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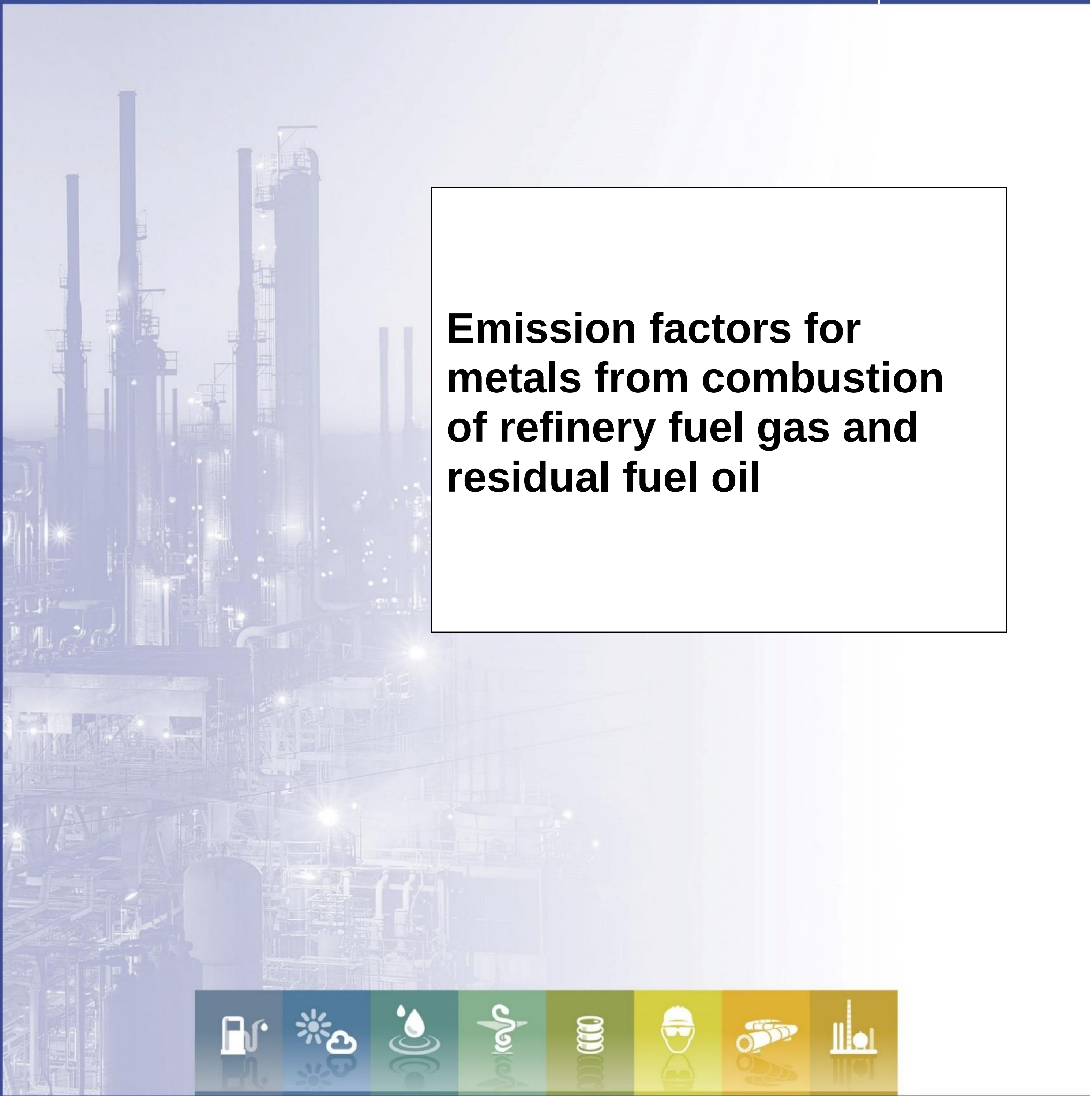
ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

report

report no. 9/16

Emission factors for metals from combustion of refinery fuel gas and residual fuel oil



Environmental science for the European refining industry

ISBN 978-2-87567-052-6

Emission factors for metals from combustion of refinery fuel gas and residual fuel oil

Prepared by the Concawe Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-69)

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ABSTRACT

This report provides emission factors for nine metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium and zinc) emitted to atmosphere during the combustion of refinery fuel gas in boilers and furnaces. It also provides a factor for nickel emissions from the combustion of refinery residual fuel oil. These factors are considered to provide more representative average emission estimates than those provided in the reference commonly used for these factors (API Publication 348) as substantially more data have been used in their derivation.

