts of certain chemical substances being emitted to the air, land and water environments. If the NPI is to achieve its aim of communicating useful and reliable information to the community, industry and governments on pollutants present in our environment, the emissions estimation techniques (EETs) used to generate inputs to the NPI need to be consistent, and the process for developing these techniques needs to be transparent. This Manual has been developed, reviewed and finalised in this context.

The NEPM contains a list of substances for which emissions will be reported on an annual basis to the Commonwealth Government, which will then compile and publish the NPI. The aggregated emissions manuals, of which this is one, have been prepared to assist State and Territory Governments in preparing these submissions, and to facilitate consistent reporting between these jurisdictions.

State and Territory Governments will also be compiling and submitting emissions data based on annual inputs from reporting facilities. These facilities are primarily industrial enterprises which use (or handle, manufacture or process) more than specified amounts of certain polluting substances, burn more than specified amounts of fuel, or consume more than certain amounts of energy. These amounts or "thresholds" (which are clearly defined in the NEPM) govern whether an industrial facility is required to report and what substances it is required to report on, and industry handbooks are being developed to help industries to prepare the information for these reports.

The aggregated emissions manuals complement these handbooks, and are intended to enable Governments to estimate emissions from non-industrial activities (e.g. transportation, domestic and commercial activities) and emissions from industry which are not reported because the relevant thresholds are not exceeded or are exempt from reporting.

Annual submissions are also to be prepared and submitted in conformance with the NPI Data Model and Data Transfer Protocol. For emissions to the air environment, this Protocol only requires jurisdictions to submit data on emissions into the particular airsheds that are listed in the Protocol, and not to the rest of each jurisdictional area. For example, under the 1998 to 2000 Memorandum of Understanding, in Victoria, emissions data are only required for the Port Phillip and Latrobe Valley Regions. In addition, emissions data are required to be submitted on a gridded basis, with each jurisdiction determining a grid domain and grid cell size necessary to meet its obligations under Section 7 of the NEPM.

Therefore, in addition to recommending and providing details and examples of appropriate emissions estimation techniques (EETs) for the relevant NPI substances, this Manual provides guidance on the spatial allocation of emissions and the use of area-based surrogates for accurately distributing the activities or sources in question.

1.3 Application of the Manual

Each of the aggregated emissions manuals provides details of:

- the NPI substances that are expected to be emitted from the relevant aggregated source type;
- the origins or sources of the emissions, and the processes that may generate them;
- the impacts of any control equipment or procedures on those emissions;
- the broad approaches that may be employed in the estimation and spatial allocation of emissions;
- details of emission factors to be used in the estimation of emissions; and
- a series of illustrative sample calculations for each estimation technique.

Each of the manuals also contains a section on "Uncertainty Analysis", which provides information and guidance to users on the reliability of the various estimation techniques, problems and issues associated with their development and application, and recommendations for their improvement. In preparing the aggregated emissions manuals it has been recognised that some jurisdictions already undertake detailed emissions inventories on a regular basis, based on relatively sophisticated methodologies. For these jurisdictions the manuals offer techniques which represent commonly available best practice for emissions estimation in Australia (i.e. techniques of high quality which can be employed by larger or more experienced jurisdictions with an acceptable expenditure of time and effort). The most recent developments in inventory methodology in Australia and overseas have been considered in selecting and documenting these techniques.

Where a more simplified methodology for emissions estimation of acceptable quality is available, it is recommended in the manual for the use of those jurisdictions which may, for the time being at least, lack the data, resources or

expertise to employ a more sophisticated approach, or not see the need for highly reliable estimates in that particular part of the inventory.

2.0 Emissions Covered by the Manual

2.1 NPI Substances

Petrol and diesel contain a mixture of volatile organic compounds (VOCs). VOCs is a general term which refers to a large and diverse group of chemicals including hydrocarbons, oxygenates and halocarbons. A number of these substances are listed in Table 2 to Annex of the NEPM.

Facilities engaged solely in the retail sale of petrol and diesel are not required to report their emissions under the NEPM for the NPI. However, States and Territories (jurisdictions) will be required to estimate and report on aggregated emissions from these sources under agreed arrangements (EA 1998). NPI substances that may be emitted from the storage and handling of these fuels are listed in Table 1.

