



Ministry for the
Environment
Manatū Mō Te Taiao

Dioxin and Furan Emissions to Air from Secondary Metallurgical Processes in New Zealand

Volume I Report

Sinclair Knight Merz
SKM

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Executive Summary

This study presents New Zealand data collected to refine estimates for polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions to air from secondary metallurgical processes. These data include the results of a comprehensive survey undertaken to characterise the size and nature of the secondary metallurgical industry, and the results of emission measurements from a range of different processing sites throughout the country.

Industry survey

The survey determined there were 82 sites falling within the scope of the study, melting approximately 91,000 tonnes of metal per year. This tonnage is greater than that estimated in 1998, where approximately 70,000 tonnes were attributed to the same process categories (Ministry for the Environment, 2000). The difference is largely accounted for by the contribution from medium- and small-scale ferrous foundries, which were mostly ignored in 1998, and offset slightly by one large site recently ceasing to process copper-based scrap (much of which may now go offshore).

Other key findings of the survey were:

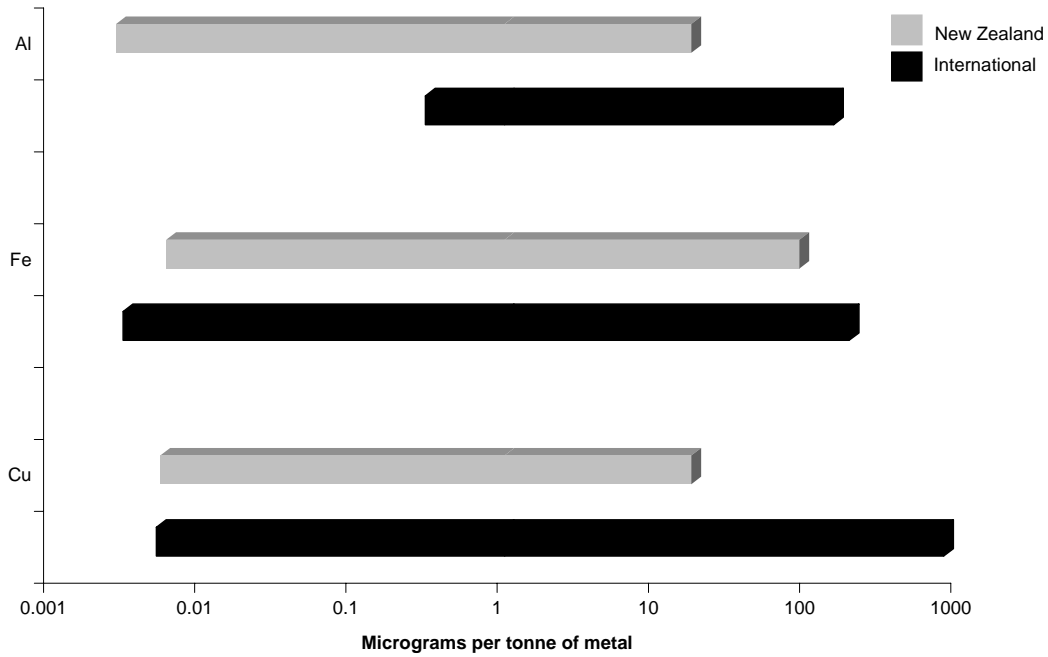
- the majority of the metal is melted in large sites, which are responsible for 71% of the total production
- the most common furnaces in use are electric induction and oil- or gas-fired crucibles
- most large and medium sites have fabric filtration for air pollution control
- the processing of dirty or contaminated scrap is confined mostly to a few large sites
- two or three sites use a thermal scrap pre-treatment process (pyrolysis, combustion, or drying).

Emission measurements

Emission testing was conducted at 12 sites covering a range of metals, furnace types and plant sizes. Twenty-four samples were collected and 30 PCDD and PCDF analyses undertaken, including some samples for which the gaseous and particulate phase were analysed separately. Even though there was considerable scatter in the measured emissions, all results fell within the range of comparable international data (see following figure).

Apart from two sites, emissions were well below the maximum emissions from overseas data when expressed as mass of PCDD and PCDF per tonne of metal melted. This indicates that, generally, emissions from the New Zealand secondary metallurgical industry are low.

New Zealand PCDD and PCDF emissions compared to international data



Sites that showed comparatively higher emissions were:

- large sites
- sites that processed dirty or contaminated scrap
- a site where the pollution control equipment was thought to have been malfunctioning.

There is no evidence, from the data collected, to show a disproportionate emission per tonne of metal melted from smaller (less-controlled) sites. The larger sites appear to contribute the majority of PCDD and PCDF emitted.

The contribution to New Zealand’s PCDD and PCDF emissions

This study estimates that the secondary metallurgical industry emits a total of 0.017 to 3.1 g I-TEQ per year to air, which is similar to the 1998 New Zealand inventory estimate of 0.126 to 3.16 g I-TEQ per year. The new data confirms the 1998 inventory estimates, but also significantly improves confidence in the estimates.

The following table presents estimates for each part of the industry sector.

Annual PCDD and PCDF emissions from the secondary metallurgical industry, 2002

Metal production sector	Basis of production estimate	Annual production (tonnes per annum)	Measured emission factors ($\mu\text{g I-TEQ tonne}^{-1}$)	Emission range (g I-TEQ per year)
Secondary steel	One large plant in Auckland (as per 1998 inventory)	170,000	0.098 – 0.37 ^a	0.017– 0.063
Ferrous foundries	Estimated from this survey	21,000	0.0058 – 89	0.00012 – 1.90
Non-ferrous metals (copper and other)	Estimated from this survey	23,200	0.0053 – 17	0.000012 – 0.394
Secondary aluminium	Estimated from this survey	47,000	0.0027 – 17	0.00013 – 0.799
Total	–	261,200	–	0.017 – 3.10

^a Data from 1998 dioxin inventory.

The total emission estimates include emissions from New Zealand’s largest secondary steel production facility located in Auckland. This site was not part of the monitoring programme for the current study because its emissions have already been well characterised. However, its emissions estimate is provided in the above table for completeness, and to provide a *national* overall figure for the secondary metallurgical industry in New Zealand.

While the 2002 estimates span a larger range of values when compared to 1998, the reliability of the data has improved. In 1998 the estimates for the secondary ferrous industry were rated as high, while production estimates and emission factors for the secondary aluminium industry were rated as having a medium and low certainty respectively. Both the production and emission factors were rated as low for the non-ferrous industry. The new data allows the production estimates and emission factors for ferrous, aluminium and non-ferrous industries all to be given at least medium or high certainty ratings.

Conclusions

The overall findings of this study are:

- the range of measured emissions from the New Zealand secondary metallurgical industry is consistent with international data
- most sites have low emissions, with a small number of large sites contributing most of the total amount of PCDD and PCDF emitted nationally
- estimates of total emissions from the sector are similar to those for the 1998 dioxin inventory, but are considered more reliable.

1 Introduction

1.1 Background

New Zealand has signed but not yet ratified the Stockholm Convention on Persistent Organic Pollutants (POPs).¹ The Convention covers 12 POPs, including polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), commonly known as dioxin, which are listed in Annex C as being unintentionally produced.

The Convention (UNEP, 2001b) sets out a series of measures designed to reduce releases of unintentionally produced POPs, with the goal under Article 5 of “their continuing minimisation and, where feasible, ultimate elimination”. Article 5 requires the development and maintenance of source inventories for the unintentionally produced POPs. Article 11 requires that parties encourage and/or undertake appropriate research and monitoring pertaining to sources and releases into the environment.

Part II of Annex C lists industrial sources with the potential for comparatively high formation and release of PCDD and PCDF to the environment: thermal processes in the metallurgical industry – in particular secondary copper, aluminium and zinc production – are all included. Part III lists thermal processes in the metallurgical industry that are not listed in Part II.

This study aims to contribute to progressing any future New Zealand obligation under the Convention by characterising emissions from thermal processes in the secondary metallurgical industry.

The *New Zealand Inventory of Dioxin Emissions to Air, Land and Water and Reservoir Sources* (Ministry for the Environment, 2000) identified the secondary metal industry as one of New Zealand’s largest industrial sources of PCDD and PCDF. This follows worldwide experience where the secondary metal sector has been identified as an important source of these pollutants.

Ferrous and non-ferrous metallurgical processes have been identified as a source of PCDD and PCDF emissions in many European countries (UNEP, 1999). Based on these national inventories, mainly for industrialised countries, iron and steel (including primary production) were estimated to contribute 10% and non-ferrous metals production 8% of the global flux for the 1995 reference year. There is, however, little information on the proportion contributed from secondary metal production.

The New Zealand dioxin inventory (Ministry for the Environment, 2000) identified uncertainties in emission estimates for non-ferrous metallurgical and foundry processes. The emission factors used were from overseas, and the applicability to New Zealand conditions was considered highly uncertain.

¹ The Government has signalled its commitment to the Convention, and has enacted amendments to the Hazardous Substances and New Organisms and the Imports and Exports Acts to enable ratification.

1.2 Study scope

This study covers those sectors within the metal production and processing industry where there were data gaps from the 1998 dioxin inventory. The inventory covered secondary steel from one large plant in Auckland, non-ferrous metals (estimated for all operations based on employee numbers), and secondary aluminium estimates for four large plants. This report updates the emission factors and production estimates for all secondary processing in New Zealand except the large steel plant in Auckland, because there is high certainty associated with that data.

The phrase ‘secondary metal processes’ in this report refers to processes for melting and refining metals including scrap, ingots, internal returns² and alloying materials. Many of these activities are sometimes referred to as ‘foundry operations’. They have been distinguished from metal production processes involving the reduction of ores and smelting. This study covers both ferrous metals and non-ferrous metals, including aluminium and copper. The principal thermal processes in the secondary metals industry encompass furnace operations and thermal pre-treatment of scrap. The study focuses on furnace emissions after an initial industry survey showed there to be limited thermal pre-treatment of scrap undertaken in New Zealand. Nonetheless, one thermal pre-treatment system was included in the test programme.

Primary metal production is considered distinct from secondary metal processing and as such is not included in this study. There are only two primary production sites in New Zealand (one steel and one aluminium), so emissions from this category can be characterised by focusing on the individual sites. There is already good information on primary steel production in New Zealand, which is undertaken by the Lurgi-Stelco direct reduction process from iron sand and coal, with a capacity of 650,00 tonnes per year and an annual PCDD and PCDF emission of approximately 0.10 g I-TEQ per year. Primary aluminium production is approximately 320,000 tonnes per year using the pre-bake Hall-Heroult process, but emissions from this source have not yet been estimated (Ministry for the Environment, 2000).

There is also limited data on secondary metal processing both in New Zealand and overseas. It was therefore considered necessary to study this part of the metals sector in order to enhance knowledge of New Zealand’s dioxin emissions to air.

In this study an industry survey was carried out to gather information on the metals sector, including process characteristics, plant sizes and pollution controls. Emission testing was then undertaken at selected sites based on the information from the survey. Sites were selected to investigate the range of small through to large production rates, and furnace and metal types commonly present in New Zealand.