KEYWORDS

Air pollution, refineries, E-PRTR, emission factors, metal emissions, refinery fuel gas, residual fuel oil.

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.org).

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SUMMARY

Concawe provides guidance to refineries on the estimation of air pollutant emissions for European Pollutant Release and Transfer Register (E-PRTR) reporting in the form of regularly updated reports. The latest is report 3/15 *Air pollutant emission estimation methods for refineries – 2015 edition.*

During the update review process for this report, the quality of the emission factors for metals from refinery fuel gas (RFG) combustion was highlighted as being of concern. The factors provided had been derived by the API from a very limited number of tests and it had correspondingly rated them, using the US EPA assessment method, as either "below average" or "poor". At the time no better factors could be identified in the public domain. Concawe subsequently undertook this study to improve the quality of these emission factors.

To permit the derivation of more representative factors, Concawe member companies were asked to respond to a questionnaire and provide data obtained during emission measurements on the stacks of RFG-fired combustion units. The information requested were:

- details of the test method used (to assure the quality of the data);
- information on the RFG consumption during the test period; and
- RFG composition and/or net calorific value (to permit the calculation of factors in units of g/GJ).

From the data provided, new emission factors have been determined for arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc and selenium. Although the latter is not an E-PRTR listed pollutant, national authorities have to report annual estimated emissions from refinery sources.

The review process for Concawe report 3/15 also identified concerns about the emission factor for nickel from the combustion of refinery residual fuel oil (RFO) as it had been derived from a single source test. For this study Concawe member companies were asked for information on the nickel content of the fuel oils fired in their refineries. A new emission factor has been determined from these data, based on the assumption that all the nickel in the oil burnt is emitted to atmosphere.

The data sets used to derive the factors are significantly larger than those from which the original factors were calculated. For gas firing, data sets from between 23 and 42 sources have been used for the new factors whereas the original factors had been derived from only one or two source tests. For oil firing 48 compositional data values from 14 refineries have been used. The new factors, therefore, can be considered to provide more representative estimates of average emissions than those currently provided in Concawe report 3/15.

It is recommended that the factors for the E-PRTR metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) from RFG and for nickel from RFO combustion in refinery boilers and furnaces currently provided in Concawe report 3/15 are replaced when the guidance is next updated.

1. INTRODUCTION

This report provides emission factors for nine metals emitted during the combustion of refinery fuel gas (RFG) in boilers and furnaces. The factors are for total emissions i.e. in both the suspended particulate and vapour phases. The metals are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn) and selenium (Se).

It also provides an emission factor for nickel emitted during the combustion of refinery residual fuel oil (RFO).

Refineries must determine annual emissions data for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn under the terms of the European Pollutant Release and Transfer Register (E-PRTR) [12]. Selenium emissions data from refinery sources also have to be reported by national competent authorities as a requirement of the Convention on Long-range Transboundary Air Pollution (CLRTAP) [13].

There is currently one source of emission factors for metals from RFG combustion in refinery sources; API Publication 348 *Air Toxics Emission Factors for Combustion Sources Using Petroleum-Based Fuels* [1]. This publication is referenced in Concawe report 3/15 *Air pollutant emission estimation methods for refineries* [4] and the EMEP/EEA *Emissions inventory guidebook* [6]. Factors for gas firing in refineries are provided elsewhere (e.g. [11]) but these have been derived from emission measurements from natural gas rather than from refinery fuel gas combustion.

API Publication 348 also provides the emission factor for nickel from RFO combustion given in both the Concawe and EMEP/EEA publications.

During the review process for the updating of the Concawe report, the quality of the metal emission factors for RFG combustion was highlighted as being of concern. The US EPA uses a rating to provide an overall assessment of the quality of a factor, e.g. rating “D” means below average and “E” means poor. The assessment [2] by the API of the factors for RFG combustion in its Publication 348 is “D” for Cr, Cu, Hg, Ni and Pb and “E” for As, Cd, Se and Zn. A major factor in these poor ratings was the limited number of test data. Eight of the nine factors were derived from only two source tests (typically comprising three test runs per source test), with data from just one test set being used for the mercury factor. Since the issue of Publication 348 the API has recommended [2] the collection of additional field data for gas-fired boilers to develop better quality emission factors for metals.

Similarly the data from only one source test were used to derive the emission factor for nickel from RFO combustion. Again, the API has recommended the collection of more test data for fuel oil-fired boilers to improve the quality of the factor.