Table 1: NPI Su	ıbstances	Typically	<pre>/ Emitted at</pre>	Service Stations ^a

Benzene	n-Hexane	Toluene	
Cyclohexane	Lead and	Total volatile organic	
•	compounds	compounds (VOCs)	
Ethylbenzene	Styrene	Xylenes	

^a Paragraph 2 (e) of Schedule A to the NEPM requires that, for the purposes of emissions estimation, a substance listed in Tables 1 and 2 of that Schedule as " (a metal) and a compound" refers only to the amount of metal that may be emitted. The EETs described in this manual have been prepared accordingly. Thus, the emission factors for metals and their compounds relate only to the amount of the metal itself that may be emitted as a part of these compounds.

2.2 Emission Sources and Related Processes

Service stations supply petrol, diesel and related products to road vehicles. Emissions are generated from the unloading of fuel from tankers to underground storage tanks, underground storage tank breathing losses, and vehicle refuelling.

There are usually two methods of unloading fuel from tankers to underground storage tanks. "Splash filling" involves lowering a fill pipe from the tanker into the storage tank (with its outlet above the liquid surface) and dispensing fuel by gravity. "Submerged loading' involves lowering the fill pipe below the fuel level. This method results in about 36% less vapour loss than splash filling.

During loading of an underground tank fuel displaces vapour. If this vapour is freely released to atmosphere the filling operation is described as "uncontrolled". If the vapour is contained and returned to the tanker, emissions to the atmosphere are reduced by about 95%. This vapour return method is known as "vapour balancing" and is achieved by installing a vapour return line from the storage tank to the tanker.

Underground storage tanks also produce emissions through breathing. Breathing occurs daily because of changes in the temperature and pressure. Losses also occur during the refuelling of motor vehicles (which is uncontrolled as fuel vapour escapes directly to the atmosphere) and also when spills occur from overfilling, nozzle drips and fuel spit-back.

2.3 Emission Controls

Emission controls for service stations include:

- use of submerged loading;
- use of vapour return lines during tanker unloading (as described above);
- good housekeeping practices and education of service station employees in new technology and good spill and leak management;
- education of the public in motor vehicle refuelling techniques; and
- reducing petrol vapour pressure, especially during summer periods.

3.0 Emissions Estimation Techniques

This section describes techniques for estimating emissions of benzene, cyclohexane, ethylbenzene, n-hexane, lead, styrene, toluene, xylenes and total VOCs from service station operations. It does not deal with emissions from other parts of the petroleum product distribution system, such as emissions from tanker loading at bulk terminals or from tankers in transit.

3.1 Approaches Employed

The best practice technique is based on the amounts of different fuel types sold in an airshed. Emissions from service stations will be related to fuel sales, fuel composition, fuel handling practices, and the types of vapour control employed.

The information that is required for this EET is as follows:

- the liquid and vapour compositions of petrol and diesel sold in an airshed;
- the annual volumes of petrol (leaded and unleaded), diesel and LPG sold in the airshed - the quantities of fuels sold in an airshed can be estimated by scaling sales data for the jurisdiction by the ratio of their populations;
- the prevalence of methods and practices for filling underground tanks in the airshed (i.e. splash or submerged, vapour balancing); and
- the location of service stations or, as an alternative, the population distribution in the airshed.

3.1.1 Estimating Total VOC Emissions

Industry associations such as the Australian Institute of Petroleum (AIP) will be able to provide consumption figures at jurisdiction level for various motor fuels, and data on typical fuel composition. Petrol sales in smaller airsheds can be estimated either on the basis of relative population, by contacting major petrol distributors in the area, or by surveying a sample of the service stations.

Information on filling methods can be provided by the AIP, regulatory authorities or petrol distributors.

Equation 1 can be used to calculate VOC emissions, based on the application of emission factors. Table 2 in Section 3.3 provides emission factors which may be used for estimating service station emissions for various fuels.

Vapour balancing controls for vehicle refuelling are not currently mandatory in Australia but may be introduced at some time in the future.

Equation 1: Estimating total VOC emissions in an airshed for different fuels using emission factors

Using estimates of fuel sales for the airshed, and the appropriate emission factor(s) for a particular fuel, total VOC emissions can be estimated as

$$E_i = EF_i * V_i * 10^{-6}$$

where

3.1.2 Speciating VOC Emissions

Petrol and diesel speciation should be based on local data at airshed level wherever possible, as fuel composition may vary with the origin and quality of crude oil and the refining technology employed. Petrol composition may also vary between jurisdictions to regulate the volatility of petrols sold in different climates.

If local data on petrol composition are not available, the data in Tables 3 and 4 may be used as default values. The data for petrol in Table 3 are assumed to apply to both leaded and unleaded petrols.

If data on the liquid composition of petrol are available but data on its vapour composition are not, the empirical formula in Equation 2 can be used to calculate the concentration of a substance in the vapour phase.