² Internal returns are offcuts and off-specification product that are generated internally and recycled to the furnace.

2 Secondary Metal Processes

2.1 Ferrous foundries

Iron and steel foundries produce castings from scrap iron, pig iron, internal returns and alloying materials. The main operations are raw material handling and preparation, melting, mould production, casting and finishing.

Alloying elements may be added to the charge, including ferro-alloys and pure elements such as ferrous silicon, ferrous manganese, ferrous chromium, copper, carbon, and nickel. Fluxes may also be added to assist refining.

Five furnace types are generally used: cupola, arc, induction, reverberatory and crucible. Cupola furnaces are the most common in the USA and Europe (US EPA, 1997; Quass et al, 2000) at least for iron, while electric arc and induction furnaces are usually used for steel. In New Zealand, cupolas are rarely used and furnaces are either electric arc or induction (Newby, 2001). Induction furnaces use a magnetic field to induce heating currents in the metal and require cleaner scrap than electric arc furnaces (EAFs).

Figure 1 provides a diagrammatic representation of an electric arc furnace and an induction furnace.

EAFs are used for melting iron and steel scrap. They allow for the melting of lower-grade scrap, but as a consequence requires appropriate flue-gas capture and cleaning. Typical EAFs have a capacity of around 200 tonnes and are operated as batch processes.

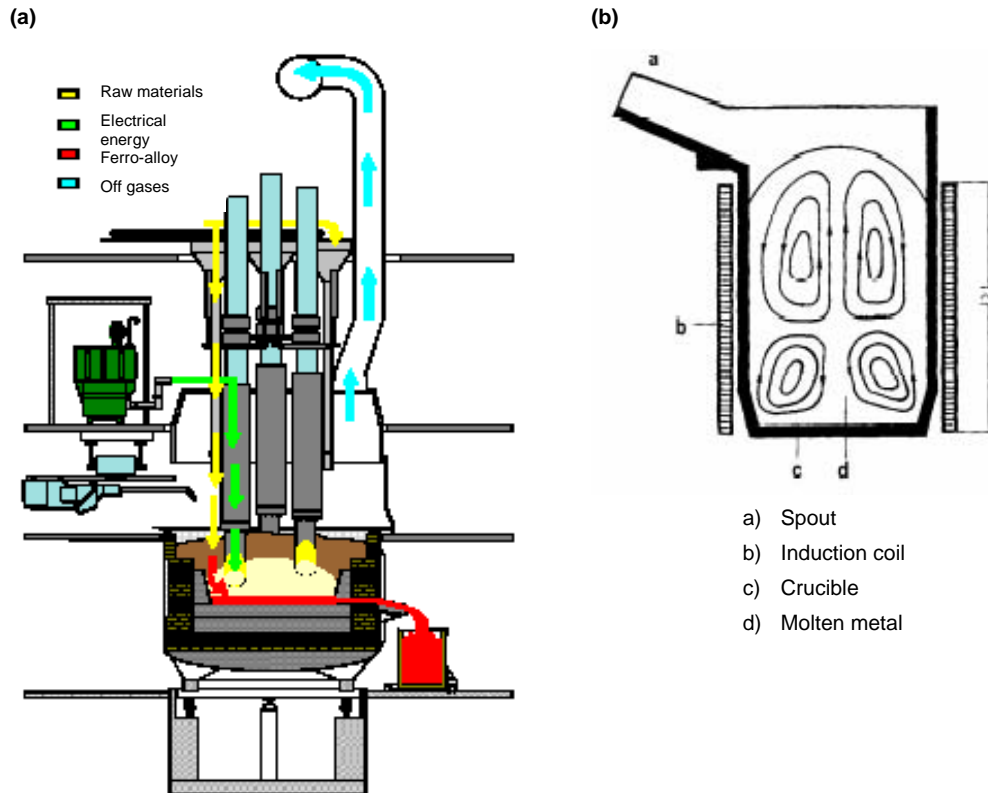
2.2 Secondary copper and alloys

Secondary copper processes generally involve scrap pre-treatment, smelting, refining, alloying and casting of copper, brass and bronze materials.

A variety of furnaces can be used. Induction furnaces are suitable where the alloy composition can be achieved without significant refining. Gas-fired rotary or reverberatory furnaces may be appropriate where degassing is needed or where there are significant quantities of slag from impurities.

In smelting operations, scrap is heated to separate the various metals by their different melting points. Smelting of low-grade copper scrap begins with melting in either a cupola blast or a rotary furnace, resulting in slag and impure copper. Copper is then charged to a converter, where the purity is increased to about 80 to 90%. A reverberatory furnace is then used to produce copper of about 99% purity.

Figure 1: Rotary electric arc furnace (a), and crucible induction furnace (b)



Source: European Commission 2001b.

Flux may be added to the copper to oxidise impurities, which are then removed as slag.

Alloying involves the addition of one or more other metals to the copper to obtain desirable qualities in the metal. Copper can be alloyed with zinc, tin, nickel, aluminium, lead and other elements to make a wide range of alloys. Common alloys are brass (copper and zinc), bronze (copper and tin), cupro-nickel, aluminium bronze and gun metal (copper with tin or zinc).

2.3 Secondary aluminium and alloys

Secondary processing of aluminium and aluminium alloys includes melting aluminium ingots or clean aluminium scrap, and melting contaminated scrap and scrap containing other metal alloys. Secondary aluminium processes may include the use of chlorine gas as a degassing agent and fluoride- or chloride-containing fluxes.

Scrap metal sources include beverage cans, slags, drosses and engineering wastes such as swarf millings and turnings.

Furnaces used include induction, rotary, resistance and reverberatory furnaces. Induction furnaces are generally used for higher grades of scrap with limited contamination. Unwanted metal contaminants may be removed by using chlorine additions and other fluxes to form a slag that can be mechanically separated. Rotary furnaces can be used for metal reclaimed from a range of less clean raw materials.

In Europe (Farrell, 2001) rotary and reverberatory furnaces are the two main types of furnace used for secondary aluminium smelting. These furnaces are heated from fuel combustion, and the molten aluminium may be pumped to one or more holding furnaces or converters for final alloying.

The reverberatory furnace can operate without salt as a flux, particularly if a metal pump is used to recirculate molten metal. This type of furnace can smelt most secondary materials and is capable of handling larger pieces of scrap. Rotary furnaces may use salt flux to reduce oxidation and/or remove some impurities (e.g. sodium, magnesium, calcium and lithium). Hearth furnaces and induction furnaces normally do not require salt fluxes.

Induction furnaces can produce hardened aluminium by blending with agents such as manganese and silicon. Crucible smelting and refining processes are used to melt small batches of aluminium scrap, typically 500 kg or less.

2.4 Other non-ferrous foundries

Non-ferrous foundries generally melt internal return and alloying ingots. Non-ferrous metal processes, other than aluminium and copper, include tin, lead and zinc.

Crucible furnaces are common for non-ferrous metal melting, which are generally smaller-scale operations at less than 500 kg per batch. Crucibles are externally heated with either combustion gases or with a thermal fluid (heated using electricity). Crucibles operate at lower temperatures than those required for melting iron and steel.

2.5 Thermal pre-treatment of scrap

Scrap metal can be contaminated with paint, organic matter (e.g. oil and cutting fluids). Organic and inorganic forms of chlorine may also be present. Scrap may be thermally pre-treated to remove contamination by burning, drying to evaporate water, or by partial pyrolysis. Burning and pyrolysis of contaminated scrap give rise to products of incomplete combustion such as particulate matter, carbon monoxide and organic compounds, and may emit PCDD and PCDF. Pyrolysis is burning without oxygen, which may suppress formation of PCDD and PCDF because of the lack of oxygen. Pyrolysis and burning units usually employ an afterburner or fabric filtration to control incomplete combustion products. Drying generally has low potential for emissions of PCDD and PCDF depending on the temperature.

Wire-stripping processes and chemical cleaning methods provide alternatives to thermal treatment.

3 Dioxin Discharges

PCDD and PCDF are not produced intentionally (other than for research). They are formed as by-products in some chemical processes, and in almost every combustion process where carbon, oxygen, hydrogen and chlorine atoms are present (Ministry for the Environment, 2000). They have low vapour pressure and mainly adsorb on to particles.

3.1 PCDD and PCDF formation mechanisms

PCDD and PCDF can be released from combustion processes through three mechanisms (Charles E Napier Ltd, 2000; US EPA 1997):

- incomplete destruction of PCDD and PCDF present in feedstock materials
- ‘in-furnace’ formation, such as via condensation of chemically related precursor compounds
- low-temperature downstream formation from simple carbon and inorganic chlorine sources (*de novo* synthesis).

Each of these mechanisms can apply to secondary metals processes.

PCDD and PCDF cannot be made without chlorine, but Charles E Napier (2000) noted that effects other than chlorine concentration dominate PCDD and PCDF formation, based on studies of the chlorine present in commercial combustion systems. Good combustion virtually eliminates furnace carry-over and flame formation of PCDD and PCDF.

3.1.1 Incomplete destruction

If combustion is inefficient, PCDD and PCDF present in materials being combusted can be emitted. Good combustion conditions rely on sufficient temperature, time and turbulence (oxygen) to ensure that any of the compounds present are completely destroyed.

3.1.2 In-furnace formation

During combustion, ring-structured hydrocarbon species (known as precursors) are formed as intermediate combustion products. If chlorine is present, these can react to form PCDD and PCDF. Precursors include chlorobenzene, chlorophenols and chlorinated biphenyls. In-furnace formation has been linked to upset conditions where incomplete combustion of fuels occurs.

3.1.3 *De novo* formation

De novo synthesis has been described as the “oxidative breakdown and transformation of macromolecule carbon structures to aromatic compounds” (Buekens et al, 2001). It generally occurs in the temperature range of 250 to 400°C, but some researchers have suggested it can occur up to 1000°C (Charles E Napier Ltd, 2000). Studies have shown that oxygen in the gas stream is essential for dioxin formation by this route. The formation mechanism also relies on the presence of degenerate graphitic carbon structures such as coal, charcoal and soot. Copper and other metals can have strong catalytic effects, while rapid cooling and certain additives can inhibit formation.

In *de novo* synthesis PCDD and PCDF are formed from chemical compounds that have little resemblance to the PCDD and PCDF molecules (i.e. from non-precursor substances). The features of *de novo* synthesis have been identified as follows:

- The carbon source of the PCDD and PCDF is likely to originate from the solid carbon matrix of fly ash.
- Divalent copper ions have been found to have a strong catalytic effect on PCDD and PCDF formation, while divalent iron, lead, and zinc appear to have only minor effects.
- The presence of molecular oxygen in the gas stream is essential for *de novo* formation, and the rate increases with the concentration of oxygen.
- Gaseous forms of chlorine such as HCl or Cl₂ appear to have little or no influence on the *de novo* synthesis reactions at concentrations found in municipal solid waste incinerator flue gases. It has been concluded that the chlorine, and also the hydrogen, found in PCDD and PCDF are likely to originate from inorganic compounds associated with carbon particles.

