National Pollutant Inventory

Emission Estimation Technique Manual

for

Leather Tanning and Finishing

Environment Australia

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EMISSION ESTIMATION TECHNIQUES
FOR
LEATHER TANNING & FINISHING

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FOR
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1.0 Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and recommended approaches for estimating emissions from facilities engaged in Leather Tanning & Finishing.

The Leather Tanning & Finishing industries covered by this Manual include facilities primarily engaged in tanning, curing, dressing, finishing, dyeing or embossing leather, animal skins or fur. This class also includes units mainly engaged in production of fellmongered wool, pelt or slipe wool.

EET MANUAL:	Leather Tanning & Finishing
HANDBOOK:	Leather Tanning & Fur Dressing
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This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

2.0 Processes and Emissions

The following section presents a brief description of the leather tanning & finishing industry.

2.1 Process Description

Tannery processes vary according to the type of leather produced - wet-blue from hides, wool skins, dewoolled or fellmongered pickled-pelts from sheepskins, finished leather or sole leather. As a result, the chemicals used and the tannery emissions can vary widely although there are similarities in some processes in different types of tanneries.

In all types of leather production, dirt and biological materials, including grease and proteins (eg. blood and hair) must be removed from the raw material. The skin collagen is then chemically stabilised with a tanning agent. Chromium III is the most widely used tannage but vegetable extracts are used for sole leathers, fish oil for chamois, and glutaraldehyde and syntans are also used to confer specific properties to leathers.

In recent times, tanneries have greatly minimised waste by the introduction of new, clean technologies and by recycling and pre-treating segregated waste streams before an appropriate effluent treatment.

These clean technologies include:

- Processing green (fresh) hides and the use of short-term preservation to eliminate salting;
- Recovery of hair through hair-saving unhairing processes to reduce BOD, nitrogen and suspended solids loads in effluent;
- Utilisation of recovered hair in compost or as a slow release high organic nitrogen fertiliser;
- Carbon dioxide (CO_2) deliming processes, which lower ammonia and nitrogen loads;
- Recycling of chromium tanning liquors;
- Efficient drums and washing processes that save both water and chemical use;
- High exhaust retans, dyes and fatliquors;
- Non-toxic dyes and pigments; and
- Aqueous finishes to replace solvents.

Important reductions are being achieved in effluent volume, BOD, Suspended Solids, Chromium, Total Nitrogen, Ammonia, Total Dissolved Solids, and Total Oxidised Sulfur. There are also reductions in air emissions of solvents and ammonia. A recent international benchmarking study with participating tanneries from Australia, Europe, USA, New Zealand, Scandinavia, South Africa, Mexico, India and South America showed that Australian tanneries had the lowest water consumption and effluent volumes per unit of output of all countries.

2.2 Emission Sources and Control Technologies

2.2.1 Emissions to Air

Air emissions may be categorised as:

Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats, open vessels, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions. Emission factor EETs are the usual method for determining losses through fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent or stack and emitted through a single point source into the atmosphere. Table 1 illustrates possible NPI-listed substance air emissions from the leather tanning & finishing industry.

Table 1 - Possible NPI-Listed Substance Air Emissions from Leather Tanning & Finishing

Emission Source	Emission Type
General Use	• Glutaraldehyde • Ammonia • Formaldehyde
Fuel Burning	• Sulfur dioxide • Oxides of Nitrogen • Carbon monoxide • Polycyclic aromatic hydrocarbons (PAHs) • Particulate Matter 10µm (PM$_{10}$)
Solvent Use	• Volatile Organic Compounds (VOCs) • Xylene • Toluene • Tetrachloroethylene (perc) • White spirit (which contains Toluene and Xylene)

Source: Department of Environment and Heritage, 1998

Air emission control technologies, are commonly installed to reduce the concentration of particulates in process off-gases before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered. Guidance on applying collection efficiencies to emission factor equations is provided in later sections.