Equation 2: Estimating the vapour concentration of a substance

If the concentration (in liquid) and boiling point of a substance are known, the vapour concentration can be calculated as

$$C_v = c * C_I * e^{aB}$$

Cv	=	Concentration of the substance in fuel vapour, % weight
С	=	6.6253 (a constant)
CI	=	Concentration of the substance in liquid fuel, % weight
а	=	-0.0376 (a constant)
В	=	Boiling point of the substance, °C

Equation 3: Estimating emission of an NPI substance in an airshed from petrol handling

Emissions of a substance from petrol handling may be calculated as

$$E_{jp} = (E_{pv} * C_{jpv} + E_{pl} * C_{jpl}) / 100$$

where

Ejp	=	Total annual emissions of species j from petrol handling, kg vr ⁻¹
E _{pv}	=	Annual VOC emissions in the airshed from evaporation of petrol, kg yr ⁻¹
Cipv	=	Concentration of species j in petrol vapour, % weight
E _{pl}	=	Annual VOC emissions in the airshed from spillage of petrol, kg yr ⁻¹
Cjpl	=	Concentration of species j in liquid petrol, % weight

and

 E_{pv} is calculated from Equation 1 by applying the emissions factors from Table 2 for evaporative operations (i.e. filling, breathing and refuelling) to sales data for the airshed, and E_{pl} is calculated by applying the spillage factor to these data

Equation 4 can be used to estimate the emissions of NPI substances from diesel handling, if the vapour composition of diesel is available for an airshed. Although liquid composition data for diesel can be obtained for various regions, no default data on the vapour composition of diesel are provided in this manual, as these data are not currently available for NPI substances.

Equation 4: Estimating emission of an NPI substance in an airshed from diesel handling

Emissions of a substance from diesel handling may be calculated as

$$\mathsf{E}_{\mathsf{jd}} = \mathsf{E}_{\mathsf{d}} * \mathsf{C}_{\mathsf{jdv}}$$

E_{jd}	=	Total annual emissions of species j from diesel handling, kg vr ⁻¹
E _d	=	Annual VOC emissions in the airshed from diesel handling, kg yr ⁻¹
\boldsymbol{C}_{jdv}	=	Concentration of species j in diesel vapour, % weight

If diesel vapour composition data can be obtained, total emissions of NPI substances (other than total VOCs) in an airshed can be calculated by combining the estimates of these emissions for the handling of petrol and diesel.

LPG consists mainly of low boiling point hydrocarbons and no NPI substances (apart from total VOCs) are present in LPG (Stamp, G.D., Elgas, August 1995, pers. comm.).

3.2 Spatial Surrogates and Spatial Allocation

The preferred method of allocation of emissions to grid cells within the airshed is to distribute emissions according to the number and location of service stations. While this technique introduces some inaccuracy by assuming the same emissions (and hence the same product throughput) for each service station, it is felt to be superior to an allocation based solely on population distribution. A more accurate method would be to distribute the emissions according to the total throughput in each grid cell, however this data may be difficult and time consuming to collect.

Petrol distributors or the Electronic Yellow Pages can provide the locations of service stations which can then be converted to co-ordinates (AMG or latitude/longitude) by a process called geocoding in a Geographic Information System (GIS). If GIS is not available, a GIS company can do the geocoding.

Emissions can be allocated according to population density if information on service station locations is not available. Allocation of more emissions to grid cells of higher population density may be inaccurate, as the siting of service stations is not based entirely on residential density. The Australian Bureau of Statistics collects population data by Collection District (CD). These data can be converted to location or population by grid cells using a program or GIS.

Equation 5: Allocating airshed emissions of a substance to grid cells

Emissions of a substance in a grid cell may be estimated as

$$\mathsf{E}_{jk} = \mathsf{E}_{j} * \mathsf{N}_{k} / \mathsf{N}$$

E _{jk}	=	Annual emissions of substance j in grid cell k, kg yr ⁻¹
Ej	=	Total annual emissions of substance j in the airshed,
		kg yr⁻¹
Nk	=	Number of service stations in grid cell k
Ν	=	Number of service stations in the airshed

3.3 *Emission and Speciation Factors*

The VOC emission factors for petrol in Table 2 have been derived by the USEPA (1995) on the basis of fuel throughput at service stations.

The VOC emission factor for diesel in Table 2 (176 mg L^{-1}) is based on typical data for New South Wales and is considered to be an acceptable default factor for calculation of evaporative emissions. If local data on the vapour pressures of both petrol and diesel used in an airshed are available, Equation 6 can be used to derive a locally applicable emission factor.