3.2 Sources of PCDD and PCDF in secondary metals processes

PCDD and PCDF emissions have the potential to occur from heat pre-treatment of scrap, melting, refining and casting operations. PCDD and PCDF may be released as a fugitive emission in addition to furnaces and thermal pre-treatment. However, there is little information on fugitive emissions³ and it is assumed that the main sources of PCDD and PCDF are the furnace and thermal pre-treatment operations.

Formation or poor destruction of PCDD and PCDF are more significant during combustion upsets or when mixing of air and combustible hydrocarbon is poor, since higher levels of organic compounds can escape furnaces at these times. When combustion conditions are optimal, PCDD and PCDF are generally effectively destroyed. Downstream formation or *de novo* synthesis is likely to be the more significant mechanism in a well-operated furnace.

³ High-volume sampling for Site L undertaken as part of this study provides an indication of casting emissions, and these appear to be low (see section 5).

3.3 Process variables affecting PCDD and PCDF emissions

There are many variables in PCDD and PCDF formation and release. Consequently, there is still a relatively low level of understanding of the PCDD and PCDF formation mechanisms, particularly for the metals industry, to the extent that the prediction of emissions is difficult. Process factors such as scrap quality, metal type, process temperatures, residence time of the exit gas in the *de novo* range and the presence of chlorine, carbon and particulate matter affect the potential for PCDD and PCDF formation. Chlorine may be present from contaminants in scrap, or from process additives such as salt fluxes.

The furnace and metal type appear to be factors, as indicated in the following examples.

The European Commission (2003) reviewed emission data from cupolas, rotary furnaces and induction furnaces with no specific air pollution controls. PCDD and PCDF levels were very low (<0.05 ng/Nm³) for aluminium melting, induction melting of iron and EAF melting of steel. Results were in a wide range (<0.01 – 3 ng/Nm³) for cupola melting and rotary melting of iron.

Copper processes have a higher potential for formation of PCDD and PCDF due to the metal's catalytic effect on the PCDD and PCDF formation mechanism. Clean raw materials, the use of electric furnaces and gas quenching all minimise the potential for PCDD and PCDF formation.

Furnace operating temperatures in ferrous foundries are high compared to those in non-ferrous foundries. This increases the potential for *de novo* formation. For non-ferrous foundries, when ingots or clean scrap are used the potential for PCDD and PCDF formation is very low because both carbon and chlorine are absent.

A study of steel plants re-melting scrap in EAFs (Öberg and Allhammar, 1989) found substantial variation in emissions due to both process variation and different efficiencies in flue-gas cleaning. Slow and continuous charging was found to optimise combustion and resulted in lower emissions. Processes free from chlorine contaminants in the input materials were still found to emit chlorinated aromatics, including PCDD and PCDF.

Furnace design is critical: small-scale, indirect-heated furnaces using clean, raw materials will have low potential for PCDD and PCDF emissions. Direct-fired furnaces, in particular using diesel or fuel oil, may result in carbonaceous particulate matter that can catalyse the formation of PCDD and PCDF, particularly in the presence of copper. Secondary measures (i.e. the use of abatement technologies) are more likely to be needed in these circumstances.

Afterburning (thermal incineration) of flue gases and fabric filtration are the main air pollution controls available for PCDD and PCDF removal.

4 Secondary Metal Production in New Zealand

4.1 Industry survey

An industry survey was used to gather data to characterise the secondary-metal-processing industry. This study covered a range of ferrous and non-ferrous foundries. The data collected included:

- the type and quantity of metals melted
- processes used, including furnace type
- air pollution controls
- furnace additives.

The survey was initially by mail, with a telephone follow-up. The survey form used is provided as Appendix A. Data was also obtained from regional councils, who hold information on some operations from their monitoring and resource consenting activities. Most of the data was collected from September through to December 2002.

Information sources used to identify metallurgical industry sites were an online telephone book search,⁴ the *New Zealand Foundry Industry Directory* (New Zealand Metal Casting Industry Association, 1995), regional councils, and a list generated from the Accident Compensation Corporation (ACC). The ACC has a database for industry premiums classified by industry type. This was searched for the following categories: basic iron and steel manufacturing; iron and steel casting and forging; aluminium smelting; copper, silver, lead and zinc smelting and refining; basic non-ferrous metal manufacturing; and non-ferrous metal casting. This study therefore represents a comprehensive compilation of the possible sites throughout New Zealand.

A list of 250 potential sites was developed and a survey was mailed to all sites. Information was requested on the basis that data for individual sites would be kept confidential.

Some thermal metallurgical operations were excluded from the survey because they did not meet the process description for the survey scope, or because good PCDD and PCDF emission data already existed. The sites excluded are discussed elsewhere, but are as follows:

- a steel mill using the direct reduction (Lurgi-Steelco) process
- a primary aluminium smelter using the pre-brake Hall-Heroult process
- a 170,000 tonne capacity secondary-steel-processing facility
- a medium-sized lead smelter.

⁴ The New Zealand Yellow Pages were searched for scrap metal recyclers, metal smelters and foundries.

4.2 Survey results

4.2.1 Survey response

Industry data was collated from all the sources discussed above; data for some sites was gathered from more than one source. Data was initially collected from regional council resource consent information, then the mail survey, followed by telephone calls. The telephone was used to gather additional information where data was incomplete and to increase the response rate from the survey.

Ninety-seven of the 250 mailed questionnaires were returned, but 58 respondents indicated the survey did not apply to them. This result gave an indication of the proportion of sites that were within the study scope. Regional council data was available for 32 sites, 11 of which returned the survey. The telephone survey gave data for 19 sites for which no other information was available.

Eighty-two secondary-metal-processing sites were confirmed, although there are data gaps for some of these due to incomplete responses.

Table 1 summarises the response rate achieved from the various information sources.

Table 1: Cumulative return rate for survey

Information source	Cumulative return rate ^a
Postal survey returns	39%
Telephone follow-up	46%
Regional council information	57%

^a Five surveys were returned undelivered, so percentages were calculated on the basis of 245 surveys.

Assumptions were needed regarding the 100 or so sites from the survey where no information was obtained. The number of surveys returned from people whose firms did not fit within the survey indicated that it was safe to assume a proportion of the non-returns did not fit within the survey. Information from the *New Zealand Foundry Industry Directory* and/or the telephone book was used to judge whether the additional sites were likely to be secondary-metal processors.

It was estimated that up to 40 additional sites were likely to fit within the study scope. The additional sites were assumed to be in the small size category, because data on larger sites is generally available from the industry itself and regional councils via their regulatory involvement with such sites. As a result, 122 sites were identified as potential secondary-metal-processing sites.

While a moderate response to the survey was achieved in terms of the number of sites, the response rate in terms of total metal melted is very high at greater than 95%. This is because the large and medium categories are responsible for the majority of the production. Any sites not identified are likely to be small and contribute little to total production. It is therefore expected that not including the additional sites will be within the bounds of error for the total production estimates.

Appendix B gives full summary tables of the survey results. A summary and a discussion of the results are provided below.

Table 2 summarises the number of metal industry sites by region.

Table 2: Metal industry sites, by region

Regional council / unitary authority	Number of confirmed operations	Regional council / unitary authority	Number of confirmed operations
Northland	1	Marlborough	0
Auckland	27	Nelson	3
Waikato	7	Tasman	0
Bay of Plenty	2	West Coast	0
Gisborne	0	Canterbury	17
Taranaki	2	Otago	5
Hawke's Bay	1	Southland	1
Manawatu-Wanganui	7	Unknown	41
Wellington	8	Total	122

4.2.2 Metal production data from survey returns

Metal production data varied in quality due to either no response or a partial response from industry participants for some questions. Some respondents were unwilling to provide details they saw as proprietary, such as total annual production figures. These figures were estimated by assuming an average number of operating hours per week multiplied by furnace production in tonnes per hour. However, due to the extensive coverage achieved from the survey, the production data collected can be assigned a medium-to-high certainty ranking, in accordance with the certainty rankings for activity statistics used in the 1998 dioxin inventory (Ministry for the Environment, 2000).

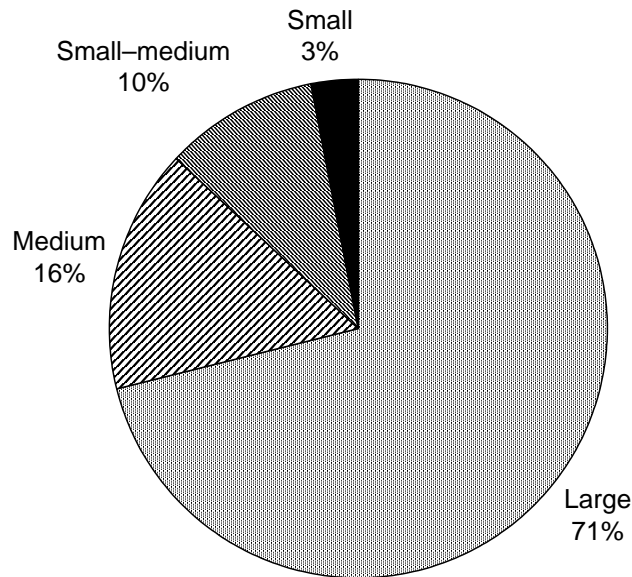
Sites were categorised according to the scale categories identified in Table 3. Six 'large' sites produce 71% of New Zealand's total production as measured by the survey. Conversely there are likely to be about 90 small operators that contribute around 3% of the total production.

Table 3: Metal industry sites, by production quantity for sites surveyed

Category	Size range (tonnes per year)	Number of sites	Total production (tonnes per year)	Percentage throughput
Large	>5,000	6	63,730	71
Medium	>1,000 to 5,000	8	14,791	16
Small-medium	>250 to 1,000	18	8,877	10
Small	≤250	90	2,799	3
Total	–	122	90,197	100

The amount of metal processed by operations according to size category, as a proportion of total industry production, is presented in Figure 2. As discussed in section 1, some very large sites were excluded from this study because emissions data has previously been assembled (Ministry for the Environment, 2000). These include one large steel plant in Auckland processing 170,000 tonnes per year of iron and steel, a large smelter of lead batteries, and a foundry associated with an aluminium producer in the South Island. If these were taken into account the production from plants in the large category would be higher than the 71% shown in Figure 2.

Figure 2: Secondary metal production, by industry size (weight percentage)



The data for production of various metals by size of industry is provided in Table 4 and the distribution is presented in Figure 3. Copper alloys include copper-based metals such as brass, bronze and gunmetal. “Other” includes lead, zinc, manganese, magnesium and tin.

