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# 1 Overview

Zinc is produced from various primary and secondary raw materials. The primary processes use sulphidic and oxidic concentrates, while in secondary processes recycled oxidised and metallic products mostly from other metallurgical operations are employed. This chapter includes information on atmospheric emissions during the production of secondary zinc. In practice, a clear distinction of primary and secondary zinc production is often difficult because many smelters use both primary and secondary raw materials.

The majority of the EU production facilities apply a hydrometallurgical production route, which is also called RLE (roast-leach-electro win) with a total production capacity of 2.1 million tonnes in 2007. RLE is a continuous process. Secondary or recycled zinc accounts for approximately 30 % of the yearly zinc consumption in Europe. Roughly 50 % of this secondary zinc is recycled within the industry (European Commission, 2014).

Secondary production is increasing in various regions of the world. This increase is as high as 5 % per year in eastern Europe.

The activities relevant for primary zinc production are:

- transport and storage of zinc ores;
- concentration of zinc ores;
- oxidation of zinc concentrates with air (roasting process);
- production of zinc by the electrochemical or the thermal process;
- after-treatment of zinc.

This chapter covers only the process emissions from these activities. Combustion emissions from zinc production are treated in chapter 1.A.2.b.

The most important pollutants emitted from these processes are sulphur dioxide, heavy metals (particularly zinc) and dust.

# 2 Description of sources

## 2.1 Process description

Primary zinc is produced from ores which contain 85% zinc sulphide (by weight) and 8–10% iron sulphide, with the total zinc concentration about 50%. The ores also contain metal sulphides such as lead, cobalt, copper, silver, cadmium and arsenic sulphide.

The ores are oxidised with air giving zinc oxide, sulphur oxide and zinc ferro-oxide. Chlorine and fluorine are removed from the combustion gas and the sulphur oxide is converted catalytically into sulphuric acid.

A secondary zinc smelter is defined as any plant or factory in which zinc-bearing scrap or zinc-bearing materials, other than zinc-bearing concentrates (ores) derived from a mining operation, are processed (Barbour *et al.*, 1978). In practice, primary smelters often also use zinc scrap or recycled dust as input material.

Zinc recovery involves three general operations performed on scrap, namely pre-treatment, melting, and refining. Scrap metal is delivered to the secondary zinc processor as ingots, rejected castings, flashing and other mixed metal scrap containing zinc (US EPA, 1995).

Scrap pre-treatment includes sorting, cleaning, crushing and screening, sweating and leaching. In the sorting operation, zinc scrap is manually separated according to zinc content and any subsequent processing requirements. Cleaning removes foreign materials to improve product quality and recovery efficiency. Crushing facilitates the ability to separate the zinc from the contaminants. Screening and pneumatic classification concentrates the zinc metal for further processing. Leaching with sodium carbonate solution converts dross and skimmings to zinc oxide, which can be reduced to zinc metal (US EPA, 1995).

Pure zinc scrap is melted in kettle, crucible, reverberatory, and electric induction furnaces. Flux is used in these furnaces to trap impurities from the molten zinc. Facilitated by agitation, flux and impurities float to the surface of the melt as dross, and are skimmed from the surface. The remaining molten zinc may be poured into moulds or transferred to the refining operation in a molten state (US EPA, 1995).

Refining processes remove further impurities from clean zinc alloy scrap and from zinc vaporised during the melt phase in retort furnaces. Molten zinc is heated until it vaporises. Zinc vapour is condensed and recovered in several forms, depending upon temperature, recovery time, absence or presence of oxygen, and equipment used during zinc vapour condensation. Final products from refining processes include zinc ingots, zinc dust, zinc oxide, and zinc alloys (US EPA, 1995).

Generally speaking, the processes used for the recycling of secondary zinc can be distinguished by the kind of raw materials employed (Rentz *et al.*, 1996):

Very poor oxidic residues and oxidic dusts, e.g. from the steel industry, are treated in rotary furnaces (Waelz furnaces), producing metal oxides in a more concentrated form. These concentrated oxides (Waelz oxides) are processed together with oxidic ores in primary thermal zinc smelters, in particular Imperial smelting furnaces, which are in use for combined lead and zinc production. In this case, a clear discrimination between primary and secondary zinc production as well as between zinc and lead production is difficult.

Metallic products prior to smelting are comminuted and sieved to separate metal grains from the oxides. Afterwards the metallic products are melted in melting furnaces, mainly of the induction type or muffle furnaces. Finally, the molten zinc is cast and in part refined to high purity zinc in distillation columns.

In New Jersey retorts it is possible to process a large variety of oxidic secondary materials together with metallic materials simultaneously. For charge preparation the oxides are mixed with bituminous or gas coal, briquetted and coked. The briquettes together with the metallic materials are charged into the retorts. The zinc vapours from the retorts are condensed by splash condensing.

# 2.2 Techniques

#### 2.2.1 Primary zinc production

#### The electrochemical zinc production process

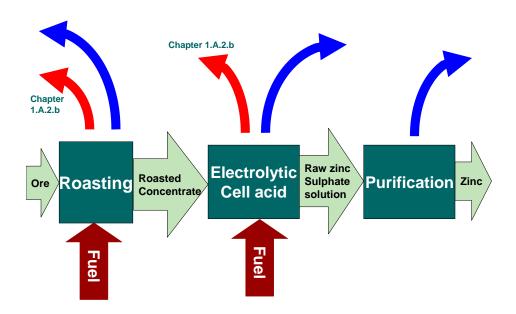
Roasted ores are leached in electrolytic cell acid. The zinc oxide dissolves in the acid solution but the zinc ferro does not. After a separation step the raw zinc sulphate solution goes to the purification process and the insoluble matter to the jarosite precipitation process.

In the jarosite precipitation process, the insoluble matter of the roast is in good contact with solution containing ammonia and iron (which also contains zinc and other metals) from the second leaching process. The iron precipitates, forming the insoluble ammoniumjarosite  $[(NH_4)_2Fe_6(SO_4)_4(OH)_{12}]$ . After separation the solution containing zinc goes to the first leaching process and the insoluble matter to a second leaching process. The insoluble matter is contacted in the second leaching process with a strong acid solution. The zinc ferro and almost all the other metals dissolve in the strong acid solution. After separation the solution containing zinc and iron is returned to the jarosite precipitation process where the iron and the insoluble matter are removed.