With regards to emission controls for PM_{10} emissions (particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10μm), in the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.

2.2.2 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries);
- Coastal or marine waters; and
- Stormwater.

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions.

The discharge of listed substances to a sewer or tailings dam does not require you to report to the NPI. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of the *NPI Guide*.)

In general, tanneries will not discharge effluent to a water body, but may alternatively discharge to the sewer, which is presently not reportable to the National Pollutant Inventory. Table 2 indicates possible NPI-listed substance water emissions from leather tanning and finishing.

Table 2 - Possible NPI-Listed Substance Water Emissions from Leather Tanning & Finishing

Substance
Chromium (III)
Manganese
Total Nitrogen
Ammonia

Source: Draft Effluent Management Guidelines for Tanning and Related Industries, 1995

2.2.3 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids and may contain listed substances. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.

Emissions to land from the leather tanning & finishing industry may be from:

- irrigation of effluent;
- solid wastes and slurries; and
- accidental spills or leaks.

The disposal of listed substances to landfill off-site does not require you to report to the NPI (see also Section Three of the *NPI Guide*).

3.0 Threshold Determination

The following information is designed to give a general idea of the composition of some of the commonly used substances in leather tanning & finishing. By determining the composition of a mixture, it is then possible to assess the amount of NPI-listed substance in that mixture, and subsequently determine whether or not a reporting threshold has been broken.

A number of NPI-listed substances are outlined below. Under each heading, the mixtures that contain the NPI-listed substances are described, along with their composition. Appendix A to the NPI Guide provides specific guidance for threshold calculations for some substances. The general rule to be applied where a substance and its compounds are listed is that the dry weight of the compound used determines if a threshold is triggered. The guidance provided below is based on a Category 1 threshold level of 10 tonnes, as set in the 1998 NPI Guide.

3.1 Tetrachloroethylene (perc)

To determine if the threshold has been triggered, it is necessary to calculate the annual amount of perc used per year.

3.2 Glutaraldehyde

To determine whether glutaraldehyde is used in a quantity exceeding the NPI threshold, and is subsequently a reportable substance, the proportion of glutaraldehyde in products used, or the amount generated in the process, needs to be determined.

3.3 Fluoride

To assist in determining if the NPI threshold for fluoride compounds is triggered, the following information may be useful:

- In hide and skin preservation;
    - 0.3% NaF is used on a hide by weight.

Therefore, it would be necessary to process approximately 3300 tonnes of hides per year before the NPI threshold is triggered and therefore reporting required.

3.4 Xylene

Xylene is a constituent of White Spirit, and therefore may be reportable if White Spirit is used in large enough quantities.

Generally White Spirit contains approximately 4.3% xylene on a weight basis.

To trigger the threshold for Xylene, approximately 232 tonnes of White Spirit would have to be used by a facility per year.

3.5 Toluene

Toluene is also a constituent of White Spirit. It is likely to be approximately 0.1% by weight of the White Spirit. For this percentage, approximately 10 000 tonnes of White Spirit would have to be used by a facility per year to be reportable.

Thinners used in finishing may contain approximately 30% Toluene. To trigger the threshold for Toluene, approximately 33 tonnes per year of such a thinner would have to be used by a facility.

It is important to note that the total usage of the substance in the processes needs to be estimated to determine if the threshold is triggered and reporting is necessary.

3.6 Fuel Burning

For tanneries burning fuel in boilers, dryers etc, the *Combustion in Boilers* Manual can be used to estimate emissions from fuel burning activities.

If 400 tonnes or more of fuel is burnt per annum, you will have to report on Category 2a substances. For above 2000 tonnes you will also need to report Category 2b substances. See also Section Two of the *NPI Guide.*

If natural gas is used, 400 tonnes equals 465 000 cubic meters.