Table 4: Metal production, by metal type for 82 sites surveyed (tonnes per year)

Industry size	Metal production (tonnes per year)			
	Al and alloys	Fe/steel	Cu alloys	Other
Large	44,000	9,000	11,000	0
Medium	1,000	6,000	1,000	7,000
Small-medium	1,000	5,000	2,000	1,000
Small	1,000	1,000	1,000	200
Total	47,000	21,000	15,000	8,200

Most of the aluminium processing takes place at large sites (94% of the total). The great majority of copper processing also takes place at large sites (73%). Small-to-medium sites process a relatively large proportion of the secondary iron and steel production (note that the single 170,000-tonne capacity plant is not included).

Figure 3: Metals processed, by industry size category (tonnes per year)

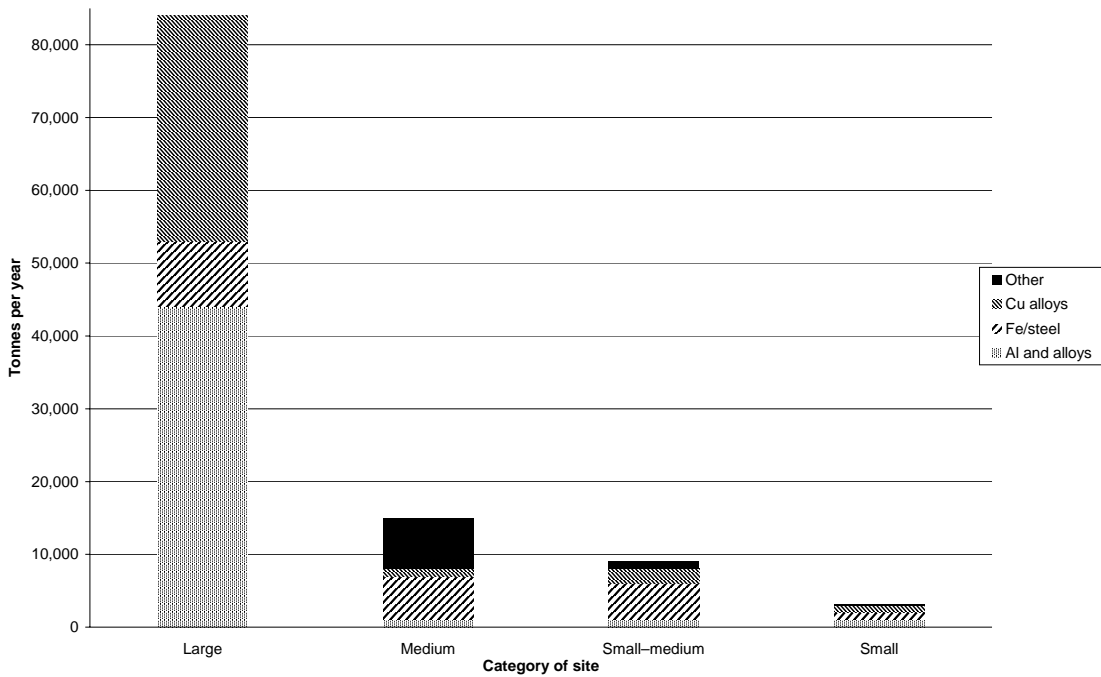
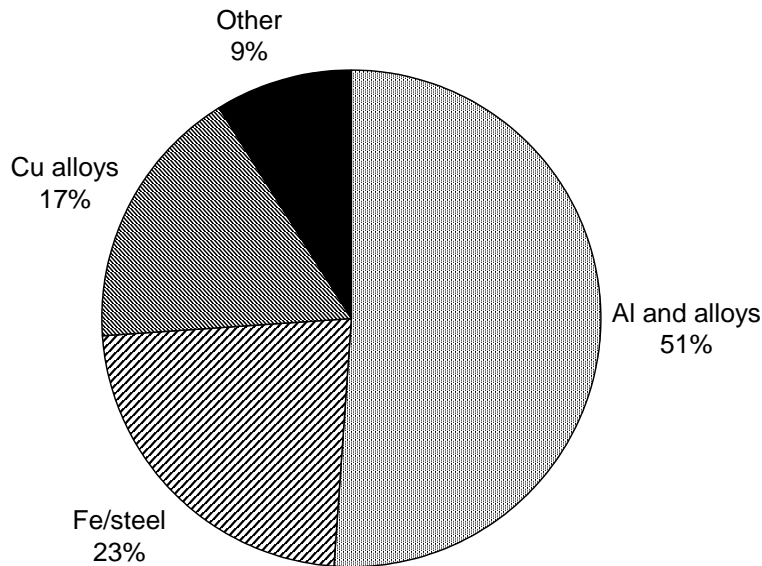


Figure 4 gives the total metal production for each metal category on a weight percentage basis.

Figure 4: Total metal production, by metal type, for 82 sites surveyed (weight %)



Excluding the 170,000 tonnes of iron and steel from the large Auckland plant, aluminium dominates secondary metal production in New Zealand. Aluminium production is mainly from four large sites, all of which were included in the test programme discussed in section 5 of this report. Iron and steel production is spread throughout a large number of plants of varying production scales and technologies. On this basis, it was considered necessary to measure a relatively larger number of sites processing iron and steel. Consequently this sector was well represented in the test programme. Copper production is mainly from one large site, which was unwilling to participate in the test programme.

4.2.3 Furnace types

Table 5 summarises data on the furnace types used within the industry. The data is only for the sites that identified having a particular furnace type. Some sites will have more than one furnace, and additional furnaces may be of the same or a different type. More detail on the total number of each furnace type was not possible due to limitations in the way that respondents completed the survey. It appears, however, that the most common types of furnaces in New Zealand are electric induction furnaces and oil- or gas-fired crucibles, and that these are used at the smaller sites. In contrast, much of the metal processing is done at large sites, which have resistance, rotary and reverberatory furnaces.

Table 5: Sites identifying furnace type

Furnace	Induction	Oil/gas-fired crucible	Arc	Resistance	Cupola	Rotary	Reverberatory	Tilting rotary	Oil/fuel oven	Other/unknown
Number of sites	35	33	5	4	2	2	1	2	1	13

Appendix B summarises furnaces used by metal type and size.

4.2.4 Air pollution control

Fabric filtration is the most common form of air pollution control. All six sites in the large-scale category have fabric filtration and five of the eight furnaces in the medium category also have fabric filters. Five sites were identified as having afterburners and three had water scrubbers. Seventy-five percent of smaller sites ventilate directly to atmosphere via extractor fans with no air pollution control.

Fume capture rates to air pollution control equipment varied from less than 50% to 100% capture (as estimated by the survey respondents). A capture rate of 75% or greater was typical.

The New Zealand industry is not known to have advanced pollution control technologies such as carbon injection or quenching prior to filtration or catalytic filtration. Lime injection, however, would normally be used with fabric filtration because of the corrosive nature of the off-gases.

Air pollution control requirements in New Zealand vary from region to region,⁵ depending on the requirements of the applicable regional plan. Operations over a specific size are required to gain resource consent for air discharges in all regions and the emissions are dealt with on a case-by-case basis. Resource consent conditions are likely to specify scrap quality (if used), air pollution control, and emission limits for particulate matter, where appropriate. Below a certain threshold the activity may be permitted by some councils and have a general requirement not to create an objectionable or offensive effect. No regions have any specific requirements relating to PCDD and PCDF emissions from metal processes that fall within the scope of this study.

Air pollution control equipment used within the industry is summarised in Appendix B.

4.2.5 Scrap quality

Data gathered on raw material was of poor quality, with the raw material type and/or quality not identified for 32 of the 82 sites. Where there was data, 78% of the sites indicated that the raw materials were clean (i.e. ingots or internally generated returns). Others stated raw materials were mixed, but did not state the contaminants present.

It is likely that the majority of dirty scrap is going to a few large sites, which are relatively well controlled. Overall the industry appears relatively clean, with little use of contaminated scrap.

Survey returns indicate that two or three sites have thermal scrap pre-treatment processes controlled by fabric filtration. Overall the rate of scrap pre-treatment is very low.

4.2.6 Furnace additives

About 20% of sites indicated that they used additives. Chlorine gas is not known to be used in New Zealand, but a few sites did identify the use of salt and other fluxes. Nitrogen gas was the most common additive identified for aluminium and copper processes. Four iron and steel sites use a combination of chlorides, fluorides and oxygen.

⁵ For example, in the Proposed Auckland Regional Plan (Auckland Regional Council, 2001) all metal-melting operations other than welding require resource consent for air discharges, while the Otago Regional Plan: Air (Otago Regional Council, 2003) provides a permitted activity for metal processing and foundries less than 250 kg/hour.

5 Dioxin Emission Testing

5.1 Testing programme

Test sites were selected by considering both the number of sites processing various metals and the total quantity of each metal melted. As discussed in section 4, a reasonable number of iron and steel sites were included in the testing programme because there is a large number of small and small-to-medium sites producing secondary iron and steel.

Unfortunately, the largest site, responsible for the majority of copper production, was unwilling to participate in the test programme. One other large site (Site F) also processes copper, and this site was included in the study; but Site F primarily processes aluminium, and emissions from melting copper and aluminium are vented to the same air pollution control equipment. It was not possible to differentiate between metals in this case, and emissions from aluminium processing are likely to have dominated the results.

Some smaller sites were included to investigate whether these were likely to be disproportionately large dischargers of PCDD and PCDF relative to their production because of, for example, poor process control and/or a lack of emission control.

There are many variables, and coverage was achieved as broad as possible within the resources available. The study has not been able to derive emission factors with a specified statistical level of confidence. Nevertheless, the data is considered to be representative of New Zealand emissions because only a few large sites are responsible for the majority of secondary metals production.

Emission testing was carried out at 12 sites throughout the North and South Islands of New Zealand. The testing programme is summarised in Table 6.

The 12 sites represent 10% of the total number of sites in New Zealand, but in terms of metal melted there is a considerably greater degree of representativeness. All four of the largest aluminium processing sites were included, accounting for 95% of the total aluminium production; 75% of the iron and steel production and 23% of the copper production were accounted for in the test programme.

Twenty-four results for total PCDD and PCDF were obtained from 30 analyses, including four gas-phase and particle-phase PCDD and PCDF analyses, and two samples collected by concurrently running two high-volume samplers. The sample train used is able to split the sample into particulate and gas phases, and this was used to investigate possible emissions controls via particulate removal. The sites expected to have the highest particulate matter emissions were used for the splits.