The raw zinc sulphate solution from the first leaching process is purified by adding zinc dust. Because of the addition of the zinc dust, copper, cobalt and cadmium are precipitated as metal. After filtration of the purified zinc sulphate solution the zinc electrolytic is separated from the solution. The electrolytically produced zinc sheets are melted in induction ovens and cast to blocks. The zinc alloys can also be produced by adding low concentrations of lead or aluminium.

Figure 2.1 below shows a generalised process scheme for the electrochemical zinc production process, as described above.

Figure 2.1 Process scheme for source category 2.C.6 Zinc production, electrochemical zinc production process



#### The thermal smelting zinc production process

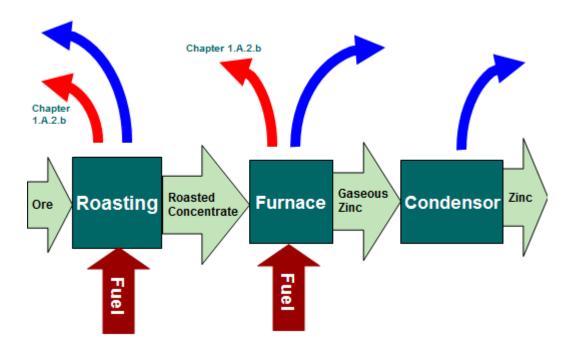
Roasted zinc is heated to a temperature of about 1100 °C (a temperature above the boiling point is needed) in the presence of anthracite or cokes. At that temperature zinc oxide is reduced and carbon monoxide is formed from the carbon source. The carbon monoxide reacts with another molecule of zinc oxide and forms carbon dioxide:

$$ZnO$$
 +  $C$   $\rightarrow$   $Zn(gas)$  +  $CO$  Reaction 1  
 $ZnO$  +  $CO$   $\rightarrow$   $Zn(gas)$  +  $CO_2$  Reaction 2  
 $CO_2$  +  $C$   $\rightarrow$   $2CO$  Reaction 3

Because reaction 2 is reversible (at lower temperatures zinc oxide is reformed) the concentration of carbon dioxide has to be decreased. The concentration of carbon dioxide is decreased by reaction with the carbon source.

Finally, the vaporised zinc is condensed by external condensers. Figure 2.2 gives an overview of the thermal smelting zinc production process.

Figure 2.2 Process scheme for source category 2.C.6 Zinc production, electrochemical zinc production process



#### 2.2.2 Secondary zinc production

A sweating furnace (rotary, reverberatory, or muffle furnace) slowly heats the scrap containing zinc and other metals to approximately 364 °C. This temperature is sufficient to melt zinc but is still below the melting point of the remaining metals. Molten zinc collects at the bottom of the sweat furnace and is subsequently recovered. The remaining scrap metal is cooled and removed to be sold to other secondary processors (US EPA, 1995).

A more sophisticated type of sweating operation involves holding scrap in a basket and heating it in a molten salt bath to a closely controlled temperature. This yields a liquid metal, which separates downwards out of the salt and a remaining solid of the other metals still free from oxidation. By arranging for heating to a sequence of temperatures, related to the melting point of the metals or alloys involved, a set of molten metal fractions with minimum intermixture can be obtained (Barbour *et al.*, 1978).

For zinc production in New Jersey retorts the raw materials containing zinc are picked up from the stockpiling area. For some raw materials a charge preparation is carried out, including comminution, sieving, and magnetic separation, so that a metallic and an oxidic fraction is obtained. Furthermore, for some raw materials dechlorination is necessary. The oxidic raw materials, like dusts and zinc drosses are mixed with bituminous coal. Subsequently, the mixture which contains about 40% zinc is briquetted together with a binding agent, coked at temperatures around 800 °C in an autogenous coking furnace and then charged to the New Jersey retorts together with small amounts of pure metallic materials. By heating with natural gas and waste gases containing carbon monoxide (CO), in the retorts temperatures of around 1 100 °C are achieved, so that the zinc is reduced and vaporised. Subsequently, the vaporised zinc is precipitated in splash-condensers and transferred to the foundry via a holding furnace. Here the so-called selected zinc is cast into ingots. The residues from the retorts are treated in a melting cyclone to produce lead-zinc-mix oxides and slag. Figure 3.1 shows a schematic diagram for secondary zinc production using New Jersey retorts. Potential sources of particulate and heavy metal emissions are indicated. The metallic fraction from charge preparation together with other metallic materials like galvanic drosses, scrap zinc, and scrap alloys are melted. The raw zinc is then sent to a liquation furnace where, in a first refining step, zinc contents of 97.5-98 % are achieved. The melted and refined zinc is also cast into ingots (Rentz et al., 1996).

The raw materials for Waelz furnaces are mainly dusts and slurry from electric arc furnaces used in the steel industry, together with other secondary materials containing zinc and lead. For transferring and charging, the dust-like secondary materials are generally pelletized at the steel plant.

After mixing, the pellets containing zinc and lead, coke as reducing agent, and fluxes are charged via a charging sluice at the upper end of the slightly sloped rotary kiln. The rotation and the slope lead to an overlaid translational and rotational movement of the charge. In a counter-current direction to the charge, air as combustion gas is injected at the exit opening of the furnace. At temperatures of around 1 200°C and with residence times of around four hours, zinc and lead are reduced and vaporised. The metal vapours are reoxidised in the gas filled space of the furnace and evacuated through the charge opening together with the waste gas. In a cleaning device, the metal oxides are collected again and as filter dust the so-called Waelz oxide with a zinc content of around 55% and a lead content of around 10% is generated. The Waelz oxide is subsequently charged into an Imperial smelting furnace which is used for combined primary zinc and lead smelting. The slag from the Waelz furnace is cooled down and granulated in a water bath. Additional oil as fuel is only needed at the start-up of the furnace, while in stationary operation the combustion of the metal vapours and carbon monoxide covers the energy demand of the process (Rentz *et al.*, 1996). A schematic representation of the Waelz process is depicted in Figure 3.2.

Secondary zinc is sometimes combined with primary material for refining. Various pyrometallurgical refining technologies can be applied, depending on the feed material and product specification. Thermal zinc refining by fractional distillation is possible in rectifying columns at temperatures around 950 °C (Rentz *et al.*, 1996).

#### 2.3 Emissions

#### 2.3.1 Primary zinc production

The main emissions to air from zinc production are:

- sulphur dioxide (SO2), other sulphur compounds and acid mists;
- oxides of nitrogen (NOX) and other nitrogen compounds;
- metals and their compounds;
- dust;
- VOCs and PCDD/F.