3.7 Chromium III

Chromium sulfate powder with a chrome content equivalent to 64% pure chromium sulfate is used

Therefore to trigger the 10 tonne threshold for Chromium III, a facility would have to use 15 tonnes of 64% powder per year.

3.8 Manganese

Manganese sulfate monohydrate, which may be used on-site, contains 89% manganese sulfate.

To trigger the threshold for manganese, a facility would have to use approximately 11 tonnes per year of manganese sulfate monohydrate.

3.9 Ammonia

For NPI reporting it is important to remember that ammonia (total) refers to ammonia (NH_3) and the ammonium ion (NH_4^+) in the solution.

Ammonia is contained in a number of substances that may be used by leather tanning & finishing facilities. These include:

- Ammonium chloride (NH_4Cl), contains 33.7% NH_4^+;

  Therefore to trigger the ammonia threshold, approximately 30 tonnes of NH_4Cl would have to be used per year.

- Ammonium sulfate ($(NH_4)_2SO_4$) contains 27% NH_4^+;

  Therefore to trigger the threshold for ammonia, approximately 37 tonnes of Ammonium sulfate would need to be used per year.

- Ammonium carbonate ($(NH_4)_2CO_3$) contains 30% NH_4^+;

  Therefore to trigger the threshold for ammonia, approximately 33 tonnes of Ammonium carbonate would need to be used per year.

- Ammonia solution contains 25% NH_4^+;

  To trigger the threshold for ammonia, 40 tonnes of ammonia solution per year would have to be used within a facility.

Note that the above threshold triggers refer to the use of that compound alone. Where more than one compound is used, the threshold will be triggered by a total usage of more than 10 tonnes of ammonia or the ammonium ion.

Wet-blue tanneries processing more than 3000 tonnes of hide per year are likely to have to report on ammonia.

3.10 Boron

Boric acid contains 17.5% boron. However, since boron and compounds are listed substances, to trigger the threshold for boron 10 tonnes of boric acid would need to be used per year

3.11 Formaldehyde

To determine the amount of formaldehyde used at a facility, it is necessary to determine the amount of formaldehyde in any products used, or determine the amount of formaldehyde that may be generated in the process.

Formalin contains 37% formaldehyde.

It is necessary to use 27 tonne of formalin in order to trigger the 10 tonne threshold for formaldehyde.

4.0 Emission Estimation Techniques

Estimates of emissions of listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in the *NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility.

The four types described in the *NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors

Select the EET, (or mix of EETs), that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of EETs that are not outlined in this handbook, your data will also be displayed as being of 'acceptable reliability'.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this handbook does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.

You should note that the EETs presented in this manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie., the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed during clean up operations.

The **usage** of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

4.1 Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement. For the sampling data to be adequate and able to be used for NPI reporting purposes, it would need to be collected over a period of time, and to be representative of operations for the whole year.

4.1.1 Sampling Data

Stack sampling test reports often provide emissions data in terms of kg/hr or g/m^3 (dry standard). Annual emissions for NPI reporting can be calculated from this data. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory license condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

Estimating Emissions from Wastewater Irrigation

If effluent is used for irrigation, it is possible to estimate emissions to land from the average concentration of particular pollutants in the effluent, and the average volume of wastewater irrigated to land per year. This method may be particularly useful for estimating emissions of Chromium III and ammonia, which may be constituents in the wastewater stream. Adjustments may need to be made for any ammonia released to air during irrigation.

The basic equation for performing this calculation is illustrated below.

Equation 1

$$E_{kpy,i} = (C_i * V) / 1\,000$$

where

$E_{kpy,i}$ = emission of pollutant i , kg/year
C_i = concentration of pollutant i in the wastewater, mg/L
V = volume of wastewater irrigated per year, m^3/year
1000 = conversion factor (1 000 000 mg/kg/1000L/m^3)

Example 1 - Using Sampling Data

This example illustrates how emissions to land of Chromium III from wastewater used for irrigation, can be calculated from sampling data that may be available from on-site monitoring.

