Pollution inventory reporting – refineries guidance note

Environmental Permitting (England and Wales) Regulations 2010

Regulation 60(1)

Version 4 December 2012

We are the Environment Agency. We protect and improve the environment and make it a better place for people and wildlife.

We operate at the place where environmental change has its greatest impact on people's lives. We reduce the risks to people and properties from flooding; make sure there is enough water for people and wildlife; protect and improve air, land and water quality and apply the environmental standards within which industry can operate.

Acting to reduce climate change and helping people and wildlife adapt to its consequences are at the heart of all that we do.

We cannot do this alone. We work closely with a wide range of partners including government, business, local authorities, other agencies, civil society groups and the communities we serve.

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1. Introduction

If we regulate your activity as an A1 installation under the Environmental Permitting (England and Wales) Regulations 2010 (EPR) you will need to submit data to the Pollution Inventory.

You need to report each year. The system opens for reporting on 1 January and the deadline for submitting is 28 February.

Our general guidance sets out how to report and provides information applicable to all businesses and industries.

In this guidance you will find helpful information specific to the refineries sector.

If your operations include production of chemicals, waste incineration or combustion please also read these guidance notes.

You can find additional information on the web:

Pollution Inventory guidance: www.environment-agency.gov.uk/pi

2. Emissions to air

2.1 Relevant pollutants

Table 2.1 gives a very brief summary of the main pollutants released by a refinery, with their main sources. Use the table as a guide only and check that there are no other pollutants emitted from your process that must be reported.

Appendix B shows UKPIA's 'Pollution Inventory – Guidance for Refineries' document, which covers the major categories of refinery emission sources. The document is split into three categories of pollutant: those that will almost certainly be emitted in quantities above the reporting threshold, those emitted but generally in quantities below the reporting threshold and those that are unlikely to be emitted by refineries.

Table 2.1 Main air pollutants emitted by refineries and their main sources

Main air pollutants	Main sources
CO_2	Process furnaces, boilers, gas turbines fluidised catalytic cracking regenerators, CO boilers, flare systems, incinerators
CO	Process furnaces, boilers, gas turbines fluidised catalytic cracking regenerators, CO boilers, flare systems, incinerators, sulphur recovery units
NOx	Process furnaces, boilers, gas turbines fluidised catalytic cracking regenerators, CO boilers, flare systems, incinerators, coke calciners
Particulate matter (including PM_{10})	Process furnaces, boilers, particularly fluidised catalytic cracking regenerators, CO boilers, incinerators, coke calciners
SOx	Process furnaces, boilers, gas turbines fluidised catalytic cracking regenerators, CO boilers, flare systems, incinerators, sulphur recovery units, coke calciners

VOCs	Storage and handling facilities, gas separation units, oil/water separation systems, fugitive emissions (valves, flanges, etc), vents, flare systems

2.2 Emission sources

2.2.1 Point source emissions

These emissions are exhausted via a stack or vent, that is a single point source into the atmosphere. Abatement equipment, for instance scrubbing units, fabric filters (bag house) can be incorporated into the exhaust system prior to discharge to atmosphere. Point source emissions will be the most significant emission sources for combustion activities taking place within refineries as well as occurring from refinery process sources (for instance vacuum distillation, catalytic cracking, sulphur recovery, and so forth).

2.2.2 Fugitive emissions

Fugitive emissions are those that are not released from a point source such as a stack. Examples of fugitive emissions from refineries include VOC emissions from piping systems, wastewater systems, storage tanks, loading and unloading systems and storage and handling. Although the release from each individual source may be small, diffuse VOC emission sources such as pumps, compressors, valves and flanges may contribute 20-50% of the total VOC emissions owing to the large number of such sources in a refinery. You only need to report fugitive emissions that leave the site to the PI so you should report vapour emissions that may have dispersed but not contained spills.

Estimation of fugitive VOC emissions is dealt with below.

2.3 Quantification of emissions

Table 2.2 indicates sources of emissions of particular relevance to refineries and indicates the further sections of this note relevant to particular release estimation techniques (RETs).

Table 2.2 Location of RETs for emissions to air from refineries

Substances emitted from refineries	Emissions to air					
	Combustion sources		Refinery process sources			Fugitives
	Oil	Gas	FCCU	SRU	Flares	
Tetrachloroethane						2.3.6
Tetrachloroethylene						Appendix C
Trichloroethylene						Appendix C
Toluene						2.3.6
Xylene						2.3.6
Zinc	Appendix C					

Take care to make sure the emission concentration and flow rate are compatible. For example, normalised emission concentrations should be multiplied by normalised volumetric flow rates or actual, measured emission concentrations multiplied by actual, measured volumetric flow rates. Normalised emission rates are quoted in terms of a standard oxygen concentration, and are usually dry gas, at a temperature of 273K and a pressure of 101.3 kPa. See Appendix A for formulae for conversion between normalised and actual emission concentrations.