Emission Source	Emission Rate (mg per litre throughput)
PETROL	
Underground tank filling	
Submerged filling	880
Splash filling	1,380
Submerged filling and vapour balance	40
Underground tank breathing/emptying	120
Vehicle refuelling	
Displacement losses (uncontrolled)	1,320
Displacement losses (controlled)	132
Spillage	80
DIESEL	176 ^b
(includes filling underground tanks, vehicle	
refuelling losses, and tank breathing)	
LPG	0.04 ^b

 Table 2: Emission Factors for Service Stations^a

^a USEPA (1995), unless otherwise indicated.

^b EPAV (1996a).

Equation 6: Deriving a local emission factor for the handling of diesel at service stations

$$\mathsf{EF}_{\mathsf{d}} = \mathsf{EF}_{\mathsf{p}} * \mathsf{P}_{\mathsf{d}} / \mathsf{P}_{\mathsf{p}}$$

EF_d	=	Emission factor for the handling of diesel in the airshed, mg L^{-1}
EF₀	=	Emission factor for the handling of petrol in the airshed
F		(i.e. the sum of the factors for filling, breathing and refuelling for petrol from Table 2), mg L^{-1}
Pd	=	Typical vapour pressure of diesel used in the airshed, kPa
Pp	=	Typical vapour pressure of petrol used in the airshed, kPa

Tables 3 and 4 provide estimates of the concentrations of organic compounds and lead in petrol liquid and vapour, which can be used for VOC speciation purposes if local data are not available.

It is acknowledged that the validity of using Equation 2 for estimating the vapour concentrations of organometallic compounds (such as in the estimation of the lead concentrations in Table 4) has not been demonstrated. However, it is considered highly desirable that estimates of lead emissions from service stations are made for the NPI, even if these estimates have a relatively low reliability and are much smaller than emissions estimates for other sources, such as motor vehicles.

Species	Species Petrol Liquid (% weight) ^a Petrol Vapour (% weigh					
Benzene	2.9 ^c	0.950				
Cyclohexane	0.2	0.0637				
Ethylbenzene	2.0	0.0791				
n-Hexane	3.5	1.73				
Styrene	0.1	0.00282				
Toluene	10.4 ^c	1.08				
Xylenes	12.2	0.433				

Table 3: Composition of Petrol

^a Ye et al (1995) unless otherwise specified.

^b Calculated from Equation 2, with the figure for styrene based on the boiling point of m-xylene.

^c Octel (1994).

	Leaded Petrol	Unleaded Petrol	
Lead content of petrol (% weight) ^a	0.0176	1.90 * 10 ⁻⁴	
Estimated lead concentration in petrol vapour (% weight) ^b	6.32 * 10 ⁻⁵	6.84 * 10 ⁻⁷	

Table 4: Lead Content of Petrol and Petrol Vapour

^a Derived from B. Challenger, AIP (July 1998) pers. comm.

^b Calculated from Equation 2.

Lead is added to petrol in the form of either tetramethyl lead (TML) or tetraethyl lead (TEL). The estimates of lead concentrations by weight in petrol vapour in Table 4 are based on the assumption that lead is present in petrol in the form of TEL.

If local data on petrol lead content and lead additives are available, Equation 2 may be used to calculate locally applicable values for lead concentration in petrol vapour (instead of the default values in Table 4). If the lead content of petrol is given in grams per litre, it needs to be converted to percentage by weight by using Equation 7.

The boiling points of TML and TEL are 110 °C and 200 °C respectively.

Equation 7: Conversion of lead content in grams per litre to percent by weight

The percentage by weight of lead in petrol liquid can be calculated from the lead content of petrol in grams per litre as follows

$$C_{cl} = Pb_p * 0.1 / D_p$$

where

then

 $C_{cl} =$ Concentration of lead in liquid petrol, % weight $Pb_p =$ Lead content of petrol, g L⁻¹ $D_p =$ Density of petrol, kg L⁻¹

3.4 Sample Calculations

Example 1: Using emission factors to calculate VOC emissions from petrol handling in an airshed

Using Equation 1 with emission factors of 40 for tank filling (i.e. the use of vapour balancing and submerged filling techniques), 120 for tank breathing losses, 1320 for vehicle refuelling (i.e. uncontrolled), and 80 for spillages (from Table 2), and assuming annual sales of 1.5 billion litres of petrol in the airshed, total VOC emissions in the airshed can be calculated as follows

 $E_{petrol} = EF_{petrol} * V_{petrol} * 10^{-6}$ = (40 + 120 + 1320 + 80) * (1.5 * 10⁹) * 10⁻⁶ = 2.34 * 10⁶ kg yr⁻¹