Other pollutants are considered to be of negligible importance for the industry, partly because they are not present in the production process and partly because they are immediately neutralised (e.g. chlorine or HC<sub>I</sub>) or occur in very low concentrations (e.g. CO). Emissions are to a large extent bound to dust (except cadmium, arsenic and mercury, which can be present in the vapour phase to varying degrees).

Dust carry-over from roasting or other pyrometallurgical processes are potential sources of direct and diffuse emissions of dust and metals. The gases are collected and treated in the gas-cleaning processes and finally in the sulphuric acid plant. Dust is removed and returned to the process. Emission of aerosols takes place in the cell house and they can contain metals in solution. The range of mist and dust emissions from these sources is 0.2 mg/Nm³ to 1.25 mg/Nm³. The melting, alloying, casting and zinc dust processes are potential emission sources of dust and metals. The range of dust emissions is reported to be 200 mg/Nm³ to 900 mg/Nm³ in the raw gas. Emissions of particulate matter and heavy metals (zinc and cadmium) also take place during the receipt and storage of the zinc ores.

Emissions of  $SO_2$  mainly arise from the roasting, electrolysis and the sulphuric acid plant. The receipt and storage of the zinc ore take place under a covering to reduce the emission. The emissions during production occur from tanks, ovens and separation equipment. These emissions can be decreased by changing some constructions.

More than 90% of the potential  $SO_2$  emissions from zinc ores is released in roasters. About 93–97% of the sulphur in the feed is emitted as sulphur oxides. Concentrations of  $SO_2$  in the off-gas vary with the type of roaster operation. The hot off-gas from a fluidised bed furnace typically contains ~10%  $SO_2$  (European Commission, 2014).

Additional  $SO_2$  is emitted from the sinter plant; the quantity depends on the sulphur content of the calcine feedstock. The  $SO_2$  concentration of sinter plant exhaust gas ranges from 0.1 to 2.4% (US EPA, 1995).

The roasting and smelting stages are potential sources of nitrogen oxides (NOX). NOX may be formed from nitrogen components that are present in the concentrates or as thermal NOX. The range for all of the processes is 20 mg/Nm³ to 400 mg/Nm³.

The formation of PCDD/F in the combustion zone and in the cooling part of the off-gas treatment system (de novo synthesis) may be possible in some processes particularly if plastic components are included in the secondary materials that are fed into a process.

The energy requirement for the different lead and zinc processes varies to a large extent. It depends on the quality of the feed and the products, the use of latent or waste heat and the production of

by-products. Please refer to the Best Available Techniques Reference (BREF) document for additional information (European Commission, 2014) with expected adoption in 2016 (1).

### 2.3.2 Secondary zinc production

Among the various process steps the melting furnace operation represents the most important source of atmospheric emissions. In general, continuous and periodical emissions can be distinguished. Continuous emissions are connected with the process as such, whereas periodical emissions occur e.g. during charging, heating, skimming or cleaning operations. The most important factors influencing emissions from scrap pre-treatment and melting are:

- the composition of the raw material, in particular the content of organic and chlorinated compounds which affects the formation of dioxins and furans;
- the utilisation of flux powder;
- the furnace type direct heating with a mixture of process and combustion waste gases reduces the content of organic compounds released from the bath;
- the bath temperature a temperature above 600 °C creates significant emissions of zinc oxide;
- the fuel type in general, natural gas or light fuel oil are used.

Continuous emissions from the melting furnace consist of combustion waste gases and gaseous effluents from the bath. The specific gas flow amounts to about 1 000 m<sup>3</sup> (STP)/Mg zinc produced.

Important periodical emissions often occur with charging and melting of the raw material. Emissions of organic compounds are mainly connected with charging operations. Furnace clearing, fluxing, ash drawing and also cleaning operations are of minor relevance. Tapping is carried out at low temperature and therefore no metal vapours are released.

In zinc distillation a high quality input material is used and therefore, emissions of compounds containing carbon or chlorine are low. Emissions mainly consist of particles containing zinc and zinc oxide and combustion waste gases (Bouscaren and Houllier, 1988).

#### 2.3.3 Particulate matter (PM)

Note that PM emission factors in the Guidebook represent primary emissions from the activities and not formation of secondary aerosol from chemical reaction in the atmosphere after release.

A number of factors influence the measurement and determination of primary PM emissions from activities and, the quantity of PM determined in an emission measurement depends to a large extent on the measurement conditions. This is particularly true of activities involving high temperature and semi-volatile emission components – in such instances the PM emission may be partitioned between a solid/aerosol phase and material which is gaseous at the sampling point but which can condense in the atmosphere. The proportion of filterable and condensable material will vary depending on the temperature of the flue gases and in sampling equipment.

A range of filterable PM measurement methods are applied around the world typically with filter temperatures of 70-160°C (the temperature is set by the test method). Condensable fractions can

<sup>(</sup>¹) The BREF document for non-ferrous metals industries is presently in the final drafting stage. A finalised version is expected to be adopted in 2016. Information concerning the status of BREF documents is available at <a href="http://eippcb.jrc.es/reference/">http://eippcb.jrc.es/reference/</a>. The previous version of the BREF was published in 2001 (European Commission, 2001).

be determined directly by recovering condensed material from chilled impinger systems downstream of a filter – note that this is condensation without dilution and can require additional processing to remove sampling artefacts. A common approach for total PM includes dilution where sampled flue or exhaust gases are mixed with ambient air (either using a dilution tunnel or dilution sampling systems) which collect the filterable and condensable components on a filter at lower temperatures (but depending on the method this can be 15-52°C).

The review identifies whether the PM emission factors (for TSP, PM<sub>10</sub> and PM<sub>2.5</sub>) represent total PM, filterable PM or whether the basis of the emission factor cannot be determined (see individual emission factor tables).

#### 2.4 Controls

#### 2.4.1 Primary zinc production

Sulphur dioxide emissions from the roasting processes are often recovered at on-site sulphuric acid plants. No sulphur controls are used on the exhaust stream of sinter plants. Extensive desulphurisation before electrothermic retorting results in practically no  $SO_2$  emissions from these devices (US EPA, 1995).

Dust control may be performed using bag filters, hot ESPs or wet scrubbers.

#### 2.4.2 Secondary zinc production

Most of the secondary zinc smelters are equipped with dust removing installations, such as baghouses. In general, emission control systems vary depending on the type of scrap being processed and the products being obtained. A distinction can be made between purely oxidised, mixed oxidised/metallic and purely metallic products.