2.3.1. Carbon dioxide emissions from refineries

The EU ETS allows CO_2 emissions to be determined by two methodologies: a calculation methodology or a measurement methodology. Where a measurement methodology is used, a requirement exists to verify the measured emissions by calculation. In both cases, it is likely that measurements of fuel burned or material flow will be available and these can be used for the determination of other emission quantities when combined with appropriate emission factors.

Specific refinery processes leading to CO_2 – emissions include:

Catalytic cracker regeneration and other catalyst regeneration calculated as follows:

(1) $E_{CO2} = A_e \times EF_{CO2} \times CF$

Where E_{CO_2} = emission of CO_2, te/yr

A_e = amount of coke burned from the catalyst, te/yr

EF_{CO2} = amount of CO_2 per tonne of coke burned based on carbon content

of coke, te/te

CF = conversion factor (taken as 1)

Refinery hydrogen production calculated as follows:

(2) $E_{CO2} = A_e \times EF_{CO2}$

Where E_{CO2} = emission of CO_2, te/yr

A_e = amount of hydrocarbon feed processed, te/yr

EF_{CO2} = emission factor (CO_2 per te of feed)

Combustion source factors

See Appendix B for refinery combustion source factors.

Emission factors are provided for the estimation of combustion products with the exception of SO_2, for which the usually preferred RET is mass balance, based on the sulphur content of the fuel. Emissions of certain trace elements can be estimated using mass balance, when fuel composition data are available. If such data are unavailable, default emission factors can be used. Emissions of NOx from oil and gas fired boilers and furnaces that do not use CEMS for annual mass emissions can be calculated from the fuel burn and NOx factors which you have agreed with us on a site specific basis.

Refinery process source factors

See Appendix B for refinery process source factors.

2.3.2 Fuel analysis and process stream data

The use of fuel analysis and process stream data to determine emissions is similar to the use of emission factors.

The basic equation used, for example, in fuel analysis emission calculations is:

(3)   E = Q_f x [Op hours] x [PC_f/100] x (MM_p / EM_f)

Where:	E	= emission of pollutant, kg/yr
	Q_f	= fuel use (kg/hr)
	PC_f	= pollutant concentration in the fuel (%)
	Op hrs	= operating hours per year, hr/yr
	MM_p	= molar mass of pollutant as emitted after combustion
	EM_f	= relative atomic mass of polluting element as present in fuel

Equation 3 is the method usually used for calculating SO_2 emissions where it is normally assumed that all of the sulphur in the fuel is converted to SO_2.

Where the pollutant concentration in the fuel is consistent over the averaging period (that is one year), equation 3 can be written as:

(4)   E = M x [PC_f/100] x (MM_p / EM_f)

Where:	E	= emission rate of pollutant in kg/yr
	M	= mass of fuel burnt in one year (kg/yr)
	PC_f	= pollutant concentration in the fuel (%)
	MM_p	= molar mass of pollutant as emitted after combustion
	EM_f	= relative atomic mass of polluting element as present in fuel

Example 1:

SO_2 emissions are calculated from oil combustion, based on fuel analysis results and fuel flow information. It is assumed that the facility operates using oil for 150 hours per year and that abatement of SO_2 does not occur.

Q_f	=	2000 kg/hr
PC_f	=	1.17%
MM_p	=	64
EM_f	=	32
Op hours	=	150 hr/yr

$E = Q_f \times PC_f \times (MM_p / EM_f) \times [\text{Op hours}]$

$= [(2000) \times (1.17 / 100) \times (64/32) \times 150] \text{ kg/yr}$

$= \textbf{7.02} \times \textbf{10}^{\textbf{3}} \textbf{ kg/year}$

$= \textbf{7.02 te/year}$

You can also use equation 3 for volatile elements such as fluorine and chlorine, as well as trace metallic pollutants, although some of these species are retained in the plant, either in the ash or in abatement equipment.

When using equation 3 or equation 4, be aware that the amounts of pollutants present in the fuel or process stream can vary significantly.

2.3.3 Fugitive VOC emissions

For the purposes of this note fugitive VOC emissions from refineries can be split into four categories:

- Process fugitives
- Tank farm fugitives
- Loading/unloading fugitives
- Drainage and effluent system fugitives

Guidance for estimation of the above releases for UK refineries can be found in two separate protocols produced by the Energy Institute. The first provides a methodology (speciation protocol), in conjunction with total VOC releases, for determining the fractional speciation of hydrocarbon emissions from oil refineries.

The second can be used to produce estimates of annual emissions of NMVOCs including fugitive VOC releases when there is insufficient information available to apply the methodology.

Process fugitives

Two methods for calculating process fugitives are presented in the VOC protocol.