Table 6: Emission testing programme

Site reference	Sample reference	Region	Process description			Size category (from survey)
			Metal	Furnace	Pollution control	
A	S1–S2	Otago	Iron and steel	Arc furnace	Fabric filter	Medium
B	S3	Auckland	Aluminium	Swarf drier	Fabric filter and afterburner	Large
	S4		Aluminium	Gas-fired crucible	Fabric filter	
	S5		Aluminium	Gas-fired crucible	Fabric filter	
C	S6–S7	Auckland	Iron/steel scrap	Induction	Fabric filter	Large
D	S8–S9	Auckland	Copper/bronze clean ingots	Electric induction batch	Fabric filter	Small
E	S10	Auckland	Aluminium internal and external scrap	Induction/remelt furnace	Fabric filter	Large
F	S11–S12	Auckland	Aluminium and copper (mixed)	Rotary/reverberatory and induction	Fabric filter	Large
G	S13–S15	Otago	Steel	Induction	Fabric filter	Small–medium
H	S16–S19	Otago	Iron and steel (mixed)	Induction furnace	Fabric filter (not working)	Medium
I	S20	Waikato	Iron and steel	Induction	Fabric filter	Medium
	S21		Manganese	Induction	Fabric filter	
J	S22–S23	Taranaki	Aluminium (mixed)	Gas-fired crucible	Fabric filter	Large
K	S24–S25	Manawatu-Wanganui	Iron and steel	Electric induction	Fabric filter	Small–medium
L ^a	S26–S27	Auckland	Iron and steel	Electric induction	None	Small
	S28–S30		Bronze	Induction	None	

^a Samples were collected by concurrently running two high-volume samplers with PUF attachments. One unit was near the furnace (S26 and S28+S29) and one near casting (S27 and S30). S28+S29 was a gas-phase particle-phase split.

5.2 Test and analytical methods

Stack emission testing was carried out using US EPA Method 0023A for determining polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans and total particulate from stationary sources. US EPA Methods 1 and 2 were used to select sample point locations and traverses. The number of sampling points was determined in accordance with ISO 9096:1992(E).

Sample times and volumes for each site are reported in Volume II, with other emission test data. A minimum sample time of 2 hours was used. Sample volumes were greater than 1.5 m³ at standard conditions and most samples were 3 to 5 m³. The sample time and/or gas volume may have been limited in some cases due to relatively short processing times and/or low flue gas flows.

Details of the sample locations are provided in Volume II.

High-volume samplers with PUF attachments were used to measure PCDD and PCDF at Site L. US EPA Reference method T-09A was used. Site L has general dilution ventilation via two roof extractor fans. Two samplers were used during each test run; one was located near the furnace operations (S26 and S28+S29) and the other nearer to the casting operations (S27 and S30). The mean concentration of the results from the High-volume samplers was used to determine the emission. The building has good-quality ventilation systems with limited escape of fugitive discharges through doors. Air concentrations within the process building were measured with all doors closed to avoid the risk of emissions escaping undetected. Building ventilation air flows were measured at the same time to give as accurate a measure as possible of building ventilation rates and to allow calculation of mass emission rates.

All XAD-2 resin cartridges were spiked with a range of isotopically labelled PCDD and PCDF standards prior to the collection of the sample. All sample collection media (XAD-2, filters and glassware) were pre-cleaned prior to use.

Following receipt at the laboratory post sampling, samples were stored at 4°C pending analysis. Each sample consisted of an XAD-2 cartridge, filters (Whatman GFC) and solvent rinses. The particulate content for each sample was determined by desiccating then weighing each filter.

Sample extraction, purification and extract work-up steps were based on US EPA 1613B methodology.⁶ Extracts were analysed by isotope dilution using high-resolution gas chromatography – high-resolution mass spectrometry (Micromass Autospec Ultima). The laboratory detection limit for air emission samples is reported at 1–10 pg/m³.

Mass of particulate was estimated by gravimetric determination. Filters were weighed in the laboratory before sampling. After sampling, filters were brought back to room temperature in a desiccator and reweighed to determine the mass of particulate. Particulate analysis results are reported to two significant figures.

PCDD and PCDF analysis results are reported to three significant figures as total mass of PCDD and PCDF in both international toxic equivalencies (I-TEQs) and World Health Organisation toxic equivalencies (WHO-TEQs).

5.3 Quality assurance

The Ministry for the Environment has previously signalled in proposed regulations that PCDD and PCDF sampling should be undertaken by IANZ- or NATA-accredited organisations (Ministry for the Environment, 2001). An IANZ-registered laboratory was used for the analysis, but no accredited stack-testing companies were available in New Zealand, nor were two prominent Australian contractors (at the time). The stack-testing company selected had, however, commenced the process of IANZ accreditation and their application has since been lodged for assessment.

One field duplicate sample was collected by running two sample trains simultaneously in the stack at Site A. The results agreed within a factor of two (S1 and S2). The congener details for all samples are provided in Appendix A of Volume II.

⁶ Method 1613B is an equivalent method to Method 8290, which is referenced in the test method US EPA 0023.

Laboratory methods were quality assured as follows.

- A laboratory glassware and reagent blank was analysed with each batch of samples and assessed for background levels.
- A matrix spike was analysed with each batch of samples to assess method precision and recovery. The matrix spike was spiked into cleaned XAD-2 resin prior to extraction.
- The high-resolution mass spectrometer (HRMS), performance, sensitivity and resolution were established for each instrumental run.
- The recoveries of all isotopically labelled surrogate standards were calculated and reported. The quality control acceptance guideline for surrogate standard recovery was 40–135 % recovery.

A variety of checking procedures were in place to ensure the integrity of all laboratory processes. These included:

- sample receipt checks
- laboratory checks
- HRMS analysis checks
- analytical data and report check
- final report check.

The analytical laboratory used regularly participates in Interlaboratory Comparison Programmes for PCDD and PCDF analysis.

No significant quality issues arose from the laboratory analysis. Background levels in laboratory blanks were insignificant with respect to levels in the samples. Matrix spike recoveries were generally within acceptable limits. In the few cases where the matrix spike recoveries of some analytes were outside the limits specified in US EPA Method 1613B, professional judgement was used in assessing and reporting the analytical data. The matrix spike recovery data for this project is reported in the laboratory data sheets provided in Volume II, Appendix A.

Some isotopically labelled surrogate standard recoveries for samples S3, S7, S8, S12, S14 and S18 were outside the method guidelines of 40–135%. The lowest recovery was 16% (OCDD for sample S7), and the highest was 140% (12378-PeCDF for sample S3). Surrogate recoveries can be influenced by a variety of factors (including the effect of co-extractives in the sample matrix on chromatographic and other laboratory processes), and are often unavoidable.

The US EPA has indicated that even where standard recoveries are outside the method guidelines accurate quantification can still be achieved. Method CARB 428 (California Air Resources Board 1990), an equivalent of US EPA Method 23A, states the following about internal standard recoveries outside the method guidelines:

This criterion is used to assess method performance. As this is an isotope dilution technique, it is, when properly applied, independent of internal standard recovery. Lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF or PCB, but may result in higher detection limits than are desired.

The technique employed is an isotope dilution technique, so the levels of PCDD and PCDF congeners are independent of internal standard recoveries. The effect on the reported levels, and in particular the total toxic equivalence for the affected samples, is therefore deemed minimal.

Sinclair Knight Merz testing specialists checked the results and calculations from the testing in detail.

5.4 PCDD and PCDF results reporting

PCDD and PCDF are reported according to varying conventions. Weightings are given to the individual congeners depending on the convention selected to calculate the total toxic equivalence of a sample. The results in this report are in both WHO (Van den Berg et al, 1998) and International (Kutz et al, 1990) TEQs (WHO-TEQ and I-TEQ). The I-TEQ has been used for the majority of the analysis to allow comparison with measurements and emission factors from other international studies.

TEQs are also reported three ways: with congeners below the limit of detection (LOD) assumed to be zero, half the LOD, and at the LOD. Common convention, particularly in New Zealand, is to include the half LOD in the TEQ calculations, and this was the proposed approach in the Ministry for Environment's dioxin action plan (Ministry for the Environment, 2001).

5.5 Dioxin measurement results

Table 7 reports the mass emissions of PCDD and PCDF per tonne of metal melted (i.e. emission factors for each process). The results are in μg TEQ per tonne of metal, with half the LOD included as per common convention in New Zealand and overseas. There is generally little difference between the I-TEQ and the WHO-TEQ results reported.

Due to the good coverage achieved from the test programme, the emission factor data can be assigned a medium-to-high certainty ranking, in accordance with the certainty rankings for emission factors used in the 1998 dioxin inventory (Ministry for the Environment, 2000). The samples with reference numbers S13+S14, S16+S17, S18+S19 and S29+S30 were separately analysed for particle and gas phase PCDD and PCDF. The results have been added together to give total PCDD and PCDF for the sample.

A summary of the results from the testing programme are presented in Appendix C of this report and full results are presented in Volume II.

The results for Sites F and H (samples S11, S12 and S18+S19) are substantially higher than those measured at other sites. Most sites have fabric filtration and reasonably clean scrap. The higher test results correlate to sites where significantly contaminated scrap was involved. In one case, the scrap had a high proportion of material coated in cutting oils;⁷ in the other case there was a large amount of mixed material. The highest result (S18+S19) may also correlate with poor fabric filter performance, although the particulate test result for this site was not unusually high.

The first sample for Site H (S16+S17) is significantly lower than the second sample (S18+S19). This was due to an error in the sampling procedure, which meant that the sampling time did not cover the main melting operations (i.e. was not representative of melting). Therefore this result has not been considered in the development of emission factors for New Zealand metal melting, although the result is reported in Table 7.

⁷ Personal comment, Stuart Keer-Kerr, K2 Environmental Ltd, 2003.

Table 7: PCDD and PCDF mass emissions per tonne of metal melted

Site reference	Sample reference	Mass PCDD and PCDF per tonne of metal ^a	
		($\mu\text{g I-TEQ tonne}^{-1}$)	($\mu\text{g WHO-TEQ tonne}^{-1}$)
A	S1	0.30	0.35
	S2	0.59	0.64
B	S3	0.20	0.20
	S4	0.0037	0.0044
	S5	0.059	0.064
C	S6	0.030	0.028
	S7	0.14	0.11
D	S8	0.0053	0.0056
	S9	0.017	0.018
E	S10	0.0027	0.0030
F	S11	4.9	5.4
	S12	17	19
G	S13 + S14 ^b	0.041	0.043
	S15	0.017	0.019
H	S16 + S17 ^{b, c}	0.072 ^c	0.076 ^c
	S18 + S19 ^b	89	95
I	S20	0.080	0.086
	S21	0.17	0.17
J	S22	0.54	0.61
	S23	0.053	0.057
K	S24	0.045	0.053
	S25	0.0058	0.0065
L ^d	Av(S26 and S27)	0.011	0.011
	Av(S28 and S29 + S30 ^b)	0.16	0.17

^a Values include half the LODs.

^b The results are added together because the samples were split into particle and gas phase PCDD and PCDF.

^c Sample not representative of metal melting.

^d Samples representative of melting and casting.

Table 8 gives the results for the emission factors by plant size and Table 9 gives results by metal.

Table 8: PCDD and PCDF mass emissions per tonne of metal, by process size

Size category	Number of samples	Mass PCDD and PCDF per tonne of metal ($\mu\text{g I-TEQ tonne}^{-1}$) ^a				
		Lowest	Highest	Average	Geometric mean	Median
Large	10	0.0027	17	2.3	0.13	0.097
Medium	5	0.080	89	18	0.73	0.30
Small-medium	4	0.0058	0.045	0.027	0.021	0.029
Small	4	0.0053	0.16	0.048	0.020	0.014

^a Values include half the LODs.