At the end of 2011 Concawe undertook a limited number of stack measurements on both an RFG-fired heater and a dual-fired (RFO and RFG) boiler at a European refinery to provide its own assessment of these factors for metal emissions. The measured mass emission data were compared to emission estimates calculated using the factors in the edition of the Concawe emission estimation guidance published at that time (Report 1/09 [3]) and since replicated in Report 3/15.

The test data from the RFG-fired unit indicated that there were significant differences between the measured and estimated emissions for cadmium, chromium, mercury and nickel. The test data from the dual-fired boiler indicated that the factor for nickel from oil combustion over-estimated emissions.

In 2013, to permit the derivation of better quality metal emission factors from fuel gas firing Concawe member companies were asked to provide, via a questionnaire, existing stack measurement campaign data from RFG-fired boilers and heaters. In response to this request a much larger set of source test data was obtained than originally used by the API to derive the factors in Publication 348, permitting the determination of the new factors provided in this report.

The conclusion that the published emission factor for nickel over-estimated emissions from oil combustion had also been reached by the UK Energy Institute [8] from measurements undertaken at three refineries. In that study very close agreement was obtained between measured emissions and those estimated using the nickel content of the fuel, assuming all of the nickel was emitted to atmosphere. Correspondingly, Concawe report 3/15 provides not only an emission factor but a recommendation that, where available, the nickel content of the fuel oil should be used to estimate emissions. To improve the quality of the default emission factor Concawe member companies were asked to provide data on the nickel content of the fuel oils fired in their refineries. The new emission factor in this report has been determined from those data.

In this report all heating values quoted are net calorific values (NCVs) and all emission factors require the use of the corresponding fuel NCV.

2. DATA GATHERING

2.1. REFINERY FUEL GAS

The Concawe questionnaire was designed to gather information on metal emissions from stack testing of units firing refinery fuel gas. Emissions data were requested either in terms of the measured concentration (mg/Nm^3, dry at 3% O_2) or as a derived mass emission (g/h). Where concentration data were provided, these were requested as either separate values for the suspended particulate and vapour phases (where these had been measured separately) or as a total emissions value.

The questionnaire established either if the pollutant was present at or above the minimum detection limit (MDL) of the test method (a "detect" value), or was below the detection limit (a "non-detect" value) in which cases the MDL value had been assigned to that data point.

Information on the test method used was requested to establish if the sampling and measurement had been undertaken according to a recognised norm and thus provide assurance on the quality of the measured data.

In order to be able to derive emission factors in units of g/GJ, information on the RFG consumption during the test period and its composition and/or net calorific value (NCV) were requested.

Questionnaires providing data on individual stack measurement campaigns were received from seven refineries. Stacks included those connected directly to combustion units (furnaces or boilers) or from combined ducts for units solely firing RFG. Some data were also received on multi-fuel (gas and oil) and natural gas combustion and also data on emissions from a gas turbine, but these have not been included in the analysis.

2.2. FUEL OIL

Data on the nickel content (in terms of mg/kg) in the residual fuel oils used in European refineries, obtained from compositional analyses using standard methods (e.g. [7]), were requested from Concawe member companies. RFO compositional data were received from fourteen refineries operated by six companies. The major factors influencing the nickel content of RFO are the concentration of nickel in the crude oil processed and the refinery process configuration. The refineries were also asked to provide the date on which the samples were taken. These were used to ensure that each point of the data set used to derive the emission factor represented a different batch of crude oil.

3. DERIVATION OF EMISSION FACTORS

3.1. REFINERY FUEL GAS

The following methodology was followed to derive emission factors for each metal.

3.1.1. Test method used

Information had been requested on the questionnaire about the test method used to perform the measurements. Where such information was not provided, the quality of the sampling and measurement method used was considered uncertain and the data sets were rejected. In addition, data were only included in the analysis if the test method applied was one of the following:

- EN 14385. Stationary source emissions. Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V.

- EN 13211. Stationary source emissions. Manual method of determination of the concentration of total mercury.

- US EPA Method 29 – Determination of metal emissions from stationary sources.

3.1.2. Determination of individual test emission factors

In the questionnaire responses, the data for metal emissions were provided either as a concentration (mg/Nm^3 – at normal conditions of 3% O_2 and dry gas) or as a mass emission (g/h), or both. If both results were given, the g/h data were used in the analyses undertaken for this report.

Where multiple tests had been undertaken on a stack, the measurement data were averaged to provide a single test data point for that source.

In order to derive an emissions factor for each test data point (EF_{test}) in g/GJ_{ncv}, the following equations were used.