The first method uses the USEPA protocol for equipment leak estimates. This protocol assumes knowledge of the number of valves/flanges/seals on a refinery and takes a tiered approach to estimating emissions.

i. **Tier 1** applies average emission factors based upon the process service.
ii. **Tier 2** applies average emission factors based on leak/no leak criteria. This requires the use of VOC monitoring equipment to measure threshold VOC concentrations at each fitting.
iii. **Tier 3** applies emission correlations based on actual VOC concentration methods determined at each fitting.

(i) Tier 1 Average emissions factors

Where no screening values are available for particular equipment types, the 'average emissions factors' presented in this section should be used. This methodology involves applying the following generic equation to estimate emissions from all sources in a stream, for a particular equipment type:

(5)   E = F x WF x N

Where: E   =   Emission rate of VOC from all sources grouped in a particular type and service (kg/hr) (e.g. values in light liquid service) equipment

F   =   Average emission factor for the particular equipment type (from table

WF   =   The average weight fraction of VOC in the stream

N   =   The number of pieces of equipment grouped in the relevant according to equipment type, service and weight fraction of VOC category

Although the average emission factors are in terms of VOCs, the equation still requires an input regarding the weight fraction of VOC in the process stream (i.e. WF) to account for any non-organic compounds. For example if the stream contains water vapour, you will need to account for this in your calculations. Example 2 illustrates the application of this methodology.

Step 1: Develop an inventory of the number and service type of fugitive sources

The number and service type (Gas/vapour, light liquid and heavy liquid) of each equipment type in the refinery must be determined. Service type definitions are given below:

- **Gas/vapour:** material in a gaseous state under operating conditions
- **Light liquid:** material in a liquid state in which the sum of the concentrations of individual constituents with a vapour pressure over 0.3 kilopascals (kPa) at 20°C ≥ 20weight percent (wt%)
- **Heavy liquid:** material that does not fall under either of the above two definitions

Step 2: Group the inventory into 'streams'

We recommend that to simplify calculations the service mode combinations identified in Step 1 (for example, valves in gas service) be grouped into 'streams' according to the approximate weight fraction of VOCs (that is WF) in each stream.

A further simplification may be to group areas of the refinery according to the 'average' weight fraction of VOCs in the process streams. It will be necessary to take account of the various service modes for each equipment type (for example, gas, light liquid and so forth) contained within that area.

Another approach may be to take the conservative assumption that all streams are approximately 100% VOCs, thereby making WF = 1.

Step 3: Note Operational hours

For the specific equipment category defined by the above two steps, you need to estimate the number of operational hours.

Step 4: Use emission factors to estimate emission rates

Use the relevant emission factors and the equation given above to calculate the emissions from each equipment type. Then add these emissions to derive a total emission rate for all equipment pieces quantified using this methodology.

Table 2.3 gives the emission factors required to estimate emissions using the steps discussed above.

Table 2.3 Average emission factors for process fugitives

Equipment type	Service	Emission factor (kg/hr/source)
Connectors	Gas	2.50×10^{-4}
	Light liquid	2.50×10^{-4}
	Heavy liquid	4.34×10^{-5}
Flanges	Gas	2.50×10^{-4}
	Light liquid	2.50×10^{-4}
	Heavy liquid	4.68×10^{-5}
Compressor seals	Gas	0.636
Pump seals	Light liquid	0.114
	Heavy liquid	3.49×10^{-3}
Valves	Gas	0.0268
	Light liquid	0.0109
	Heavy liquid	9.87×10^{-5}
Open ended lines	All	2.30×10^{-3}
Pressure relief valves	Gas	0.16
Sampling connections	All	0.015
Other	Heavy liquid	5.18×10^{-5}

Notes:

The emission factors given above are for non-methane VOCs only.

The following example shows the application of the average emission factor approach.

Example 2:

1. A particular section of the refinery has 300 valves (Step1)
2. 200 of these are in gas service (Step 1)
3. Within this smaller group of valves in gas service, it is ascertained that 100 valves are, on average, 80 weight percent NMVOCs, 10 % methane, and 10% water vapour (Step 2);
4. It is estimated that this group of valves operates for 5500 hours per year (Step3);
5. The appropriate emission factor for valves in gas service is 0.027 kg/hr/source (from table 2.4) (Step 4). Emissions from this group of valves are thus estimated by using the following parameters:

6. The final emission estimate for the group of 100 valves specified above is approximately 11,900 kg NMVOCs/year

The above steps would then be repeated again for the remaining 200 valves that were not included in the above estimate for that section of the refinery. Similarly, emissions need to be calculated from other potential fugitive emission sources in that section, followed by the next refinery 'section' and so on until fugitive emissions from the entire refinery have been quantified.

(ii) Tier 2 Leak/no-leak method

Screening using a portable monitoring device is required for this methodology. This method relies on a 'leak'/no leak' criterion. Take the following steps:

Step 1: Measure leaks from fugitive sources

A leak is typically defined and recorded if a screening value of > 10000 ppmv is returned by an appropriate calibrated monitoring instrument. Therefore, the emission factor you choose from table 2.4 will depend on whether the component tested returns a pass (a reading ≥ 10000 ppmv), or fail (a reading < 10000 ppmv).