Example 2: Calculating emissions of an NPI substance (benzene) from petrol handling in an airshed

Using Equation 3 and the same petrol sales and emission factors as Example 1, but separately calculating VOCs from evaporation and spillage respectively, benzene emissions in the airshed can be derived as follows

$$E_{pv} = (40 + 120 + 1320) * (1.5 * 10^{9}) * 10^{-6}$$

= 2.22 * 10⁶ kg yr⁻¹
$$E_{pl} = 80 * (1.5 * 10^{9}) * 10^{-6}$$

= 1.20 * 10⁵ kg yr⁻¹
$$E_{benzene,p} = [E_{pv} * C_{benzene,pv} + E_{pl} * C_{benzene,pl}] / 100$$

 $= (2.22 * 10^{6} * 0.950 + 1.20 * 10^{5} * 2.9) / 100$ = 24 600 kg yr⁻¹

Example 3: Allocating airshed emissions of benzene to a grid cell

Using the result from Example 2 with Equation 5, and assuming 350 and 8 service stations in the airshed and grid cell, benzene emissions in the cell are

 $\begin{array}{rcl} E_{jk} & = & E_{j} * N_{k} / N \\ & = & 24 \ 600 * 8 / 350 \\ & = & 562 \ kg \ yr^{-1} \end{array}$

4.0 Uncertainty Analysis

4.1 Data Reliability

The reliability of the EETs is essentially dependent on the quality of data on fuel throughput and composition, and fuel handling and tank filling methods. If industry associations and/or petrol distributors are consulted, data of high reliability should be obtained.

Should data on petrol composition in vapour not be available for the NPI substances in question, the default information in Tables 3 provides an approach of medium reliability.

4.2 Reliability of Emission Factors

USEPA emission factors are used as the basis for this technique. If the emission factors for petrol were derived for Australian jurisdictions, they would provide greater accuracy, especially for the range of climatic conditions that are encountered.

Data on liquid petrol composition is freely available for most petrols, however the vapour composition data is calculated using Equation 2, which is of medium reliability. The default vapour concentration estimates for lead (Table 4) have low reliability. More accurate data from recent measurements of petrol vapour in Australia is desirable.

4.3 Problems and Issues Encountered

There is no reliable technique for estimating the vapour concentrations of lead for petrol, as discussed above. Vapour composition of diesel is not readily available.

4.4 Recommendations for Further Work

The following work would increase the reliability of the EETs for service stations:

- collection of local data on the composition of petrol and diesel vapour, especially the concentrations of NPI substances; and
- the development of airshed databases on the location, size and emission control practices of service stations.

5.0 Glossary of Terms and Abbreviations

AE AIP CSIRO EET EF EPAV GIS NEPC NEPM NPI USEPA VOC	Aggregated emissions Australian Institute of Petroleum Commonwealth Scientific and Industrial Research Organisation Emissions estimation technique Emission factor Environment Protection Authority (Victoria) Geographic information system National Environment Protection Council National Environment Protection Measure National Environment Protection Measure National Pollutant Inventory United States Environmental Protection Agency Volatile organic compound
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6.0 References

Dames and Moore (1996). *National Pollution Inventory, Emissions Estimation Techniques Report,* vol 1, Environment Australia.

EA (1998). National Pollution Inventory Guide, Environment Australia.

EPAV (1996a). *Metropolitan Air Quality Study, Air Emissions Inventory*, Environment Protection Authority of New South Wales, Sydney.

EPAV (1996b). National Pollutant Inventory: Technical Report on the Air *Emissions Trials for the National Pollutant Inventory*, vol 2, AGPS, Commonwealth of Australia.

Nelson, P. F., Quigley, S. M and Smith M. Y. (1983). "Sources of Atmospheric Hydrocarbons in Sydney: A Quantitative Determination Using a Source Reconciliation Technique", *Atmos. Environ.*, vol 17, pp 439-449.

Octel (1994). Petrol Surveys 1994, Octel, Australia.

USEPA (1995). Compilation of Air Pollutant Emission Factors, Stationary Point and Area Sources, AP-42, vol I, 5th edn, United States Environment Protection Agency, Research Triangle Park, North Carolina, USA.

Ye, Y., Weeks, I. A., Galbally, I. E., Duffy, B., and Nelson, P. (1995). *Benzene, Toluene, Xylenes and 1,3-Butadiene Concentrations in Emissions from a Representative Portion of the Australian Car Fleet,* Final report to Commonwealth Environment Protection Agency and Department of Environment, Sports and Territories, CSIRO, Aspendale, Victoria.