3.1.2.1. Mass emission data supplied

If data in g/h were provided, the following equation was used:

EF_{test} = emissions in g/h / (NCV of fuel x quantity of gas fired)

If the fuel composition but not the NCV was provided, the NCV was derived from the compositional analysis. If neither NCV data nor fuel composition were given in the dataset, a default value for the NCV of RFG of 48.07 MJ/kg provided in the Refinery BREF [5], Section 9.6.2, Annex B.2.3 was used.

3.1.2.2. Concentration data supplied

For data provided in terms of mg/Nm^3, the methodology given in the Refinery BREF, Section 9.6 (the so-called 'Bubble approach' methodology) was used to estimate the flue gas volume.

The following default values provided in the methodology were used:

- NCV for the fuel as fuel oil equivalent (FOE) = 41.868 MJ/kg

- Flue gas factor for RFG = 11.34 Nm^3/kg FOE

The following equations were used to derive emissions factors for each test data point:

Flue gas flow = fuel flow x flue gas factor
Mass of FOE (kg) = mass of fuel x NCV_{fuel} / NCV_{FOE}
EF_{test} = concentration in mg/Nm^3 x flue gas factor / NCV_{FOE}

3.1.3. Treatment of data points below detection limit (BDL) value

The US EPA recommended procedure ([9], Appendix B) for the treatment of data below the minimum detection limit (MDL) was used in the development of emission factors. When the data set contained a mix of values that were above and below the MDL, the test values identified as BDL were replaced with values equivalent to half of their MDL. If a replacement value exceeded the highest data value that was measured above the MDL, the replacement value was not used in the calculation of an average emissions factor.

3.1.4. Procedure for identifying statistical outliers

The US EPA recommended procedure ([9], Appendix C) for identifying statistical outliers was used. This assumes that all emissions test data values follow log normal distributions. Every test value in the data set was therefore log transformed prior to conducting outlier tests.

If there were three to 24 test values in the data set, the Dixon Q test was used to determine outliers. If there were 25 or more test values for analysis, the Rosner test was used to identify outliers. All outlier tests were performed using a 95% confidence level. If any outliers were identified they were removed from the data set.

The ProCAL statistical software package available on the US EPA Site Characterization and Monitoring Technical Support Center website [10] was used for outlier identification.

3.1.5. Calculation of emission factors

The mean and median values of each set of individual test emission factors (EF_{test}) was calculated. The overall emission factor was determined using the protocol in Concawe report 3/15 [4], section 5.3. This states that the factor is the mean value of the data set, except where the latter is excessively skewed and the mean value is greater than ten times the median value, when the latter is used.

3.2. FUEL OIL

3.2.1. Calculation of Ni emission factor

The value of the nickel content in each of the analysed oil samples was provided in terms of mg/kg.

To determine individual emission factors for each sample (EF_{sample}) in g/GJ, the nickel concentration value was divided by the net calorific value (NCV) in MJ/kg. For those samples where the NCV had not been supplied, a default value for the NCV of RFO of 40.0 MJ/kg provided in the Refinery BREF [5], Table 3.54, was used.

Where a refinery provided the analytical data for more than one RFO sample, the frequency of sampling was checked. When more than one sample had been taken within a four week period the average value of EF_{sample} was derived for those samples. This procedure was applied to ensure that only one value of EF_{sample} was derived for any batch of crude oil processed. Following this procedure, the number of values of EF_{sample} in the database totalled 48.

The set of individual sample emission factor values (EF_{sample}) was tested to determine any statistical outliers using the procedure described in **Section 3.1.4.** The overall emission factor was determined using the protocol described in **Section 3.1.5.**

4. SUMMARY OF THE RESULTS

4.1. DERIVED EMISSION FACTORS

4.1.1. Refinery fuel gas

Emission factors were derived following the methodology outlined in **Section 3.1**. The individual emission factors calculated for each source for each pollutant are given in **Appendix 1**, along with the results of the statistical analyses. In all cases the mean value is less than ten times the median value. The mean values, therefore, provide the emission factors for all metals.

Table 1 provides the emission factors derived in this report and compares them to those provided in API Publication 348 and Concawe report 3/15.

The emission factors for metals from RFG combustion provided in Concawe report 3/15 are the same as in API Publication 348, except for zinc. The data used to derive the factor for zinc in API Publication 348 are significantly skewed with the value of the mean being more than ten times greater than the median. Concawe report 3/15, therefore, provides the median value as the emission factor for zinc. The EMEP/EEA Guidebook provides the same emission factors as Concawe report 3/15, except for selenium which is not included in the latter as it is not an E-PRTR pollutant.