Table 9: PCDD and PCDF mass emissions per tonne of metal, by metal type⁸

Metal type	Number of samples	Mass PCDD and PCDF per tonne of metal ($\mu\text{g I-TEQ tonne}^{-1}$) ^a				
		Lowest	Highest	Average	Geometric mean	Median
Ferrous	11	0.0058	89	8.2	0.10	0.045
Copper and other ^b	5	0.0053	17	3.5	0.13	0.16
Aluminium ^b	8	0.0027	17	2.9	0.15	0.13
All non-ferrous	12	0.0027	17	1.9	0.096	0.11

^a Values include half the LODs.

^b Includes sample S12, where both aluminium and copper were being melted.

Measured emission concentrations are summarised in Table 10. Data could not be normalised by correcting to 11% O₂ as per the normal convention, because the oxygen concentration at the sampling points was essentially ambient for all the sites. This is because many of the ventilation systems are open systems designed to draw in air from the general workspace, rather than directly ventilating the furnaces as an enclosed system. The air extracted from the furnace is therefore diluted by the workspace air. The precision of the oxygen measurements are such that corrections to 11% O₂ are meaningless when O₂ concentrations approach 21%.

The low PCDD and PCDF concentrations measured are due to dilution from workspace air. Consequently, it is not advisable to compare the results with concentration-based discharge standards.

The individual O₂ concentrations for all sites are given in the Volume II report.

⁸ A total of 23 samples are reported because sample S16 + S17 was not representative of melting operations, as discussed.

Table 10: PCDD and PCDF emission concentrations

Site reference	Sample reference	PCDD and PCDF concentration (ng/m ³ , 0°C, dry) ^a	
		I-TEQ	WHO-TEQ
A	S1	0.014	0.016
	S2	0.024	0.026
B	S3	0.021	0.021
	S4	0.00049	0.00059
	S5	0.0010	0.0011
C	S6	0.0019	0.0018
	S7	0.0090	0.0070
D	S8	0.0013	0.0014
	S9	0.0016	0.0018
E	S10	0.0011	0.0012
F	S11	0.10	0.11
	S12	0.57	0.61
G	S13 + S14 ^b	0.0066	0.0069
	S15	0.0019	0.0022
H	S16 + S17 ^b	0.015	0.016
	S18 + S19 ^b	7.9	8.4
I	S20	0.0037	0.0040
	S21	0.0076	0.0079
J	S22	0.059	0.067
	S23	0.0040	0.0043
K	S24	0.0079	0.0093
	S25	0.0012	0.0013
L	S26+27	0.000036	0.000037
	S28+S29 + S30 ^b	0.00036	0.00038

^a Values include half the LODs.

^b The results are added together because the samples were split into particle and gas phase PCDD and PCDF.

5.6 Particulate matter measurement results

Table 11 presents particulate matter results. All sites tested other than Site L had fabric filtration. Although the stack testers reported that the fabric filter for Site H was not functioning properly, the results are still within the range for the sites with fabric filters. Particulate matter concentrations are not necessarily an indication of pollution control performance because of dilution due to ventilation of general workplace air. This is indicated by the oxygen concentrations measured at the sampling points, which were at or approaching 21%. For Site L the results are from the monitoring workplace atmosphere using the high-volume samplers and are representative of building air.

Table 11: Particulate matter emission concentrations

Site reference	Sample reference	Particulate matter concentration (mg/m ³ , 0°C, dry) ^a
A	S1	17.8
	S2	7.3
B	S4	0.02
	S5	0.67
C	S6	< 0.6
	S7	< 0.6
D	S8	4.1
	S9	2
E	S10	15.7
F	S11	7.2
	S12	< 4
G	S13 + S14 ^b	0.6
	S15	0.1
H	S16 + S17 ^b	34
	S18 + S19 ^b	14
I	S20	0.2
	S21	0.1
J	S22	0.38
	S23	1.09
K	S24	< 0.6
	S25	< 0.2
L	S26 (furnace)	0.83
	S27 (casting)	0.28
	Average S26 and S27	0.56
	S28, S29 + S30 ^b	Damaged filter; analysis not possible

^a Values include half the LODs.

^b The results are added together because the samples were split into particle and gas phase PCDD and PCDF.

5.7 Relationship of PCDD and PCDF to particulate matter

It is possible to obtain a general indication of the distribution of PCDD and PCDF between the particulate and gas phase by analysing the filter material and XAD traps separately. Table 12 gives the results of the four samples for which this was done.

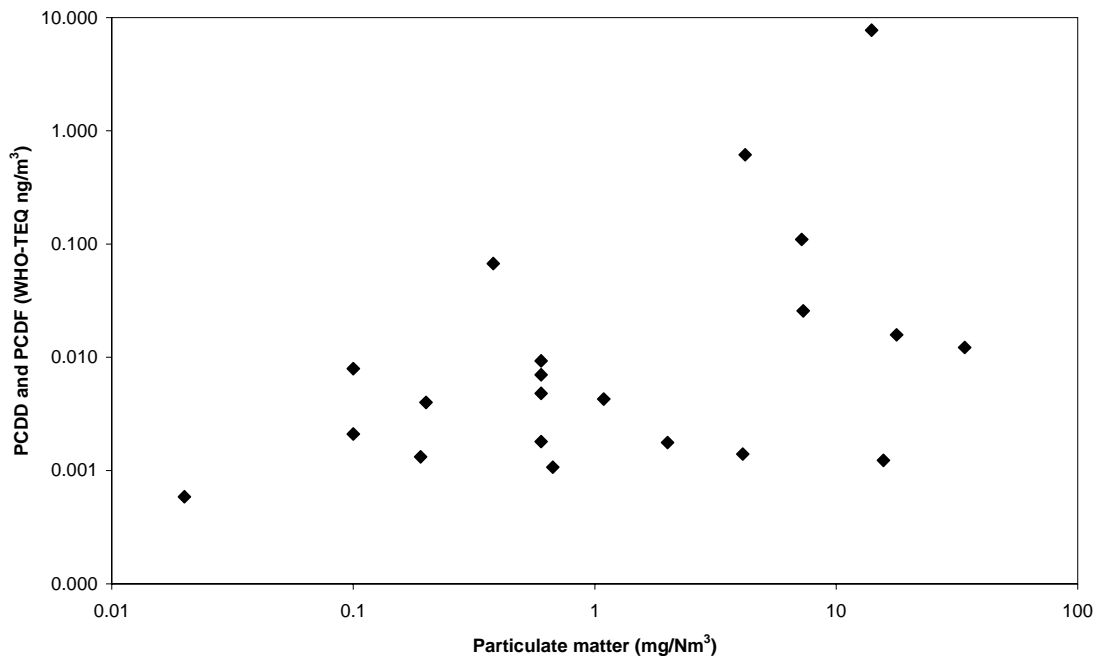
The results indicate that the majority of PCDD and PCDF is associated with the particulate phase. It should be recognised, however, that split analysis of the filters and XAD traps may only give a crude indication of the proportion of PCDD and PCDF found in particulate. This is because the results can be affected by the characteristics of the sampling method rather than the true distribution within the flue gas.

Table 12: Particle-bound PCDD and PCDF

Sample reference	Process	Concentration (ng I-TEQ per m ³)			Percentage particle bound
		Particle bound	Gas phase	Total	
S13 + S14	Steel induction furnace fabric filter	0.005	0.002	0.007	70
S16 + S17	Iron and steel (mixed) induction furnace (fabric filter not working)	0.012	0.003	0.015	79
S18 + S19	Iron and steel (mixed) induction furnace (fabric filter not working)	7.3	0.6	7.9	92
S28 + S29	Bronze induction furnace (fugitive)	0.00077	0.000029	0.00080	96

Figure 5 is a log-log graph showing the correlation between measured levels of particulate matter and PCDD and PCDF for each sample. There is a reasonable degree of scatter in the relationship. This is not unexpected because of the range of variables and the complex factors associated with PCDD and PCDF formation. Nevertheless, low PCDD and PCDF results tend to correlate with low particulate matter results.

Figure 5: Measured particulate matter emissions vs PCDD and PCDF concentration



The results in Table 12 and the correlation in Figure 5 generally confirm that a high level of particulate control will contribute to minimising PCDD and PCDF emissions in New Zealand, although other variables such as the condition of scrap may have a larger influence.

6 Comparison with International Data

6.1 Data limitations

The secondary metal sector is characterised by a wide variety of furnace types operated in different modes and with a range of air pollution controls. Furthermore, the input materials being processed will vary considerably. Taken together, these factors mean that emissions can be expected to vary widely from plant to plant, over time, and with changes to the operation of an individual plant.

Emissions of PCDD and PCDF from the secondary metal sector have not been comprehensively studied internationally. Much of the data that is available is derived from tests in Germany, where standards of pollution control on plants and controls over input materials are likely to be among the most stringent in the world. Consequently, the relatively low emission factors from these studies may not be representative of other countries. Conversely, some data is available for older plants with practices that are no longer carried out, or where air pollution control has improved.

In some cases systems are in place to collect particulate matter from flue gases. The filter or cyclone dusts may contain PCDD and PCDF at high levels and these become a further discharge to the environment upon disposal to land.

6.2 Ferrous foundries

The US EPA *Draft Dioxin Reassessment* (US EPA, 2000) contains emission factors for ferrous foundries. The emission factors used were from data reported from Germany for a variety of furnaces. The mean of the data was 1.26 $\mu\text{g I-TEQ tonne}^{-1}$ of metal feed, although the factors spanned four orders of magnitude.

Testing by the California Air Resources Board⁹ (CARB) had been undertaken but was not considered to be representative of the US industry. The CARB testing was based on batch-operated cupola furnaces charged with pig iron, scrap iron, steel scrap, coke and limestone, with an oil-fired afterburner and a fabric filter (US EPA, 2000). The CARB data gave an emission factor of 0.37 $\mu\text{g I-TEQ tonne}^{-1}$ of metal feed (0.42 $\mu\text{g WHO-TEQ tonne}^{-1}$).

German testing of electric arc furnaces showed a wide range of emissions factors (Working Group, 1996). Flue gas treatment using fabric filters appeared to capture about 90% of the PCDD and PCDF. Emissions ranged from about 0.025 to 5 $\mu\text{g I-TEQ tonne}^{-1}$ (product). It should be noted that runs using a plant with scrap pre-heat gave emission concentrations about 10 times higher than the other data. (No emission factor could be calculated from the data available, but it would likely be of the order of 20–50 $\mu\text{g I-TEQ tonne}^{-1}$.)

⁹ AB-2588 facility test report.

Tysklind et al (1989) tested an EAF continuously charging with a mixed scrap containing a variable chlorine content, and measured 0.8–30 µg Nordic-TEQ tonne⁻¹ dry without fabric filtration and 0.2–7.7 µg Nordic-TEQ tonne⁻¹ with fabric filtration. The worst case was batch charging of an open furnace with materials containing cutting oils, which resulted in 190 µg Nordic-TEQ tonne⁻¹. The reported emission factors were 13 µg Nordic-TEQ tonne⁻¹ for batchwise charging and 7.7 µg Nordic-TEQ tonne⁻¹ for continuous charging.