From a tanning operation, 100 000 m^3 of wastewater was used for irrigation in one year. The average concentration of Chromium III in this wastewater is 5 mg/L.

From Equation 1

$$E_{kpy,chromium\ III} = (C_{chromium\ III} * V)/1000$$

Using the information from the tanning operation,

$$E_{kpy,chromium} = (5\ mg/L * 100\ 000\ m^3/year)/1\ 000$$
$$= 500\ kg/year.$$

Therefore, from this tanning operation, 0.5 tonne per year of chromium III is emitted to the land via irrigation. This effluent is irrigated over a large area, say 200 hectares.

4.1.2 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system provides a continuous record of emissions over time, usually by reporting pollutant concentration.

Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

You should note that prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies your relevant environmental authority's requirement for NPI emission estimations.

4.2 Mass Balance

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.

4.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

4.3.1 Fuel Analysis

Fuel analysis is an example of an engineering calculation and can be used to predict SO_2, metals, and other emissions based on application of conservation laws, if fuel rate is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulfur, which may be converted into other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is the following:

Equation 2

$$E_{kpy,i} = Q_f * \text{pollutant concentration in fuel} * (MW_p / EW_f) * OpHrs$$

where:

$E_{kpy,i}$ = emissions of pollutant i, kg/yr
Q_f = fuel use, kg/hr
MW_p = molecular weight of pollutant emitted, kg/kg-mole
EW_f = elemental weight of substance in fuel, kg/kg-mole
OpHrs= operating hours, hr/yr

For instance, SO_2 emissions from coal combustion can be calculated based on the concentration of sulfur in the coal. This approach assumes complete conversion of sulfur to SO_2. Therefore, for every kilogram of sulfur (EW = 32) burned, two kilograms of SO_2 (MW = 64) are emitted. The application of this emission estimation technique is shown in Example 2.

Example 2 - Using Fuel Analysis

This example illustrates how SO_2 emissions can be calculated from coal combustion based on fuel analysis results and the fuel flow information from a tannery facility. The facility is assumed to operate 1500 hours per year.

$E_{kpy,SO2}$ = may be calculated using Equation 2

Fuel flow	=	2 000 kg/hr
Weight percent sulfur in fuel	=	0.5%

$$\begin{aligned} E_{kpy,SO2} &= Q_f * \text{pollutant concentration in fuel} * (MW_p / EW_f) * OpHrs \\ &= (2\,000) * (0.5/100) * (64/32) * 1\,500 \\ &= 20.0 \text{kg/hr} * 1\,500 \text{ hr/yr} \\ &= 30\,000 \text{ kg/yr} \end{aligned}$$

As the majority of leather tanning and finishing facilities use natural gas as their fuel source, the fuel analysis equation above may not be applicable.

For more information on fuel analysis techniques, please refer to the *Combustion in Boilers* EET Manual

4.4 Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. Presently there are no emission factors available for assistance in estimating emissions from leather tanneries and finishing plants. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted, divided by the unit weight, volume, distance, or duration of the activity emitting the substance.

Emission factors are used to estimate a facility’s emissions by the general equation:

Equation 3

$$E_{kpy,i} = [A * OpHrs] * EF * [1 - (CE_i / 100)]$$

where :

$E_{kpy,i}$ = emission rate of pollutant i, kg/yr
A = activity rate, t/hr
$OpHrs$ = operating hours, hr/yr
EF_i = uncontrolled emission factor of pollutant i, kg/t
CE_i = overall control efficiency for pollutant i, %.

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources. The emission factor must be reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

4.4.2 Predictive Emission Monitoring (PEM)

Predictive emission monitoring is based on developing a correlation between pollutant emission rates and process parameters. A PEM allows facilities to develop site-specific emission factors, or emission factors more relevant to their particular process.

Based on test data, a mathematical correlation can be developed which predicts emissions using various parameters.