Table 1 Comparison of the emissions factors for metals from gas firing

Pollutant	EF derived in this report g/GJ	References		EF in references g/GJ	Ratio of derived EF to that in references
		API Publication 348	Concawe report 3/15		
As	3.52E-04	X	X	3.43E-04	1.03
Cd	2.19E-03	X	X	7.12E-04	3.08
Cr	6.69E-03	X	X	2.74E-03	2.44
Cu	3.29E-03	X	X	2.22E-03	1.48
Pb	1.61E-03	X	X	1.79E-03	0.9
Hg	3.72E-04	X	X	8.60E-05	4.32
Ni	7.37E-03	X	X	3.60E-03	2.05
Se	1.56E-03	X		3.07E-04	3.72
Zn	1.70E-02	X		6.83E-01	0.025
			X	2.55E-02	0.67

The derived emission factors for As and Pb are in good agreement with those provided in Concawe report 3/15, whilst those for Cu, Ni and Zn are in reasonable agreement (i.e. approximately within a factor of two). The factor for Zn in API Publication 348 is heavily biased by the skewed nature of the data set used by the API possibly explaining the large difference between it and the derived factor. Those for Cd, Cr, Hg and Se are in less agreement, being up to four times higher than the factors in Concawe report 3/15 and/or API Publication 348.

Table 2 provides the number of source tests used to derive the emission factors in API Publication 348 and in this report.

Table 2 Number of source tests used to derive the emissions factors for metals from RFG combustion

Pollutant	Number of source tests	
	API Publication 348	**This report**
As	2	33
Cd	2	33
Cr	2	35
Cu	2	30
Pb	2	42
Hg	1	23
Ni	2	35
Se	2	25
Zn	2	29

This shows that the data sets used to derive the factors in this report are significantly larger than those from which the factors in API Publication 348 were calculated. The new factors, therefore, can be considered to provide more representative estimates of average emissions.

4.1.2. Residual fuel oil (nickel)

The emission factor for nickel was derived following the methodology outlined in **Section 3.2**. The individual sample emission factors calculated from the RFO compositional data are given in **Appendix 2.**

Table 3 provides the emission factor derived in this report and compares it to that provided in API Publication 348 and Concawe report 3/15.

Table 3 Comparison of the emissions factors for nickel from residual fuel oil firing

EF derived in this report g/GJ	EF in API 348 and Concawe 3/15 g/GJ	Ratio of derived EF to that in references
7.73E-01	1.03E-00	0.75

The emission factor was derived from 48 values of the nickel content of RFO assuming that all of the metal is emitted to atmosphere. This provides a slightly conservatively high emission factor as it assumes no production of metallic based eutectics (slag) within the combustion unit. The factor is in reasonable agreement (i.e.

within a factor of two) with the factor provided in API Publication 348 which was derived from only one set of stack measurements.

4.2. RECOMMENDATIONS

It is recommended that the factors for the E-PRTR metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) from RFG combustion in boilers and furnaces given in **Table 4** are used by refineries to estimate emissions for E-PRTR reporting purposes.

Table 4 Recommended emissions factors for metals from refinery gas and oil firing

Pollutant	Refinery Fuel[1]	Emission Factor g/GJ[2]
Arsenic	RFG	3.52E-04
Cadmium	RFG	2.19E-03
Chromium	RFG	6.69E-03
Copper	RFG	3.29E-03
Lead	RFG	1.61E-03
Mercury	RFG	3.72E-04
Nickel	RFG	7.37E-03
	RFO	7.73E-01
Selenium	RFG	1.56E-03
Zinc	RFG	1.70E-02

Table notes:

1. RFG = refinery fuel gas. RFO = refinery residual fuel oil
2. In this report all heating values quoted are net calorific values (NCVs) and all emission factors require the use of the corresponding fuel NCV.

Due to the wide range of nickel contents of fuel oils burnt in refineries the recommendation provided in Concawe report 3/15 to use, where available, the nickel content of the fuel oil to estimate emissions is affirmed. Where a default emission factor for nickel from RFO combustion is required that provided in **Table 4** should be used.

The emission factors given in **Table 4** should replace those currently provided in Concawe report 3/15 when it is next revised.

5. REFERENCES

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APPENDIX 1 DATA AND STATISTICAL RESULTS – REFINERY FUEL GAS

This Appendix provides the data sets used to calculate the emission factors for the nine metals and recommended emission factors derived from those data sets. The data sets comprise the individual emission factors derived for each stack test (EF_{test}). The data sets are tabulated in decreasing size order. The sets do not contain any BDL values or outliers removed from the analysis under the procedures outlined in **Section 3.1.3** and **Section 3.1.4**. Where these procedures have been applied, the number of data points removed from the original data set and their values are given in the tables of data set properties.