Step 2: Estimate the VOC emission rate

Emissions are estimated for each of the equipment types listed using the following equation:

(6)   E = (FG x NG) + (FL x NL)

Where: E = VOC emission rate for the equipment type (kg/hr)

FG = Emission factor for sources with screening values ≥ 10000 ppmv (kg/hr/source)

NG = For the particular equipment type of concern, the number of sources with screening values ≥ 10000 ppmv

FL = Emission factor for sources with screening values < 10000 ppmv (kg/hr/source)

NL = For the particular equipment type of concern, the number of sources with screening values ≥ 10000 ppmv

Step 3: Note operational hours

For the specific equipment pieces screened, the annual number of operational hours needs to be estimated. This is required to derive annual emissions based on the hourly emission rates.

Step 4: Determine total VOC emissions

If all process fugitive sources have been screened, total VOC emissions from all sources can be determined by adding emission rates from each individual equipment component.

Table 2.4 presents the emission factors required to estimate emissions using the steps discussed above.

Table 2.4 Leak/no leak emission factors for process fugitives

Equipment type	Service	LEAK (>=10000 ppmv) emission factor	NO LEAK (<10000 ppmv) emission factor
Connectors/flanges	All	0.0375	0.00006
Valves	Gas	0.2626	0.0006
	Light liquid	0.0852	0.0017
	Heavy liquid	0.00023	0.00023
Pump seals	Light liquid	0.437	0.012
	Heavy liquid	0.3885	0.0135
Compressors	Gas	1.608	0.0894
Pressure relief valves	Gas	1.691	0.0447
Open ended lines	All	0.01195	0.0015

(iii) Tier 3 Correlation equations

You can only use this method if screening values (ppmv) are obtained through a fugitive leak screening programme. The required screening value (SV) data is collected using an appropriate calibrated monitoring instrument.

The following points are important to note when using this methodology:

- emission estimates are for 'total organic compounds' (TOC) and, as a consequence, a correction must be made to convert the estimates to NMVOCs (to exclude methane);
- emission factors are on a 'per source' basis
- each individual screening value must be entered into the correlation equation to predict emissions for an equipment piece. It is important **not** to average screening values and then enter the average value into the correlation equation to estimate emissions

Follow the steps to determine fugitive emissions using the correlation equation approach.

Step 1: Measure leaks from fugitive sources

For each piece of equipment tested, the recorded screening value will fall into one of three categories. The correct estimation methodology must be used for each category as follows:

1. For 'zero' readings (no emission detected), consult step 2 to estimate emissions.
2. For screening values between the lower and upper detection limits of the monitoring device, use step 3.
3. For values greater than the upper detection limit of the monitoring device (a 'pegged' emission reading), use step 4.

Step 2: Use of zero default factors

If no emissions are detected (below detection limit), then use the 'default zero emission rate' emission factors (see table 2.5), unless the lower detection limit of the monitoring device is >1 ppmv. In this case, use half the detection limit.

Step 3: Use of correlation factors to determine leak

If screening values (SV) are determined through testing (measured level is between the lower and upper detection limits), use the 'correlation equations' presented in table 2.5 to determine the leak from each relevant component tested.

Step 4: Use of pegged emission rate

If pegged screening values are detected, use the 'pegged emission rate' emission factors presented in table 2.5.

Step 5: Correct TOC readings to VOC estimate

Once emissions have been estimated from each source, convert the emissions from TOCs to VOCs. To do this, additional information is required on the approximate weight % of VOCs and TOCs in the process streams from which the emissions originate. This is then combined with the emission estimate for each equipment component as follows:

(7) $E_{VOC} = E_{TOC} \times (WP_{VOC} / WP_{TOC})$

Where: E_{VOC} = The VOC emission rate from the equipment (kg/hr)

E_{TOC} = The TOC emission rate from the equipment (kg/hr) calculated using the emission factors for correlations from table 2.5

WP_{VOC} = The concentration of VOC in the equipment in weight %

WP_{TOC} = The concentration of TOC in the equipment in weight %

If a number of equipment pieces can be grouped because they share the same process stream and thus have similar VOC/TOC ratios, TOC emissions can be added for this equipment group prior to performing Step 5, thereby reducing the number of calculations required.

Step 6: Note operational hours

For the specific equipment pieces tested, you should estimate the annual number of operational hours. This information is required to derive annual emissions based on the hourly emission rates.

Step 7: Determine total VOC emissions

If all process fugitive sources have been tested, total VOC emissions from all sources can be determined by adding the emissions from each individual equipment component.