5.0 Emission Estimation Techniques: Acceptable Reliability and Uncertainty

This section is intended to give a general overview of some of the inaccuracies associated with each of the techniques. Although the National Pollutant Inventory does not favour one emission estimation technique over another, this section does attempt to evaluate the available emission estimation techniques with regards to accuracy.

Several techniques are available for calculating emissions from leather tanneries. The technique chosen is dependent on available data, available resources, and the degree of accuracy sought by the facility in undertaking the estimate. In general, site-specific data that is representative of normal operations is more accurate than industry-averaged data, such as the emission factors.

5.1 Direct Measurement

Use of stack and/or workplace health and safety sampling data is likely to be a relatively accurate method of estimating air emissions. However, collection and analysis of samples from facilities can be very expensive and especially complicated where a variety of NPI-listed substances are emitted and where most of these emissions are fugitive in nature. Sampling data from a specific process may not be representative of the entire manufacturing operation, and may provide only one example of the facility’s emissions.

To be representative, sampling data used for NPI reporting purposes needs to be collected over a period of time, and to cover all aspects of production.

In the case of CEMS, instrument calibration drift can be problematic and uncaptured data can create long-term incomplete data sets. However, it may be misleading to assert that a snapshot (stack sampling) can better predict long-term emission characteristics. It is the responsibility of the facility operator to properly calibrate and maintain monitoring equipment and the corresponding emissions data.

5.2 Mass Balance

Calculating emissions from tanneries using mass balance appears to be a straightforward approach to emission estimations. However, it is likely that few Australian facilities are likely to consistently track material usage and waste generation with the overall accuracy needed for application of this method. Inaccuracies associated with individual material tracking or other activities inherent in each material handling stage can result in large deviations of total facility emissions. Because emissions from specific materials are typically below 2 percent of gross consumption, an error of only ± 5 percent in any one step of the operation can significantly skew emission estimations.

5.3 Engineering Calculations

Theoretical and complex equations or *models* can be used for estimating emissions from tanning processes.

Use of emission equations to estimate emissions from leather tanning & finishing facilities is a more complex and time-consuming process than the use of emission factors. Emission equations require more detailed inputs than the use of emission factors but they do provide an emission estimate that is based on facility-specific conditions.

5.4 Emission Factors

Every emission factor has an associated emission factor rating (EFR) code. This rating system is common to EETs for all industries and sectors and therefore, to all Industry Handbooks. They are based on rating systems developed by the United States Environmental Protection Agency (USEPA), and by the European Environment Agency (EEA). Consequently, the ratings may not be directly relevant to Australian industry. Sources for all emission factors cited can be found in Section 6.0 of this Manual. The emission factor ratings <u>will not</u> form part of the public NPI database.

When using emission factors, you should be aware of the associated EFR code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived.

The EFR system is as follows:

A - Excellent
B - Above Average
C - Average
D - Below Average
E - Poor
U - Unrated

6.0 References

Agricultural and Resource Management Council of Australia and New Zealand, and the Australian and New Zealand Environment and Conservation Council. 1995. *Draft Effluent Management Guidelines for Tanning and Related Industries.* National Water Quality Management Strategy, Department of Conservation & Natural Resources, Victoria, Australia.

Communication from Catherine Money, CSIRO Wool Technology on behalf of the Australian Association of Leather Industries to Alison Wiltshire, National Pollutant Inventory Unit, Queensland Department of Environment and Heritage, September 1998.

National Pollutant Inventory Homepage
http://www.npi.gov.au

The following Emission Estimation Technique Manuals referred to in this Manual are available at the NPI Homepage and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Combustion in Boilers;
- Emission Estimation Technique Manual for Combustion Engines;
- Emission Estimation Technique Manual for Fuel & Organic Liquid Storage; and
- Emission Estimation Technique Manual for Sewage and Wastewater Treatment.