The data sets indicate the below detection limit (BDL) data points but the table provides their replacement values of half of the minimum detection limit (MDL) values (see **Section 3.1.3**).

The tables of data set properties include the number of data points, mean and median values and the values of some statistical parameters.

A1.1 Arsenic

Table A1.1 Emission factors calculated for each test (EF_{test})

EF_{test} (g/GJ)		EF_{test} (g/GJ)		EF_{test} (g/GJ)	
8.76E-04		4.02E-04		1.88E-04	BDL
7.74E-04		3.96E-04	BDL	1.67E-04	
7.45E-04		3.51E-04		1.42E-04	BDL
7.43E-04		3.38E-04		1.35E-04	
7.12E-04	BDL	3.29E-04		1.32E-04	BDL
6.04E-04	BDL	2.97E-04		1.07E-04	BDL
5.74E-04		2.56E-04		9.45E-05	
5.61E-04		2.56E-04		4.24E-05	BDL
5.55E-04		2.55E-04	BDL	4.19E-05	BDL
5.51E-04		2.51E-04		3.00E-05	BDL
4.58E-04		2.43E-04		2.33E-05	BDL

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.2 Properties of data set

Number of sources	33
Mean value	3.52E-04
Median value	2.97E-04
Mean to median ratio	1.2
Variance	6.02E-08
Standard deviation	2.45E-04
Coefficient of variation	0.7
Number of “non-detects” [1]	12
Detect ratio [2]	0.64
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 3.52E-04 g/GJ

A1.2 Cadmium

Table A1.3 Emission factors calculated for each test (EF_{test})

EF test (g/GJ)		EF test (g/GJ)		EF test (g/GJ)	
2.28E-02		6.18E-04	BDL	2.16E-04	
1.49E-02		3.96E-04	BDL	2.07E-04	BDL
7.85E-03		3.87E-04	BDL	1.35E-04	
6.93E-03		3.54E-04	BDL	1.31E-04	
4.11E-03		3.54E-04		1.16E-04	BDL
3.10E-03		2.92E-04		1.16E-04	BDL
2.82E-03		2.70E-04		8.94E-05	BDL
1.48E-03		2.62E-04	BDL	4.41E-05	
1.48E-03		2.43E-04		1.70E-05	BDL
1.38E-03		2.38E-04	BDL	1.69E-05	BDL
6.81E-04		2.36E-04	BDL	9.32E-06	BDL

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.4 Properties of data set

Number of sources	33
Mean value	2.19E-03
Median value	2.92E-04
Mean to median ratio	7.5
Variance	2.30E-05
Standard deviation	4.80E-03
Coefficient of variation	2.19
Number of “non-detects” [1]	14
Detect ratio [2]	0.58
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 2.19E-03 g/GJ

A1.3 Chromium

Table A1.5 Emission factors calculated for each test (EF_{test})

EF test (g/GJ)		EF test (g/GJ)		EF test (g/GJ)	
1.15E-01		2.54E-03	BDL	9.51E-04	
1.79E-02		2.41E-03	BDL	9.34E-04	BDL
1.34E-02	BDL	2.02E-03		9.10E-04	
1.29E-02		1.92E-03	BDL	7.08E-04	BDL
1.19E-02		1.74E-03		5.26E-04	
9.20E-03		1.70E-03		4.09E-04	
7.91E-03		1.42E-03		3.78E-04	
6.92E-03		1.25E-03		2.97E-04	
4.97E-03		1.13E-03		2.71E-04	BDL
3.65E-03		1.12E-03	BDL	2.70E-04	
3.09E-03		1.07E-03		1.49E-04	BDL
2.62E-03		1.02E-03	BDL		

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.6 Properties of data set

Number of sources	35
Mean value	6.69E-03
Median value	1.70E-03
Mean to median ratio	3.9
Variance	3.73E-04
Standard deviation	1.93E-02
Coefficient of variation	2.88
Number of “non-detects” [1]	10
Detect ratio [2]	0.71
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 6.69E-03 g/GJ

A1.4 Copper

Table A1.7 Emission factors calculated for each test (EF_{test})