The control efficiency of dust removing installations is often very high, reaching 99.9%. Both primary gases and fugitive dust emissions are reduced in baghouses to concentrations below 10 mg/m³.

Afterburners are reported for non-ferrous-metal industry in the United States of America. Also wet scrubbers may be used.

# 3 Methods

## 3.1 Choice of method

Figure 3.1 presents the procedure to select the methods for estimating process emissions from the zinc industry. The basic approach is as follows:

- If detailed information is available: use it.
- If the source category is a key category, a Tier 2 or better method must be applied and detailed input data must be collected. The decision tree directs the user in such cases to the Tier 2 method, since it is expected that it is more easy to obtain the necessary input data for this approach than to collect facility level data needed for a Tier 3 estimate;
- The alternative of applying a Tier 3 method, using detailed process modelling is not explicitly included in this decision tree. However, detailed modelling will always be done at facility level and results of such modelling could be seen as "facility data" in the decision tree.

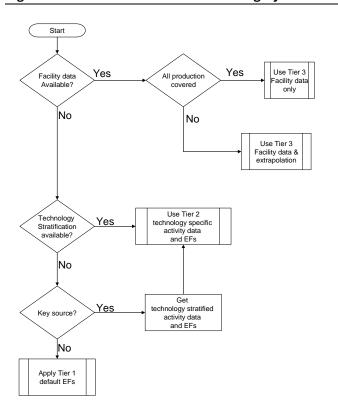


Figure 3.1 Decision tree for source category 2.C.6 Zinc production

# 3.2 Tier 1 default approach

### 3.2.1 Algorithm

The Tier 1 approach for process emissions from primary zinc production uses the general equation:

$$E_{pollutant} = AR_{production} \times EF_{pollutant}$$
 (1)

Where:

E<sub>pollutant</sub> = the emission of the specified pollutant

 $AR_{production}$  = the activity rate for the zinc production

EF<sub>pollutant</sub> = the emission factor for this pollutant

This equation is applied at the national level, using annual national total primary zinc production. Information on the production of primary zinc, suitable for estimating emissions using the simpler estimation methodology (Tier 1 and 2) is widely available from United Nations statistical yearbooks or national statistics.

Tier 1 emission factors assume an 'averaged' or typical technology and abatement implementation in the country and integrate all sub-processes in zinc production.

In cases where specific abatement options are to be taken into account a Tier 1 method is not applicable and a Tier 2 or Tier 3 approach must be used.

#### 3.2.2 Default emission factors

The Tier 1 approach needs emission factors for all relevant pollutants, which integrate all subprocesses within the industry from inputting raw materials to the final shipment of the products off site. The default emission factors suggested for primary and secondary zinc production are given in Table 3.1.

Emissions of  $NO_x$  and CO are assumed to originate mainly from combustion and are discussed in chapter 1.A.2.b. All other emissions are assumed to originate primarily from the process and are therefore discussed in the present chapter. The emission factors for heavy metals were obtained from the BREF and from Theloke et al. (2008) (Tier 1 EF). These average emission factors are representative for the EU-27, Albania, Belarus, Croatia, Iceland, Former Yugoslav Republic of Macedonia, Moldova, Norway, the European part of Russia, Serbia and Montenegro, Switzerland, and Ukraine. The share of  $PM_{10}$  and  $PM_{2.5}$  is estimated by using the distribution given in Visschedijk et al. (2004).

Emission factors in BREF documents are mostly given in ranges. The range is interpreted as the 95% confidence interval, while the geometric mean of this range is chosen as the value for the emission factor.

Table 3.1 Tier 1 emission factors for source category 2.C.6 Zinc production.

Tier 1 default emission factors								
	Code	Name						
NFR source category	2.C.6 Zinc production							
Fuel	NA							
Not applicable	HCH							
Not estimated		/IVOC, NH <sub>3</sub> , BC, As, ( pranthene, Indeno(			rene, Benzo(a)fluoranthene,			
Pollutant	Value	Unit		onfidence	Reference			
			int	erval				
			Lower	Upper				
SO <sub>x</sub>	1350	g/Mg zinc	200	9000	European Commission (2014)			
TSP	15	g/Mg zinc	3	73	European Commission (2014)			
PM <sub>10</sub>	13	g/Mg zinc	3	66	Visschedijk et al. (2004) applied on TSP			
PM <sub>2.5</sub>	12	g/Mg zinc	2.4	58	Visschedijk et al. (2004) applied on TSP			
Pb	0.2	g/Mg zinc	0.01	3	European Commission (2014)			
Cd	0.04	g/Mg zinc	0.004	0.42	European Commission (2014)			
Нg	0.04	g/Mg zinc	0.001	1.55	Ratio from Theloke et al. (2008) applied on Zn			
As	0.03	g/Mg zinc	0.01	0.1	European Commission (2014)			
Zn	5	g/Mg zinc	1	21	European Commission (2014)			
PCB	2	μg/Mg zinc	0.3	11	Note 1			
PCDD/F	5	μg I-TEQ/Mg zinc	0	1000	UNEP (2005)			

**Notes:** The EF for PCB may be revised in the future based on new information from UNEP: Toolkit for Identification and Quantification of Releases of Dioxins and Furans and Other Unintentional POPs: http://chm.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/Overview/tabid/372/Default.aspx

These PM factors represent filterable PM emissions only (excluding any condensable fraction). A conventional plant is assumed, using electrostatic precipitators (ESP), settlers and scrubbers for abatement and having moderate control of fugitive sources. The heavy metal emission factors assume limited control.

#### 3.2.3 Activity data

Information on the production of zinc suitable for estimating emissions using the simpler estimation methodology (Tier 1 and 2) is widely available from United Nations statistical yearbooks or national statistics.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 4.7.2.3 'Choice of activity statistics' (IPCC, 2006).

# 3.3 Tier 2 technology-specific approach

#### 3.3.1 Algorithm

The Tier 2 approach is similar to the Tier 1 approach. To apply the Tier 2 approach, both the activity data and the emission factors need to be stratified according to the different techniques that may occur in the country. The different techniques used in the production of primary zinc are discussed in subsection 2.2.1 of the present chapter.