A study of nine Swedish steel plants remelting scrap in an EAF (Öberg and Allhammar, 1989) gave dioxin emissions in the range <0.23–9.0 µg TEQ (Eadon) tonne⁻¹ product.

The *European Dioxin Inventory Stage II* (Quass et al, 2000) emission factor for 1985 was 3 µg I-TEQ tonne⁻¹. This was three times higher than the ‘typical’ factor presented in the Stage I report, but within the Stage I range of 0.3–5.7 µg I-TEQ tonne⁻¹. Emission factors have been lowered over time to reflect a decrease in installations using scrap pre-heating devices and improved flue-gas cleaning. The reference also reported tests carried out on “cold blast cupolas” for producing cast-iron and steel. Six tests gave emission concentrations of between 0.003 and 0.184 ng I-TEQ/m³, yielding an average emission factor of 0.35 µg I-TEQ tonne⁻¹ of product with a maximum of 1.45 µg I-TEQ tonne⁻¹ of product.

Table 13 summarises emission factors for liquid steel from the *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases* (UNEP, 2001a). These are also mainly drawn from testing in Germany.

UNEP recommends that an emission factor of 3 µg TEQ tonne⁻¹ of liquid steel is used for EAFs based on tests from plants using clean scrap and virgin iron with some afterburners and fabric filters.

Emissions from EAFs using dirty scrap and containing cutting oils or plastic, and plants with scrap pre-heating and with poor controls, have been found to have higher emissions of PCDD and PCDF. In such cases, UNEP recommends an emission factor of 10 µg TEQ tonne⁻¹ of liquid steel.

Where controls are placed on scrap to exclude cutting oils and heavily contaminated scrap, and gas cleaning with secondary combustion and fabric filtration are used, emissions below 0.1 µg TEQ tonne⁻¹ of liquid steel can be achieved.

Table 13: UNEP iron foundry emission factors

Process	Emission factor (µg I-TEQ tonne ⁻¹ of liquid steel)
Cold air cupola or rotary drum with no gas cleaning	10
Rotary drum with fabric filter	4.3
Cold air cupola with fabric filter	1
Hot air cupola or induction furnace with fabric filter	0.03
EAFs designed for low emissions using clean scrap or virgin iron	0.1

6.3 Secondary copper

The European Stage I inventory gives a typical emission factor of 50 µg I-TEQ tonne⁻¹ of refined copper, with a minimum and maximum value of 5 and 500 µg I-TEQ tonne⁻¹ respectively. The factor was assigned high uncertainty because it was based on a poor data pool. Measurements from the French inventory programme suggested that emission factors were lower, but the Stage I figure was maintained for the European Stage II inventory because there was insufficient evidence to show that the French data were representative of European secondary copper installations.

Emission factors reported for German shaft furnaces or converters and reverberatory furnaces ranged from 5.6 to 110 µg I-TEQ tonne⁻¹ and from 0.005 to 1.56 µg I-TEQ tonne⁻¹ respectively. Emission factors reported for two smelter and casting furnaces in Sweden, in which relatively clean scrap was used as input, were 0.024 and 0.04 µg I-TEQ tonne⁻¹. A smelter in Austria was reported to have an emission factor of 4 µg I-TEQ tonne⁻¹.

A study was conducted of a plant with electrically heated melters fed with copper and zinc to produce brass ingots in Portugal (Coutinho et al, 2001). The study yielded emission factors ranging from 0.09 to 0.4 µg I-TEQ tonne⁻¹. The exhaust system had two gas treatment lines including cooling (to prevent *de novo* synthesis), cyclones and fabric filtration.

UNEP's published emission factors for the secondary copper industry are summarised in Table 14.

Table 14: UNEP secondary copper and brass emission factors

Process		Emission factor (µg TEQ tonne ⁻¹ of brass or copper)
Copper	Basic technology – mixed materials with simple fabric filtration	800
	Well controlled – scrap copper with afterburners and fabric filters	50
	Optimised for PCDD/PCDF control (i.e. rapid water quench or activated carbon)	5
Brass	Simple melting furnace	1
	Induction furnace with air pollution control	0.1

The US EPA dioxin inventory (US EPA, 2000) discusses releases from secondary copper production. The earliest US data relates to a batch-fed cupola-type blast furnace controlled by a gas-fired afterburner and a fabric filter processing a mixture of scrap copper-containing materials and considerable plastic contamination. Emissions were determined to be 779 µg I-TEQ tonne⁻¹ of scrap (810 µg WHO-TEQ tonne⁻¹).

Further testing was carried out on another cupola blast furnace system producing blister copper and fitted with afterburner, cooling tower and fabric filter. Emissions from this plant were 16,618 µg I-TEQ tonne⁻¹ of scrap (16,917 µg WHO-TEQ tonne⁻¹). This plant was operated under reducing conditions.

A third plant was tested which operated under oxidising conditions. The feed was relatively pure and clean, and the rotary furnace was equipped with a primary quench and venturi scrubber. Emissions were reported at 3.6 µg I-TEQ tonne⁻¹ of scrap (3.66 µg WHO-TEQ tonne⁻¹).

6.4 Secondary aluminium

A Portuguese study of secondary aluminium production gave emission factors ranging from 47 to 200 $\mu\text{g I-TEQ tonne}^{-1}$ (Coutinho et al, 2001). Salts fluxes such as sodium chloride, potassium chloride and fluoride were added to the process. There was no treatment of air emissions from these furnaces.

In the US, four facilities were tested in 1995 and two facilities were tested in 1992. The results of testing are summarised in Table 15 (US EPA, 2000).

Table 15: US factors from test data for secondary aluminium

Process	Emission factor ($\mu\text{g I-TEQ tonne}^{-1}$)
Top-charge melt furnace; clean scrap	0.3 ^a
Sweat furnace pre-cleaner, and reverberatory furnace with afterburner	3.2 ^b
Roasting dryer and reverberatory furnace with afterburner and fabric filter (lime addition on the furnace fabric filter)	13 ^b
Roasting dryer and reverberatory furnace with afterburner and fabric filter (lime addition on the furnace fabric filter)	36 ^a
Uncontrolled	52 ^a
Venturi scrubber	22 ^a

^a Charge material.

^b Aluminium product.

The average value in the US tests from the six facilities was 21.1 $\mu\text{g I-TEQ tonne}^{-1}$ of charge material, including the value with very clean scrap.

For the European Stage I inventory, default emission factors ranged from 5 to 100 $\mu\text{g I-TEQ tonne}^{-1}$ with a typical value of 22 $\mu\text{g I-TEQ tonne}^{-1}$, which was used for the estimation in Stage II. Data from 11 facilities tested in Germany had emission factors calculated at 0.01–167 $\mu\text{g I-TEQ tonne}^{-1}$ of charge material. The mean emission factor for the facilities was 42 $\mu\text{g I-TEQ tonne}^{-1}$ of charge material (Working Group, 1996).

UNEP (2001a) has published emission factors for the secondary aluminium industry per tonne of aluminium, as summarised in Table 16.

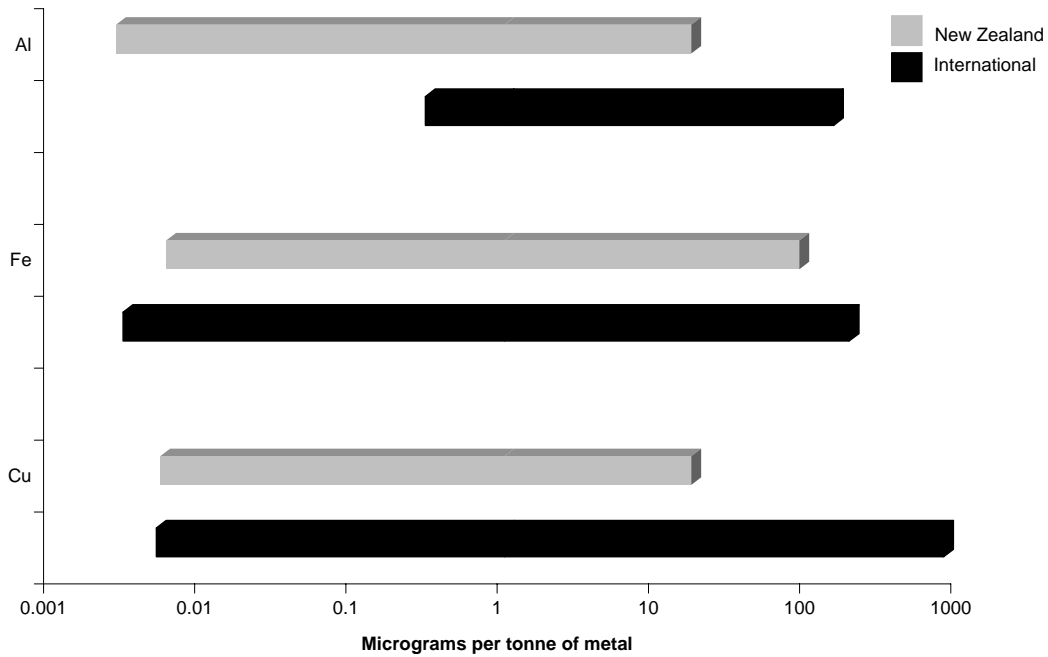
Table 16: UNEP secondary aluminium emission factors

Process	Emission factor ($\mu\text{g TEQ tonne}^{-1}$ of aluminium)
Thermal processing with simple or no dust removal	150
Thermal processing; well-controlled fabric filters with lime injection/afterburners	35
Drying (pre-treatment) of shavings	10
Optimised for PCDD/PCDF control, scrap-cleaning lime injection, afterburners, fabric filters and activated carbon	0.5

6.5 New Zealand measurements compared to international data

Figure 6 provides a comparison of the range of New Zealand measurement data compared to data measured in overseas studies for aluminium (Al), iron and steel (Fe) and copper (Cu). The range of measurements reflects the range of process variables; in particular, scrap quality and air pollution control. Apart from the results for two sites, emissions were well below overseas data, indicating the New Zealand industry generally has low emissions.

Figure 6: PCDD and PCDF emissions per tonne of metal compared to international data



7 The New Zealand Dioxin Inventory

7.1 Basis of the 1998 inventory

The New Zealand dioxin inventory for the reference year 1998 (Ministry for the Environment, 2000) provided a national estimate of PCDD and PCDF emissions to air, land and water, and of quantities present in reservoir sources. Annual emission estimates were derived for each source from an activity statistic and an emission factor.

The total annual estimate for emissions to air in New Zealand was between 14 and 51 g I-TEQ per year. The secondary metals sector was estimated to contribute between 0.126 and 3.16 g I-TEQ per year. The categories used were secondary steel, non-ferrous metals and secondary aluminium production. Table 17 summarises the data used to estimate total annual emissions for 1998.