Table 2.5 Correlation equations for process fugitive emissions

Equipment type	Default zero emission	Pegged emission rate (kg/hr)		Correlation equation (kg/hr)
		10,000 ppmv	100,000 ppmv	
Connector	7.5×10^{-6}	0.028	0.03	leak = 1.53×10^{-6} (SV)$^{0.735}$
Flange	3.1×10^{-7}	0.085	0.084	leak = 4.61×10^{-6} (SV)$^{0.703}$
Valve	7.8×10^{-6}	0.064	0.14	leak = 2.29×10^{-6} (SV)$^{0.746}$
Open-ended line	2.0×10^{-6}	0.03	0.079	leak = 2.20×10^{-6} (SV)$^{0.704}$
Pump seal	2.4×10^{-5}	0.074	0.16	leak = 5.03×10^{-5} (SV)$^{0.610}$
Other	4.0×10^{-6}	0.073	0.11	leak = 1.36×10^{-5} (SV)$^{0.589}$

The second method is a crude estimation which assumes that fugitive VOC emissions from plant and pipework represent 0.03wt% of the actual material processed in the refinery (including all thermally processed material but not product blend stocks).

Thus annual process fugitives = 0.0003 x annual refinery throughput (tonnes).

This method should only be used in the absence of available data on the number of valves, flanges, pump seals, and so forth. for the refinery under consideration.

Tank farm fugitives

For a detailed coverage of estimation of emissions from both floating and fixed roof tanks refer to section 2 of the VOC protocol.

Loading/unloading fugitives

For a detailed coverage of estimation of emissions from both controlled and uncontrolled loading operations refer to section 3 of the VOC protocol.

Drainage and effluent system fugitives

For a more detailed coverage of estimation of emissions from drains, separators, air flotation units and biological treatment facilities refer to section 1.9 of the VOC protocol.

2.3.6 Speciation of VOC emissions

The VOC speciation protocol provides a methodology for determining the fractional speciation of hydrocarbon emissions from oil refineries. The results are reported as the mass fraction of the annual hydrocarbon emissions providing individual annual mass release data for the following PI substances:

- benzene;
- toluene;
- xylene (all isomers);
- 1,3-butadiene;
- 1,2-dichloroethane;
- 1,1,2,2-tetrachloroethane.

3. Emissions to water

Emissions of substances to water can be either direct to controlled waters or indirect, following transfer to off-site effluent treatment plant. Guidance on what constitutes an emission or a transfer is contained in the general PI Guidance document.

3.1 Relevant pollutants

Water discharges from refinery processes can be contaminated by a variety of substances. The main ones and their main sources are illustrated in table 3.1. Use the table as a **guide** only, and check that there are no other pollutants emitted from the process.

Table 3.1 Main water pollutants generated by refineries

Main water pollutants	Main sources
Phenols	Distillation units, visbreaker, catalytic cracking, ballast water
Organic chemicals (TOC)	Distillation units, hydro treatment, visbreaker, catalytic cracking, hydro cracking, spent caustic, storage tanks water heel drainings
Benzene, toluene, xylene	Distillation units, hydro treatment, catalytic cracking, visbreaker, storage tanks water heel drainings

All of the following determinands in table 3.2 below are generally measured directly from the effluent discharge unless otherwise indicated.

Table 3.2 Determinands measured in refinery effluent discharges

Determinand measured in effluent discharge	Notes
Arsenic	
Benzene	API factor of 6µg/l applied to process water
Cadmium	
Chromium	
Copper	
Ethyl benzene	
Lead	
Mercury	
Nickel	
Nitrogen – total	
Phenols	
Total organic carbon	
Toluene	API factor of 1µg/l applied to process water
Xylene	API factor of 0.25µg/l applied to process water
Zinc	

3.2 Emission sources

More generally, emissions to water arise from the following sources:

• Process water, steam and wash water. These waters become contaminated with process fluids, dissolved gases and apart from oil, will also have taken up hydrogen sulphide, ammonia and phenols. The process water is treated in several steps before discharge to the environment.

• Cooling water, once-through or circulating systems. This stream is theoretically free of oil. However, leakage into once-through systems, even at low concentrations, can result in significant mass losses because of the large volume of water involved.

• Rainwater from process areas. This type of water has not been in contact with the process fluids, but it comes from rainfall on surfaces which are possibly oil-contaminated. This water is typically treated prior to discharge to the environment.

The resulting discharges of the above substances depend on the 'in process' preventative measures (good housekeeping, re-use) and the presence and technical standards of wastewater treatment facilities.

4. Off-site waste transfers

Wastes must be classified by the List of Waste Regulations (LOW) 6-digit code(s) and by the relevant Waste Framework Directive disposal or recovery code(s) (D&R).

There is no reporting threshold for hazardous wastes, which are indicated by an asterisk in the LOW. For all other LOW/D&R code combinations, a reporting threshold of 5 tonnes applies.

Any transfer of waste off-site to a third party is covered by the Duty of Care provisions of the Environmental Protection Act 1990. This includes the requirement to describe the waste and record the quantity. You need to use data generated in compliance with Duty of Care requirements to complete the PI return.