The Tier 2 approach is as follows:

Stratify zinc production in the country to model the different product and process types occurring in the national zinc industry into the inventory by:

- defining the production using each of the separate product and/or process types (together called 'technologies' in the formulae below) separately; and
- applying technology specific emission factors for each process type:

$$E_{pollutant} = \sum_{technolog \not es} AR_{production technolog y} \times EF_{technolog y pollutant} \tag{2}$$

where:

AR<sub>production,technology</sub> = the production rate within the source category, using this specific technology

EF<sub>technology,pollutant</sub> = the emission factor for this technology and this pollutant

A country where only one technology is implemented will result in a penetration factor of 100 % and the algorithm reduces to:

$$E_{pollutant} = AR_{production} \times EF_{technologypollutant}$$
 (3)

where:

 $E_{pollutant}$  = the emission of the specified pollutant

AR<sub>production</sub> = the activity rate for the zinc production

EF<sub>pollutant</sub> = the emission factor for this pollutant

The emission factors in this approach will still include all sub-processes within the industry from inputting raw materials until the produced zinc is shipped to the customers.

### 3.3.2 Technology-specific emission factors

Applying a Tier 2 approach for the process emissions from zinc production calls for technology-specific emission factors. These are provided in the present subsection. A BREF document for this industry is available at <a href="http://eippcb.jrc.es/pages/FActivities.htm">http://eippcb.jrc.es/pages/FActivities.htm</a>. In subsection 4.3.1 of the present chapter emission factors derived from the emission limit values (ELVs) as defined in the BREF document are provided for comparison.

The present subsection provides technology-specific emission factors for the two techniques for primary zinc production described in this chapter; the electrochemical process and the thermal smelting process (see section 0Error! Reference source not found. and 0Error! Reference source no t found.). However, not many specific emission factors are available for these two processes.

As for the Tier 1 approach, emissions of  $NO_x$  and CO are assumed to originate mainly from combustion and are discussed in chapter 1.A.2.b. All other emissions are assumed to originate primarily from the process and are therefore discussed in the present chapter.

Emission factors in the BREF documents are mostly given in ranges. The range is interpreted as the 95 % confidence interval, while the geometric mean of this range is chosen as the value for the emission factor in the tables below.

#### **Primary zinc production**

Table 3.2 presents emission factors that can be used for primary zinc production; unabated. Table 3.3 presents emission factors from the BREF, relevant to the current technology level in the EU-28. However, data were not available for all pollutants (only for the values referenced in Theloke *et al.*, 2008). For the unabated emission factors, the PM<sub>10</sub> emission was estimated from the composition of particulate matter emitted from zinc oxide kilns given in the SPECIATE database (US EPA, 2011) and the emission of heavy metals given by Theloke et al. (2008). The share of TSP and PM<sub>2.5</sub> was estimated by using the distribution given in Visschedijk et al. (2004). The Zn/Pb ratio was assumed to be the same as the Tier 1 EF (Table 3.1). The emission factors presented in these tables should therefore be handled with care. Abatement efficiencies for particulates are provided separately in section 3.3.3.

Table 3.2 Tier 2 emission factors for source category 2.C.6 Zinc production, primary zinc production, unabated.

Tier 2 default emission factors							
	Code Name						
NFR source category	2.C.6	Zinc production					
Fuel	NA						
SNAP (if applicable)	040309	Zinc production					
Technologies/Practices	Primary	zinc production					
Region or regional conditions							
Abatement technologies	Unabate	ed					
Not applicable	HCH						
Not estimated		, NMVOC, SO <sub>x</sub> , NH <sub>3</sub> , )fluoranthene, Ben			nzo(a)pyrene, o(1,2,3-cd)pyrene, HCB		
Pollutant	Value	Unit	95 % co	nfidence	Reference		
			inte	rval			
			Lower	Upper			
TSP	210	g/Mg zinc	105	420	Visschedijk et al. (2004) applied on PM <sub>10</sub>		
PM <sub>10</sub>	170	g/Mg zinc	85	340	US EPA (2011, file no. 2050110)		
PM <sub>2.5</sub>	130	g/Mg zinc	65	260	Visschedijk et al. (2004) applied on PM <sub>10</sub>		
Pb	35	g/Mg zinc	10	70	Theloke et al. (2008)		
Cd	5	g/Mg zinc	2	8	Theloke et al. (2008)		
Hg	5	g/Mg zinc	2	8	Theloke et al. (2008)		
Zn	80	g/Mg zinc	40	160	European Commission (2001)/same ratio to Pb as in Tier 1		
PCB	0.9	μg/Mg zinc	0.3	2.8	Note 1		
PCDD/F	5	μg I-TEQ/Mg zinc	0	1000	UNEP (2005)		

**Notes:** The EF for PCB may be revised in the future based on new information from UNEP: Toolkit for Identification and Quantification of Releases of Dioxins and Furans and Other Unintentional POPs: <a href="http://chm.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/Overview/tabid/372/Default.aspx">http://chm.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/Overview/tabid/372/Default.aspx</a>. These PM factors represent filterable PM emissions only (excluding any condensable fraction).

Table 3.3 Tier 2 emission factors for source category 2.C.6 Zinc production, primary zinc production assuming average technology in the EU-28.

Tier 2 default emission factors								
	Code	Code Name						
NFR source category	2.C.6	Zinc production						
Fuel	NA							
SNAP (if applicable)		inc production						
Technologies/Practices	Primary z	inc production						
Region or regional conditions	EU-28							
Abatement technologies	Current to	echnology level						
Not applicable	HCH							
Not estimated		NMVOC, SO <sub>x</sub> , NH <sub>3</sub> , E luoranthene, Benzo			(a)pyrene, 2,3-cd)pyrene, HCB			
			95 % coi	nfidence	Reference			
Pollutant	Value	Unit	interval					
			Lower	Upper				
TSP	15	g/Mg zinc	3	73	European Commission (2014)			
PM <sub>10</sub>	13	g/Mg zinc	2.7	66	Visschedijk et al. (2004) applied on TSP			
PM <sub>2.5</sub>	12	g/Mg zinc	2.4	58	Visschedijk et al. (2004) applied on TSP			
Pb	0.17	g/Mg zinc	0.01	3	European Commission (2014)			
Cd	0.04	g/Mg zinc	0.004	0.42	European Commission (2014)			
Hg	0.6	g/Mg zinc	0.1	1.5	Ratio from Theloke et al. (2008) applied on Zn			
Zn	5	g/Mg zinc	1	21	European Commission (2014)			
PCB	0.9	μg/Mg zinc	0.3	2.8	Note 1			
PCDD/F	5	μg I-TEQ/Mg zinc	0	1000	UNEP (2005)			
SO <sub>x</sub>	1350	g/Mg zinc	200	9000	European Commission (2014)			

**Notes:** The EF for PCB may be revised in the future based on new information from UNEP: Toolkit for Identification and Quantification of Releases of Dioxins and Furans and Other Unintentional POPs: http://chm.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/Overview/tabid/372/Default.aspx

These PM factors represent filterable PM emissions only (excluding any condensable fraction).