EF test (g/GJ)		EF test (g/GJ)		EF test (g/GJ)	
1.04E-02		4.16E-03	BDL	1.76E-03	
8.34E-03		3.99E-03		1.70E-03	BDL
6.13E-03		3.82E-03		1.34E-03	
6.00E-03		3.49E-03		1.27E-03	BDL
5.98E-03		2.84E-03		1.14E-03	
5.63E-03		2.06E-03		1.03E-03	
5.17E-03		2.04E-03		3.24E-04	
4.89E-03		1.98E-03	BDL	2.70E-04	
4.67E-03		1.86E-03	BDL	1.68E-04	BDL
4.30E-03		1.84E-03	BDL	9.32E-05	BDL

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.8 Properties of data set

Number of sources	30
Mean value	3.29E-03
Median value	2.45E-03
Mean to median ratio	1.34
Variance	6.34E-06
Standard deviation	2.52E-03
Coefficient of variation	0.766
Number of “non-detects” [1]	8
Detect ratio [2]	0.73
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 3.29E-03 g/GJ

A1.5 Lead

Table A1.9 Emission factors calculated for each test (EF_{test})

EF test (g/GJ)		EF test (g/GJ)		EF test (g/GJ)	
8.34E-03		1.93E-03		8.97E-04	
3.70E-03		1.74E-03		5.13E-04	
3.65E-03		1.68E-03	BDL	4.59E-04	
3.59E-03		1.64E-03	BDL	4.16E-04	
3.47E-03		1.53E-03		4.05E-04	
3.40E-03		1.21E-03		3.94E-04	
2.99E-03		1.11E-03	BDL	3.90E-04	BDL
2.77E-03		1.08E-03		3.81E-04	BDL
2.63E-03		1.03E-03		2.98E-04	
2.56E-03		1.01E-03		1.76E-04	BDL
2.07E-03		9.93E-04		1.62E-04	
2.03E-03		9.91E-04		1.54E-04	
2.00E-03		9.70E-04		8.76E-05	
1.98E-03		8.98E-04		4.24E-05	BDL

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.10 Properties of data set

Number of sources	42
Mean value	1.61E-03
Median value	1.09E-03
Mean to median ratio	1.47
Variance	2.36E-06
Standard deviation	1.54E-03
Coefficient of variation	0.952
Number of “non-detects” [1]	7
Detect ratio [2]	0.83
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 1.61E-03 g/GJ

A1.6 Mercury

TableA1.11 Emission factors calculated for each test (EF_{test})

EF_{test} (g/GJ)		EF_{test} (g/GJ)		EF_{test} (g/GJ)	
1.77E-03		3.47E-04	BDL	1.59E-04	BDL
9.91E-04		3.24E-04		1.40E-04	BDL
9.27E-04	BDL	3.03E-04	BDL	1.40E-04	BDL
6.04E-04	BDL	2.16E-04	BDL	1.38E-04	BDL
4.87E-04	BDL	2.10E-04		1.70E-05	BDL
4.16E-04		2.06E-04	BDL	1.68E-05	BDL
3.91E-04		1.89E-04	BDL	9.00E-06	BDL
3.87E-04	BDL	1.62E-04			

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.12 Properties of data set

Number of sources	23
Mean value	3.72E-04
Median value	2.16E-04
Mean to median ratio	1.72
Variance	1.58E-07
Standard deviation	3.97E-04
Coefficient of variation	1.068
Number of “non-detects” [1]	16
Detect ratio [2]	0.3
“Non-detects” removed	0
Outliers removed	0

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 3.72E-04 g/GJ

A1.7 Nickel

Table A1.13 Emission factors calculated for each test (EF_{test}) (after removal of one outlier)

EF_{test} (g/GJ)		EF_{test} (g/GJ)		EF_{test} (g/GJ)	
8.27E-02		2.97E-03		1.41E-03	
6.81E-02		2.86E-03		1.25E-03	BDL
1.35E-02	BDL	2.85E-03		1.20E-03	
9.71E-03	BDL	2.75E-03		1.12E-03	
9.40E-03		2.69E-03		1.03E-03	BDL
8.65E-03		2.24E-03		8.73E-04	BDL
7.23E-03		2.13E-03		6.99E-04	
6.91E-03		2.02E-03		5.67E-04	
4.38E-03	BDL	1.94E-03		4.79E-04	
3.90E-03		1.89E-03		1.68E-04	BDL
3.65E-03		1.78E-03		1.49E-04	BDL
3.21E-03		1.46E-03			

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.14 Properties of data set

Number of sources	35
Mean value	7.37E-03
Median value	2.24E-03
Mean to median ratio	3.29
Variance	3.01E-04
Standard deviation	0.0174
Coefficient of variation	2.356
Number of “non-detects” [1]	9
Detect ratio [2]	0.77
“Non-detects” removed	0
Outliers removed	1
Value of outlier	6.41E-01