4.1 Relevant wastes

The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process. Oil refinery waste normally covers three categories of materials:

- Oily and non-oily sludges. These originate from various sources such as crude and product tank bottoms, desalters, alkylation units, boiler feed water preparation, biotreaters, the cleaning of heat exchanger bundles and equipment, oil spills and soil remediation. In terms of volume oily sludge's represent the largest waste category from refineries. Bio-sludge production only takes place if a refinery operates a biotreater.
- Other wastes are produced from many of the refining processes petroleum handling operations and wastewater treatment. Both hazardous and non-hazardous wastes are generated. Spent catalysts originate from the reformers, catalytic crackers, hydro crackers, hydrodesulphurisation and hydro treating units.
- Non-refining wastes, for instance domestic-type waste, demolition and construction wastes.

4.2 Transboundary shipments of hazardous waste

You must report the annual quantities of any transboundary hazardous waste shipments taking place to the PI.

Appendix A Normalisation of emission concentrations

In many cases, pollutant emission concentrations to air are reported as normalised concentrations, the actual measured emission concentration having been adjusted to a normalised temperature (273K), oxygen, pressure and/or water vapour concentration. In calculating mass emissions to air, it is important that either the actual release concentration is multiplied by the actual volumetric flowrate, or the normalised concentration is multiplied by the normalised volumetric flowrate

The following equations can be used to correct measured concentrations and flowrates for temperature, oxygen, pressure and water vapour content.

Concentrations

To correct for moisture concentration to dry (0% oxygen)

$$C_d = C_m \times (100/(100 - \%H_2 0))$$

Where: C_d is the dry concentration

C_m is the measured concentration
$\%H_2 0$ is the measured water vapour percentage

To correct the % oxygen to dry basis (if required – may already be measured dry)

$$O_2(dry) = O_2 m \times (100/(100 - \%H_2 0))$$

Where: $O_2(dry)$ is the dry oxygen percentage
$O_2 m$ is the measured oxygen percentage

To correct to normalised oxygen concentration

$$C_{corr} = C_d \times (20.9 - O_2 norm)/(20.9 - O_2(dry))$$

Where: C_{corr} is the corrected concentration for oxygen concentration
O_{2norm} is the stated normalised oxygen percentage

To correct for temperature

$$C_{normT} = C_{corr} \times ((273 + T_m)/273)$$

Where: C_{normT} is the normalised concentration for temperature
T_m is the measured temperature in degrees centigrade

To correct for pressure

$$C_{norm} = C_{normT} \times (101.3/P_m)$$

Where: C_{norm} is the normalised concentration
P_m is the measured pressure in kPa

Volumetric flowrates

To correct for moisture concentration to dry (0% oxygen)

$$Q_d = Q_m \times ((100 - \%H_2O))/100$$

Where: Q_d is the dry volumetric flowrate
Q_m is the measured volumetric flowrate
$\%H_2O$ is the measured water vapour percentage

To correct the % oxygen to dry basis (if required – may already be measured dry)

$$O_2(dry) = O_{2m} \times (100/(100 - \%H_2O))$$

Where: $O_2(dry)$ is the dry oxygen percentage
O_{2m} is the measured oxygen percentage

To correct to normalised oxygen concentration

$$Q_{corr} = Q_d \times (20.9 - O_2(dry))/(20.9 - O_{2norm})$$

Where: Q_{corr} is the corrected volumetric flowrate for oxygen concentration
O_{2norm} is the stated normalised oxygen percentage

To correct for temperature

$$Q_{normT} = Q_{corr} \times (273/(273 + T_m))$$

Where: Q_{normT} is the normalised volumetric flowrate for temperature
T_m is the measured temperature in degrees centigrade

To correct for pressure

$$C_{norm} = C_{normT} \times (P_m/101.3)$$

Where: C_{norm} is the normalised volumetric flowrate
P_m is the measured pressure in kPa

Appendix B UKPIA Pollution Inventory guidance for refineries

This guidance document was produced by UKPIA's Refinery Emissions Working Group and was developed through a review of relevant industry guidance; In particular, information from the US Environment Protection Agency's Airchief program[1], the American Petroleum Institute[2] and the Canadian Petroleum Products Institute.

This document is designed to be an aid for compiling Pollution Inventory (PI) submissions from petroleum refineries, and covers the major categories of emission sources; process emissions, combustion emissions, wastewater and so forth.

This table addresses all the pollutants which we consider potentially emitted from a typical oil refinery. For pollutants not contained within this table a return of 'not applicable' is in most cases to be expected, to indicate that this pollutant is not knowingly discharged by the site.

Emissions to air

Category 1: These emissions are almost certainly produced by refineries in volumes above the reporting threshold (i.e. returns are expected for these substances).