#### Secondary zinc production

Table 3.4 presents an average set of emission factors that can be used for secondary zinc production without abatement techniques. Table 3.5**Error! Reference source not found.** presents emission factors for the typical zinc production in the EU-28 using currently installed technology. However, unabated emission factors were not available for all pollutants (only for the values referenced in Theloke *et al.*, 2008). The PM<sub>10</sub> emission has been estimated from the composition of particulate matter emitted from zinc oxide kilns given in the SPECIATE database (US EPA, 2011) and the emission of heavy metals given by Theloke et al. (2008). The share of TSP and PM<sub>2.5</sub> is estimated by using the distribution given in Visschedijk et al. (2004). Regarding the EFs concerning abated emissions the reduction of TSP is assumed to be as efficient as the reduction of heavy metals. The Zn/Pb ratio is

assumed to be the same as the Tier 1 EF (Table 3.1). Separate abatement efficiencies supplied for particulates are presented below in section 3.3.3.

Table 3.4 Tier 2 emission factors for source category 2.C.6 Zinc production, secondary zinc production, unabated.

Tier 2 default emission factors								
	Code	N	Name					
NFR source category	2.C.6	Zi	nc production					
Fuel	NA							
SNAP (if applicable)	040309 Z	nc production						
Technologies/Practices	Secondary	zinc productior	1					
Region or regional conditions								
Abatement technologies	Unabated							
Not applicable	HCH							
Not estimated			₃, BC, Cr, Cu, Ni, nzo(k)fluoranthe		oyrene, .2,3-cd)pyrene, HCB			
			95 % co	nfidence	Reference			
Pollutant	Value	Unit	inte	erval				
			Lower	Upper				
TSP	425	g/Mg zinc	215	850	Visschedijk et al. (2004) applied on PM <sub>10</sub>			
PM <sub>10</sub>	340	g/Mg zinc	170	680	US EPA (2011, file no. 2050110)			
PM <sub>2.5</sub>	255	g/Mg zinc	125	510	Visschedijk et al. (2004) applied on PM <sub>10</sub>			
Pb	65	g/Mg zinc	40	100	Theloke et al. (2008)			
Cd	35	g/Mg zinc	20	50	Theloke et al. (2008)			
Hg	0.006	g/Mg zinc	0.003	0.009	Theloke et al. (2008)			
As	5.9	g/Mg zinc	3.0	9.0	Theloke et al. (2008)			
Zn	150	g/Mg zinc	75	300	European Commission (2001)/same relation to Pb as in Tier 1			
PCB	0.0031	μg/Mg zinc	0.001	0.0093	Note 1			
PCDD/F	100	μg I-TEQ/Mg zinc	0.3	1000	UNEP (2005)			

**Notes:** The EF for PCB may be revised in the future based on new information from UNEP: Toolkit for Identification and Quantification of Releases of Dioxins and Furans and Other Unintentional POPs: http://chm.pops.int/Implementation/UnintentionalPOPs/ToolkitforUPOPs/Overview/tabid/372/Default.aspx

These PM factors represent filterable PM emissions only (excluding any condensable fraction).

Table 3.5 Tier 2 emission factors for source category 2.C.6 Zinc production, secondary zinc production assuming average technology in the EU-28.

Tier 2 default emission factors									
	Code	N							
NFR source category	2.C.6	Zi	nc production						
Fuel	NA								
SNAP (if applicable)	040309 Zinc pr	oduction							
Technologies/Practices	Secondary zinc	production							
Region or regional conditions	EU-28								
Abatement technologies	Current techno	logy level							
Not applicable	HCH								
Not estimated			Cu, Ni, Se, Benzo(a)p I,2,3-cd)pyrene, HCB		luoranthene,				
Pollutant	Value	Unit	95 % confid	ence interval	Reference				
Pollutarit	value	Offic	Lower	Upper					
TSP	32	g/Mg zinc	14	73	European Commission (2014)				
PM <sub>10</sub>	29	g/Mg zinc	13	66	Visschedijk et al. (2004) applied on TSP				
PM <sub>2.5</sub>	26	g/Mg zinc	11	58	Visschedijk et al. (2004) applied on TSP				
Pb	0.95	g/Mg zinc	0.3	3	European Commission (2014)				
Cd	0.23	g/Mg zinc	0.13	0.42	European Commission (2014)				
Hg	0.0015	g/Mg zinc	0.0009	0.0019	Ratio from Theloke et al. (2008) applied on Zn				
As	0.03	g/Mg zinc	0.01	0.1	European Commission (2014)				
Zn	9	g/Mg zinc	4	21	European Commission (2014)				
PCB	3.6	μg/Mg zinc	1.2	11	Note 1				
PCDD/F	5	μg I-TEQ/Mg zinc	0	1000	UNEP (2005)				
SO <sub>x</sub>	1000	g/Mg zinc	500	2000	European Commission (2014)				

**Notes:** The EF for PCB may be revised in the future based on new information from UNEP: Toolkit for Identification and Quantification of Releases of Dioxins and Furans and Other Unintentional POPs: <a href="http://chm.pops.int/Implementation/ToolKit/Meetings/7thExpertMeeting2012/tabid/2906/mctl/ViewDetails/EventModID/876/EventID/326/xmid/9376/Default.aspx">http://chm.pops.int/Implementation/ToolKit/Meetings/7thExpertMeeting2012/tabid/2906/mctl/ViewDetails/EventModID/876/EventID/326/xmid/9376/Default.aspx</a>.

These PM factors represent filterable PM emissions only (excluding any condensable fraction).

# 3.3.3 Abatement

A number of add on technologies exist that are aimed at reducing the emissions of specific pollutants. The resulting emission can be calculated by replacing the technology-specific emission factor with an abated emission factor as given in the formula:

$$EF_{technologyabated} = \eta_{abatement} \times EF_{technologyunabated}$$
 (4)

Where

EF technology, abated = the emission factor after implementation of the abatement

 $\eta$  abatement = the abatement efficiency

EF technology, unabated = the emission factor before implementation of the abatement

Typical abatement efficiencies and pollutant flue gas concentrations related to a specific abatement technique can be found in the revised BREF document on the non-ferrous metal industries (European Commission, 2014).