Table notes:
1. “Non-detects” are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of test values

Derived emission factor = 7.37E-03 g/GJ

A1.8 Selenium

Table A1.15 Emission factors calculated for each test (EF_{test}) (after removal of one high "non-detect")

EF test (g/GJ)		EF test (g/GJ)		EF test (g/GJ)	
4.15E-03		2.24E-03	BDL	6.18E-04	BDL
3.67E-03	BDL	1.49E-03	BDL	2.97E-04	
3.28E-03		1.36E-03	BDL	2.38E-04	BDL
2.95E-03	BDL	1.32E-03	BDL	2.16E-04	
2.66E-03		9.67E-04	BDL	1.89E-04	
2.62E-03	BDL	9.21E-04	BDL	1.55E-04	
2.43E-03	BDL	7.95E-04		1.35E-04	
2.43E-03	BDL	7.83E-04			
2.32E-03	BDL	7.74E-04			

Table note:
BDL means measurement value was below minimum detection limit.
Data point in table = 0.5 x minimum detection limit value.

Table A1.16 Properties of data set

Number of sources	25
Mean value	1.56E-03
Median value	1.32E-03
Mean to median ratio	1.18
Variance	1.48E-06
Standard deviation	0.00122
Coefficient of variation	0.78
Number of "non-detects" [1]	14
Detect ratio [2]	0.44
"Non-detects" removed	1
Value of "non-detect" removed	1.01E-02
Outliers removed	0

Table notes:
1. "Non-detects" are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of data points

Derived emission factor = 1.56E-03 g/GJ

A1.9 Zinc

Table A1. 17 Emission factors calculated for each test (EF_{test})

EF test (g/GJ)	EF test (g/GJ)	EF test (g/GJ)
4.94E-02	2.00E-02	5.90E-03
3.79E-02	1.98E-02	5.90E-03
3.78E-02	1.66E-02	4.10E-03
3.66E-02	1.60E-02	3.60E-03
3.36E-02	1.24E-02	3.50E-03
3.19E-02	9.90E-03	3.20E-03
3.01E-02	9.60E-03	3.00E-03
2.57E-02	9.20E-03	1.10E-03
2.48E-02	9.00E-03	7.00E-04
2.28E-02	7.70E-03	

Table A1.18 Properties of data set

Number of sources	29
Mean value	1.70E-02
Median value	1.24E-02
Mean to median ratio	1.37
Variance	1.85E-04
Standard deviation	0.0136
Coefficient of variation	0.802
Number of "non-detects" [1]	0
Detect ratio [2]	1.0
"Non-detects" removed	0
Outliers removed	0

Table notes:
1. "Non-detects" are data points with value < minimum detection limit (MDL) value
2. Detect ratio = number of data points ≥ MDL value / total number of data points

Derived emission factor = 1.70E-02 g/GJ

APPENDIX 2 DATA AND STATISTICAL RESULTS – RESIDUAL FUEL OIL

Table A2.1 provides the data set used to calculate the overall emission factor for nickel. The data set comprises the individual emission factors (EF_{sample}) derived from sample analysis data. **Table A2.2** provides the results of the statistical analysis of the data set.

A 2.1 Nickel

Table A2.1 Emission factors calculated from sample analysis data (EF_{sample})

EF_{sample} (g/GJ)	EF_{sample} (g/GJ)	EF_{sample} (g/GJ)	EF_{sample} (g/GJ)
1.31E-01	4.00E-01	6.45E-01	1.06E+00
2.68E-01	4.71E-01	6.80E-01	1.09E+00
2.85E-01	4.75E-01	6.99E-01	1.15E+00
2.97E-01	5.00E-01	7.14E-01	1.25E+00
3.08E-01	5.13E-01	7.88E-01	1.30E+00
3.10E-01	5.13E-01	8.38E-01	1.36E+00
3.28E-01	5.15E-01	8.50E-01	1.37E+00
3.35E-01	5.38E-01	8.50E-01	1.46E+00
3.70E-01	5.73E-01	9.60E-01	1.51E+00
3.73E-01	5.75E-01	9.83E-01	1.53E+00
3.95E-01	6.00E-01	1.04E+00	1.86E+00
4.00E-01	6.25E-01	1.06E+00	1.98E+00

Table A2.2 Properties of data set

Number of data points	48
Mean value	0.773
Median value	0.653
Mean to median ratio	1.22
Variance	0.199
Standard deviation	0.446
Coefficient of variation	0.577
Outliers removed	0

Derived emission factor = 7.73E-01 g/GJ

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ISBN 978-2-87567-052-6
9 782875 670526 >