Determinand	Method[1]	Emission Source	Reference	Factors and guidance
Ammonia	C	FCCU Regen[2]	AP42	FCCU (uncontrolled): 0.155kg/1000L
	C	SRU to stack[3]	Industry experience	1 ppm in SRU flue gas
	C	SWS to flare	Industry experience	Flared SWS gas x 0.002
CO	C	Combustion	AP42 AP42	RFG: $1.34\ E^0$ kg/1000m^3 (0.082 lb/MBTU) RFO: $6.00\ E^{-1}$ kg/1000L (0.033 lb/MBTU)
	M	FCCU Regen	Onsite analyser	Measurement
CO_2	C	Site combustion and process	EU ETS	Guidance from EU Commission and API – as part of EUETS
Chlorine[5]	E	Reformers	Industry experience	BRT from catalyst regeneration[6]
Dinitrogen oxide[7] (nitrous oxide)	C	Combustion	EEA Corinair[8]	RFG: $2.16\ E^{-2}$ kg/1000m^3 (22 g/million grams)
			AP42 AP42 AP42	NG (uncontrolled): $3.52\ E^{-2}$ kg/1000m^3 NG (low-NOx- burner): $1.02\ E^{-2}$ kg/1000m^3 RFO: $1.32\ E^{-2}$ kg/1000L
	E	Process	Industry experienc	n/a for non-combustion plant
1,2 Di-chloroethane	M	Site	IP Speciation Protocol	Based on speciation surveys
Hydrogen sulphide[10]	C	SRU to flare	CPPI	0.5% of measured H$_2$S content in gas flared (98% combusted, 1.5% reacted with CO)
Methane[11]	C	Combustion[12]	AP42	RFO (industrial boiler): $1.20\ E^{-1}$ kg/1000L NG: $3.68\ E^{-2}$ kg/1000m^3
	C	Fugitive	Industry Experience	RFG flow x Me content x 0.03%
	C	FCCU regen	Industry Experience	$4.9\ E^{-3}$ kg/1000m^3 exhaust gas flow
	C	Incomplete flare	Industry	
		combustion	Experience	
NOx	C	Combustion	EA	Site specific factors agreed for combustion plant

	C/M	FCCU regen	EA	Site specific EA agreed factors or emission analyzer
	C	FCCU regen	AP42	2.04 E^{-1} kg/1000L cracker feed
	C	Flare	Industry experience	0.068 lbs/MMBtu gas flared (HHV)
	C	SWS to flare (stoichiometric conversion of combusted ammonia to NOx)	Industry experience	
Particulate Matter	C	Combustion	AP42 AP42	RFO: 1.1S + 0.39 kg/1000L (where S=%sulphur in fuel) RFG/NG: 1.22 E-1 kg/1000m3
	M	FCCU regen13	BS 3504: 1983	Continuous analyser or spot analysis
PM_{10}	C	Combustion	AP42	RFO: 86% of total particulate RFG/NG: 100% of total particulate
		FCCU	CPPI	PM10: 70% of total particulate
Sulphur oxides	C	Combustion	Industry experience	Fuel sulphur content x flow rate
	M	FCCU regen	EA	Continuous analyser or spot analysis
	C	FCCU regen	AP42	1.41 E^{0} kg/1000L of FCC feed
	C	SRU to stack	Industry experience	Based upon sulphur unit efficiency (% sulphur not removed)
	C	Flare	Industry experience	Flared gas sulphur content x flow rate
Toluene	M/C	Site/Fugitive	IP Speciation Protocol	In-house data based on site speciation protocol
NMVOC	M/C	Site/Fugitive	IP Estimation Protocol	Modified by measured data as it becomes available from LDAR programmes.
PAH's (Total)[15]	C	Combustion	API/WSPA	RFO: Sum of Borneff Six[15] : 1.39 E^{-6} kg/1000L NG: Sum of Borneff Six: 1.10 E^{-7} kg/1000m^3
	C	FCCU	CARB16	9.3 E^{-8} kg/1000L fresh feed (6.71 E^{-6} lbs/MBar)
Benzo(a)pyre ne	C	Combustion	AP42	RFO: 1.05 E^{-7} kg/1000L NG: 9.60 E^{-9} kg/1000m^3
	C	FCCU	CARB	4.0 E^{-9} kg/1000L fresh feed (2.60 E^{-7} lbs/MBar)
Benzene	M/C	Combustion	Industry experience	N/A for combustion plant
Nickel	C	Combustion	AP42	RFO: 1.01 E^{-2} kg/1000L
	C/M	FCCU	Industry experience	Cat Cracker particulates x 584 ppm
Vanadium	C	Combustion	AP42	RFO: 3.82 E^{-3} kg/1000L
	C/M	FCCU	Industry Experience	Cat cracker particulates x 1053 ppm
Zinc	C	Combustion	AP42	RFO: 3.49 E^{-3} kg/1000L

Category 2: These emissions may be produced by refineries but are generally below the reporting threshold (N.B. This position is yet to be fully re-evaluated against reporting thresholds introduced by the Pollution Inventory Schedule from 2006, Ref. 2, although the threshold values have been updated in the Appendix C tables). Further clarification may be required (further clarification may be required by reporting sites).