Table 3.6, Table 3.7 and Table 3.8 present default abatement efficiencies for particulate matter,  $SO_x$  and heavy metal emissions. The particulate matter (PM) efficiencies for older abatement equipment are based on AP 42 (US EPA, 1998), while efficiencies for modern equipment are based on the draft BREF document for the large combustion plants sector (European Commission, 2013). It should be noted that the efficiencies from the LCP BREF are primarily based on observations made for fly ash from coal-fired power plants. For other types of dust efficiencies may be lower. The abatement efficiencies for heavy metals are based on Theloke et al. (2008) and the  $SO_x$  abatement efficiency for sulphuric acid plants is taken from the BREF (European Commission, 2014). Final abatement efficiency is dependent on the state of the abatement installed.

Table 3.6 Dust abatement efficiencies (η<sub>abatement</sub>) for source category 2.C.6 Zinc production

Tier 2 Abatement efficiencies								
	Code	Name						
NFR Source Category	2.C.6	Zinc production	Zinc production					
Fuel	NA	not applicable						
SNAP (if applicable)	040309b	Zinc production						
Abatement technology	Pollutant	Efficiency		onfidence erval	Reference			
		Default Value	Lower	Upper				
	particle > 10 μm	78.7%	36.2%	92.9%	US EPA (1998)			
Multicyclone	10 μm > particle > 2.5 μm	75.8%	27.5%	91.9%				
	2.5 µm > particle	75.0%	25.0%	91.7%				
	particle > 10 μm	77.6%	32.7%	92.5%	US EPA (1998)			
Spray tower	10 μm > particle > 2.5 μm	74.4%	23.2%	91.5%				
	2.5 µm > particle	72.5%	17.5%	90.8%				
	particle > 10 μm	95.1%	85.3%	98.4%	US EPA (1998)			
ESP + spray tower	10 μm > particle > 2.5 μm	94.6%	83.8%	98.2%				
	2.5 µm > particle	96.3%	88.8%	98.8%				
	particle > 10 μm	98.2%	94.5%	99.4%	US EPA (1998)			
Wet ESP	10 μm > particle > 2.5 μm	96.4%	89.2%	98.8%				
	2.5 µm > particle	94.4%	83.1%	98.1%				
	particle > 10 μm	>99.95%			European Commission			
Modern ESP	10 μm > particle > 2.5 μm	>99.95%			(2013)			
	2.5 µm > particle	97.4%	>96.5%	>98.3%				
	particle > 10 μm	71.9%	15.7%	90.6%	US EPA (1998)			
Crossflow packed bed scrubber	10 μm > particle > 2.5 μm	67.9%	3.8%	89.3%				
	2.5 µm > particle	76.9%	30.6%	92.3%				
Floating bed	particle > 10 μm	79.6%	38.8%	93.2%	US EPA (1998)			
scrubber	10 μm > particle > 2.5 μm	76.8%	30.4%	92.3%				

	2.5 µm > particle	75.0%	25.0%	91.7%	
	particle > 10 μm	96.7%	90.0%	98.9%	US EPA (1998)
Venturi Scrubber	10 μm > particle > 2.5 μm	96.2%	88.6%	98.7%	
	2.5 µm > particle	92.3%	77.0%	97.4%	
	particle > 10 μm	>99.9%			European Commission
Modern Venturi scrubber	10 μm > particle > 2.5 μm	99.9%			(2013)
	2.5 µm > particle	99.0%	98.5%	99.5%	1
	particle > 10 μm	99.1%	97.4%	99.7%	US EPA (1998)
Dry + secondary scrubber	10 μm > particle > 2.5 μm	98.3%	95.0%	99.4%	
	2.5 µm > particle	97.5%	92.5%	99.2%	1
	particle > 10 μm	98.1%	94.3%	99.4%	US EPA (1998)
Coated fabric filter	10 μm > particle > 2.5 μm	96.3%	88.8%	98.8%	
	2.5 µm > particle	94.4%	83.1%	98.1%	
	particle > 10 μm	>99.95%			European Commission
Modern fabric filter	10 μm > particle > 2.5 μm	>99.9%			(2013)
	2.5 µm > particle	>99.6%			

Table 3.7 SO<sub>x</sub> abatement efficiencies (η<sub>abatement</sub>) for source category 2.C.6 Zinc production

Tier 2 Abatement efficiencies								
	Code	Name						
NFR Source Category	2.C.6	Zinc production						
Fuel	NA	not applicable	not applicable					
SNAP (if applicable)	040309b	Zinc production	Zinc production					
Abatement	Pollutant	Efficiency	95% confid	ence interval	Reference			
technology		Default Value	Lower	Upper				
Single contact sulphuric acid plants	SO <sub>x</sub>	97.6%	96%	99.10%	European Commission (2014)			
Double contact sulphuric acid plants	SO <sub>x</sub>	99.6%	99.20%	99.97%	European Commission (2014)			

Table 3.8 Metal abatement efficiencies ( $\eta_{abatement}$ ) for source category 2.C.6 Zinc production

Tier 2 Abatement efficiencies								
	Code	Name						
NFR Source Category	2.C.6	Zinc production						
Fuel	NA	not applicable	not applicable					
SNAP (if applicable)	040309b	Zinc production	Zinc production					
Abatement	Pollutant	Efficiency	95% confid	lence interval	Reference			
technology		Default Value	Lower	Upper				
Dry ESP	Hg	5%	0%	68%	Theloke et al. (2008)			
	Cd	84.7%	54%	95%	Theloke et al. (2008)			
	Ni	84.7%	54%	95%	Theloke et al. (2008)			
	As	84.7%	54%	95%	Theloke et al. (2008)			

	Pb	84.7%	54%	95%	Theloke et al. (2008)
State of the art fabric	Hg	10%	0%	70%	Theloke et al. (2008)
filter	Cd	99.99%	99.97%	99.997%	Theloke et al. (2008)
	Ni	99.99%	99.97%	99.997%	Theloke et al. (2008)
	As	99.99%	99.97%	99.997%	Theloke et al. (2008)
	Pb	99.99%	99.97%	99.997%	Theloke et al. (2008)
	PCDD/F	10%	0%	70%	Theloke et al. (2008)

#### 3.3.4 Activity data

Information on the production of zinc suitable for estimating emissions using Tier 1 and 2 estimation methodology is widely available from United Nations statistical yearbooks or national statistics.

For a Tier 2 approach these data need to be stratified according to technologies applied. Typical sources for these data might be industrial branch organisations within the country or questionnaires submitted to the individual zinc works.

Further guidance is provided in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, volume 3 on Industrial Processes and Product Use (IPPU), chapter 4.7.2.3 'Choice of activity statistics' (IPCC, 2006).

# 3.4 Tier 3 emission modelling and use of facility data

#### 3.4.1 Algorithm

There are two different methods to apply emission estimation methods that go beyond the technology-specific approach described above:

- detailed modelling of the zinc production process;
- facility-level emission reports.

#### **Detailed process modelling**

A Tier 3 emission estimate using process details will make separate estimates for the consecutive steps in the zinc production process.

#### **Facility-level data**

Where facility-level emission data of sufficient quality (see the guidance chapter on QA/QC in Part A of the Guidebook) are available, it is good practice to use these data. There are two possibilities:

- the facility reports cover all zinc production in the country;
- facility-level emission reports are not available for all zinc plants in the country.

If facility level data cover all zinc production in the country, it is good practice to compare the implied emission factors (reported emissions divided by national zinc production) with the default emission factor values or technology-specific emission factors. If the implied emission factors are outside the 95 % confidence intervals for the values given below, it is good practice to explain the reasons for this in the inventory report

If the total annual zinc production in the country is not included in the total of the facility reports, it is good practice to estimate the missing part of the national total emissions from the source category, using extrapolation by applying:

$$E_{Total,pollutant} = \sum_{Facilities} E_{Facility,pollutant} + \left(National\ Production - \sum_{Facilities} Production_{Facility}\right) \times EF$$
 (5)

where:

E<sub>total,pollutant</sub> = the total emission of a pollutant for all facilities within the source

category

E<sub>facility,pollutant</sub> = the emission of the pollutant as reported by a facility

Production $_{total}$  = the production rate in the source category

Production<sub>facility</sub> = the production rate in a facility

EF<sub>pollutant</sub> = the emission factor for the pollutant

Depending on the specific national circumstances and the coverage of the facility-level reports as compared to the total national zinc production, it is good practice to choose the emission factor (*EF*) in this equation from the following possibilities, in decreasing order of preference:

- technology-specific emission factors, based on knowledge of the types of technologies implemented at the facilities where facility level emission reports are not available;
- the implied emission factor derived from the available emission reports:

$$EF = \frac{\sum_{Facilities}}{\sum_{Facilities}} Production_{Facility}$$
(6)

• the default Tier 1 emission factor. This option should only be chosen if the facility level emission reports cover more than 90 % of the total national production

#### 3.4.2 Tier 3 emission modelling and use of facility data

Zinc kilns are major industrial facilities and emission data for individual plants might be available through a pollutant release and transfer registry (PRTR) or another emission reporting scheme. When the quality of such data is assured by a well developed QA/QC system and the emission reports have been verified by an independent auditing scheme, it is good practice to use such data. If extrapolation is needed to cover all zinc production in the country either the implied emission factors for the facilities that did report or the emission factors as provided above could be used.

The emission factor for ore handling is calculated with the following formula:

$$E = M_{dust} \cdot M_{ore} \cdot M_{metals} \cdot M_{productionzinc}^{-1}$$
(7)

where:

 $M_{dust}$  = loss of mass during receipt of ore (weight percentage)

 $M_{ore}$  = yearly average received mass of zinc ores (tonnes)

 $M_{metals}$  = average weight percentage of metals in dust

 $M_{production,zinc}$  = total yearly produced mass zinc (tonnes)

The emission factor, summarizing all processes with vaporisation of off-gas containing heavy metal is calculated using:

$$E = F_{gas} \cdot d \cdot C_{metals} \cdot M_{productionzinc}^{-1}$$
(8)

Where:

 $F_{gas}$  = gas flow of a certain subprocess that emits heavy metals to air

 $(m^3/yr)$ 

d = duration of the period of emission of HMs to air (per subprocess) (yr)

 $C_{metals}$  = average concentration of heavy metals in emitted gas (g/m<sup>3</sup>)

 $M_{production,zinc}$  = total yearly produced mass zinc (tonnes)

# 3.4.3 Emissions can vary widely depending on the ore used and the abatement measures applied. Activity data

Since PRTR generally do not report activity data, such data in relation to the reported facility-level emissions are sometimes difficult to find. A possible source of facility-level activity data might be the registries of emission trading systems.

In many countries national statistics offices collect production data at the facility level but these are in many cases confidential. However, in several countries national statistics offices are part of the national emission inventory systems and the extrapolation, if needed, could be performed at the statistics office, ensuring that the confidentiality of production data is maintained.

# 4 Data quality

## 4.1 Completeness

Care must be taken to include all emissions, from combustion as well as from processes. It is good practice to check, whether the emissions, reported as 'included elsewhere' (IE) under source category 2.C.6 are indeed included in the emission reported under combustion in source category 1.A.2.b.

## 4.2 Avoiding double counting with other sectors

Care must be taken that the emissions are not double counted in processes and combustion. It is good practice to check that the emissions reported under source category 2.C.6 are not included in the emission reported under combustion in source category 1.A.2.b.

#### 4.3 Verification

#### 4.3.1 Best Available Technique emission factors

BAT emission limit values are available from the BREF document for the non-ferrous metal industry (European Commission, 2001).

The BREF document describes the technologies necessary to achieve BAT emission levels. For zinc production, no generic emission concentrations are given that may be compared against the Tier 1 estimate. However, some numbers for different techniques and processes are available from the BREF document and may be used for verification purposes.

# 4.4 Developing a consistent time series and recalculation

No specific issues.

# 4.5 Uncertainty assessment

No specific issues.

#### 4.5.1 Emission factor uncertainties

The quality class of the emission factors is estimated to be about B. Please refer to the general guidance chapter on uncertainties in Part A of the Guidebook for an explanation of how this relates to the 95 % confidence intervals in the emission factor tables.

#### 4.5.2 Activity data uncertainties

No specific issues.

# 4.6 Inventory quality assurance/quality control (QA/QC)

No specific issues.

# 4.7 Gridding

No specific issues.

# 4.8 Reporting and documentation

No specific issues.

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# 6 Point of enquiry

Enquiries concerning this chapter should be directed to the relevant leader(s) of the Task Force on Emission Inventories and Projection's expert panel on Combustion and Industry. Please refer to the TFEIP website (www.tfeip-secretariat.org) for the contact details of the current expert panel leaders.