Determinand	Method[1]	Emission Source	Reference	Factors and guidance
Hydrogen Chloride	E	Reformer	Industry experience	Brt from catalyst regeneration[6]
	E	Combustion	Industry experience	brt[9]
Fluorine and inorganic compounds as HF	E	HF Alkylation	HF Detection Equipment	brt when undetected
HCFCs	C	Process Refrigerants	Industry experience	Estimate from fridge units' make-up rate
Tetrachloroethylene	E	Site/Fugitive	Industry experience	Industry consensus brt or n/a
Trichloroethylene	E	Site/Fugitive	Industry experience	Industry consensus brt or n/a
Arsenic	C	Combustion	AP42	RFO: $1.58\ E^{-4}$ kg/1000L
Mercury	C	Combustion	AP42	RFO: $1.36\ E^{-5}$ kg/1000L

Category 3: These substances are unlikely to be produced by refineries (no returns are expected for these substances)

Determinand	Method[1]	Emission source	Reference	Factors and guidance
Dioxins	E	Combustion	IP/ENTEC	Industry consensus[14] indicates refineries not a source of dioxin emissions – assume brt

Substances listed in the Pollution Inventory Schedule but not included in these tables are considered to be not applicable to refinery emissions and *n/a* should be entered in the PI return.

Notes:

1. In method column M=measurement, C=calculation, E=estimation (engineering judgement)
2. When CO boiler is present NH_3 emissions from FCCU are considered negligible (see CPPI 9.3.4)
3. Sour water stripper overhead gas to the sulphur recovery unit is included in this calculation
4. AP42: suggestion of formation in sulphur recovery unit but no mention of factors
5. Losses of free chlorine from cooling towers (used as biocide) considered negligible on basis that chlorine will be dissolved in water droplets
6. Chlorine used in regeneration of catalyst (reactivation of active sites)
7. It is anticipated that N_2O emissions will be included in future phases of the EUETS – estimation methodologies may therefore require adaptation when EU monitoring and reporting decisions are published
8. http://reports.eea.eu.int/EMEPCORINAIR3/en/Group%201.pdf
9. CPPI: "For process units which are subject to strict fugitive emission control, for example HF, the emissions may be considered negligible and assumed to be zero."
10. Not stated on PI list of pollutants, but reportable as "Other individual acid forming gases"
11. It is anticipated that methane emissions will be included in future phases of the EUETS – estimation methodologies may therefore require adaptation when EU monitoring and reporting decisions are published
12. Emission source is unburnt residuals in heater flue gases
13. CPPI "PM emissions from catalytic cracking units stem primarily from catalyst fines entrained in the exhaust gas from the catalyst regenerator."
14. Barnes, "UK Oil Refining and Atmospheric Emissions of Dioxins" (2004) and ENTEC, "Development of UKCost Curves for Abatement of Dioxin Emissions to Air" (2003)
15. http://www.arb.ca.gov/app/emsinv/catef_form.html
16. Industry Experience suggests that no metals are emitted from the combustion of natural gas or refinery fuel gas
17. Data collected by AEA 1999 based on analysis of FCCU catalyst fines

Releases to controlled waters and transfers in wastewater

Wherever possible data should be net of incoming cooling water quality, but where this would result in a negative return (removal of pollutants from incoming waters) make a brt return.

Category 1: These emissions are almost certainly produced by refineries in volumes above the reporting threshold (i.e. returns are expected for these substances)

Determinand	Method	Emissions Source	Reference	Factors and Guidance
Benzene	M / C	Effluent Treatment Facilities		Effluent quality measured data – brt if bio treated
	C	Process Water	API	6 µg/litre process water
Toluene	M / C	Effluent Treatment Facilities		Effluent quality data
	C	Process Water	API	1 µg/litre process water
Xylene	M / C	Effluent Treatment Facilities		Effluent quality data
	C	Process Water	API	0.25 µg/litre process water
Nitrogen	M	Effluent Treatment Facilities		Effluent quality data (14/17 since ammoniacal)
Phenols	M	Effluent Treatment Facilities		Effluent quality data (72/94 for "as C")
TOC	M	Effluent Treatment Facilities		Effluent quality data
Arsenic	M	Effluent Treatment Facilities		Effluent quality data
Cadmium	M	Effluent Treatment Facilities		Effluent quality data
Chromium	M	Effluent Treatment Facilities		Effluent quality data
Copper	M	Effluent Treatment Facilities		Effluent quality data
Lead	M	Effluent Treatment Facilities		Effluent quality data
Mercury	M	Effluent Treatment Facilities		Effluent quality data
Nickel	M	Effluent Treatment Facilities		Effluent quality data
Zinc	M	Effluent Treatment Facilities		Effluent quality data

Substances listed in the Pollution Inventory but not included in these tables are considered to be not applicable to refinery emissions so will be recorded as n/a in the PI return, unless site specific information is available.

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