Table 17: PCDD and PCDF estimates from secondary metals, 1998

Metal production sector	Basis of production estimate	Annual production (tonnes per annum)	Emission factor range ($\mu\text{g I-TEQ tonne}^{-1}$)	Emission range g I-TEQ per year to air
Secondary steel	One large plant in Auckland; excluded small iron and steel foundries	170,000	0.098 – 0.37	0.017– 0.063
Non-ferrous metals (includes a lead smelter)	Total production based on the number of employees in the sector	20,000 – 36,000	5 – 35	0.1 – 1.3
Secondary aluminium	Three large sites in Auckland and one in New Plymouth; included other non-ferrous metal production from these sites	35,000	0.26 – 52.2	0.0091 – 1.8
Total	–	225,000 – 241,000	–	0.126 – 3.16

Source: Ministry for the Environment, 2000.

The secondary metal sector was identified as a reasonably significant contributor to the national emissions from industrial sources, but there was a large uncertainty associated with the estimates due to uncertainty in both the emission factors and the activity statistics.

The emission estimate for secondary steel was based on one plant with an EAF processing steel scrap with a rated capacity of 170,000 tonnes per year, which represented 90% of New Zealand’s iron and steel production at the time. This site was excluded from the present study, as discussed elsewhere. Six samples from the plant over a six-month period gave emissions in the range 0.0064 to 0.239 ng I-TEQ/Nm³ with a mean of 0.0127 ng I-TEQ. This corresponded to an emission factor of 0.098–0.37 $\mu\text{g I-TEQ tonne}^{-1}$. The activity statistic and emission factors were both rated as having high certainty. The estimates for total PCDD and PCDF from the 1998 inventory did not include iron and steel foundries.

Non-ferrous metal production estimates from the 1998 inventory included brass, copper, bronze and lead. Non-ferrous metal foundries in New Zealand were estimated to produce between 0.5 and 30 tonnes per day. The large number of small operators in the sector was identified as a limiting factor in being able to predict accurate production data. Information was used from the Metal Casting Industry Association and the number of employees in the sector to estimate total production at between 20,000 and 36,000 tonnes per year. This figure is similar to the survey results from the present study (see section 4) of 23,200 tonnes per annum, noting that one large secondary copper operation has recently ceased operation.

In 1988 no emission data were available for non-ferrous metals other than tests on a secondary lead smelter (described below), and activity data were extrapolated. An emission factor range of 5 to 35 $\mu\text{g I-TEQ tonne}^{-1}$ was used, sourced from the UK inventory (Her Majesty's Inspectorate of Pollution, 1995).

A factor for New Zealand lead smelting was derived from New Zealand emission testing of 0.45 $\mu\text{g I-TEQ tonne}^{-1}$, consistent with US emission factors for lead. The operation used a gas-fired rotary kiln with fabric filtration. Lead smelting has not been revised as part of this study due to the availability of specific test data, although this site was not accounted for separately in the 1998 inventory.

The 1998 inventory identified that there were four main sites in New Zealand processing secondary aluminium. The total aluminium production from these sites was estimated at 35,000 tonnes per year. No estimate was made for production from small aluminium foundry operations. The survey estimate from the present study, which includes all New Zealand operations, gave 47,000 tonnes, suggesting the 1998 estimates were reasonable and there has been no significant change.

For secondary aluminium production an emission factor range of 0.26–52.2 $\mu\text{g I-TEQ tonne}^{-1}$ was used, which was based on the data reported in the US inventory (US EPA, 1998). The activity statistic was rated as having medium certainty and the emission factor was rated as low certainty.

7.2 Revised dioxin inventory 2002

The inventory previously included emissions from one secondary iron and steel plant, which has a capacity to produce 170,000 tonnes per year. Other ferrous metal plants, particularly foundries, were investigated in the current study. Secondary iron and steel production was found to involve an additional 21,000 tonnes per year.

Table 18: Updated PCDD and PCDF estimates for the secondary metals sector, 20002/03

Metal production sector	Basis of production estimate	Annual production (tonnes per annum)	Measured range ($\mu\text{g I-TEQ tonne}^{-1}$)	Geometric mean ^a ($\mu\text{g I-TEQ tonne}^{-1}$)	Emission range (g I-TEQ per year to air)
Secondary steel	One large plant in Auckland (as per 1998 inventory)	170,000	0.098 – 0.37 ^b	NA	0.017 – 0.063
Ferrous foundries	Estimated from 2002 survey	21,000	0.0058 – 89	0.10	0.00012 – 1.90
Non-ferrous metals (copper and other)	Estimated from 2002 survey	23,200	0.0053 – 17	0.13	0.000012 – 0.394
Secondary aluminium	Estimated from 2002 survey	47,000	0.0027–17	0.15	0.00013 – 0.799
Total	–	261,200	–	–	0.017 – 3.10

^a Taken as the geometric mean of the measured data.

^b Data from 1998 dioxin inventory.

A comparison of data in Tables 17 and 18 shows that tonnes of metal melted have not changed significantly from the estimates in the 1998 inventory. The emission factors developed from the emission-testing programme in New Zealand are similar to those used in 1998, and this is offset by the additional metal production estimates.

While the 2002 estimates span a larger range of values when compared to 1998, the reliability of the data has improved. In 1998 the estimates for the secondary ferrous industry were rated as high. However, production estimates and emission factors for the secondary aluminium industry were rated as having a medium and low certainty respectively, while both the production and emission factors were rated as low for the non-ferrous industry. The new data allows the production estimates and emission factors for ferrous, aluminium and non-ferrous industries all to be given at least medium or high certainty ratings.

Emissions calculated using the geometric mean of the results, as reported in Table 18, are low at 0.012 g I-TEQ per year. Including secondary steel, this gives a range for annual emissions of 0.029 to 0.075 g I-TEQ. But care is needed with this type of estimate because some of the large sites had high emissions, which are effectively ignored by this type of averaging.

An important observation from the measurement programme is that larger sites contribute the major portion of dioxin because they process the majority of the metal. The smaller sites do not appear to contribute a disproportionate amount of dioxin relative to their size and/or production levels. While the flue gases are not always as well controlled as in large plants, it appears that the majority of the poor-quality scrap is confined to the larger sites.

8 International Regulation and Best Practice

8.1 United States

In the United States the US EPA promulgates National Emission Standards for Hazardous Air Pollutants (NESHAP) for Source Categories through the Federal Register, which define the Maximum Achievable Control Technology (MACT) standard.

US National Emission Standards for Hazardous Air Pollutants for Secondary Aluminium Production, Final Rule (US EPA, 23 March 2000) MACT standard for PCDD and PCDF, for affected plants, is to upgrade or install a fabric filter or a lime-injected fabric filter (i.e. a fabric filter to which lime or other alkaline reagent is continuously injected). Alternatively, plants may be required to add a thermal incinerator or afterburner, a thermal incinerator and a lime-injected fabric filter, and/or apply pollution prevention techniques to limit the type of scrap charged and the type and amount of fluxing agents used. Many of these measures are designed to control pollutants other than PCDD and PCDF; for example, lime will help control acid gases such as HCl and SO₂. Table 19 summarises the PCDD and PCDF emission limits specified in the standard.

Table 19: Secondary aluminium NESHAPs (US EPA, 23 March 2000)

Source	Emission limit
Thermal chip drier (that is a major or area source)	2.5 µg TEQ per tonne feed
Scrap drier/de-lacquering kiln (that is a major or area source)	0.25 µg TEQ per tonne feed
Scrap drier/de-lacquering kiln (that is a major or area source) equipped with an afterburner with a 1-second residence time at 750°C	5.0 µg TEQ per tonne feed
Sweat furnace (used to reclaim aluminium from scrap containing iron)	0.8 ng/Nm ³
Group 1 furnace (that is a major or area source) ^a	15 µg TEQ per tonne feed

^a A Group 1 furnace means a furnace that melts, holds or processes aluminium that contains paint, lubricants or coating, or processes clean charge with reactive fluxing (gas, liquid or solid flux that results in a HAP emission).

US National Emission Standards for Hazardous Air Pollutants from Iron and Steel Foundries were proposed in December 2002 (US EPA, 23 December 2002), which include emission limits for metal and organic hazardous air pollutants (HAPs) and operating limits for capture systems and control devices. Carbon monoxide (CO) limits are set as a surrogate for organic HAPs from cupolas. NESHAPs are set for three furnace types: cupolas, electric induction and electric arc. The primary method for reducing organic HAP emissions from cupolas is identified as afterburning at about 700°C or higher. Emission test data suggested that well-controlled cupolas are well below the detection limit for current EPA methods. For existing and new sources, the MACT standard for organic HAP emissions is a CO emission limit of 200 parts per million by volume (ppmv). Organic HAP emissions from electric induction furnaces are not considered significant, and no MACT has been set, although scrap quality and pre-heaters are considered to be integral to induction furnace operation, and volatile organic compounds (VOC) have been used as a surrogate for organic HAP from scrap pre-heating. Afterburners are the MACT floor for existing and new scrap pre-heating and must achieve a 98% or greater reduction in VOC or 20 ppmv. The EPA believes this level of control to be achievable by afterburners and most scrap pre-heaters employing direct flame pre-heating. The MACT floor for organic HAPs from EAFs is the implementation of a scrap selection and inspection programme to minimise the

organic impurities. This is because the organic HAP concentrations are already so low that no technically feasible control technologies could be identified.

MACT requirements for ferro-alloys were promulgated on 20 May 1999.¹⁰

8.2 Japan

Regulatory limits for new facilities in Japan (Nakamura, 2000) have been set for EAFs for steel scrap recycling and the manufacture of aluminium alloys. The limits are 0.5 ng-TEQ/Nm³ and 1.0 ng-TEQ/Nm³ respectively.

8.3 European Union

The European Commission (EC) promulgates guidance on best available techniques (BAT) for individual industry sectors through the Integrated Pollution and Prevention Control (IPPC) sector reference documents. The guidance is adopted into regulations and guidance documents through local jurisdictions within the European Union.

Key BAT considerations for secondary metals are: purchasing and inspecting scrap to avoid contaminated material; furnace design; suitable raw material pre-treatment and process controls, including blending raw materials; optimising temperature and optimising pressure and gas flow to control combustion. Operator training and the use of the correct feed material for the particular furnace or process are also considered to be important.

Techniques considered to be BAT for preventing and destroying PCDD and PCDF in the non-ferrous metals sector are (European Commission 2001a):

- correctly designed and operated afterburners and rapid quenching of the hot gases to less than 250°C to minimise *de novo* synthesis
- optimising combustion conditions using oxygen injection in the upper part of a furnace to ensure complete combustion of furnace gases
- activated carbon absorption in a fixed bed or moving bed reactor, or by injection into the gas stream and fabric filtration
- very high-efficiency dust removal, such as using ceramic filters, high-efficiency fabric filters,
- a catalytic oxidation stage, or fabric filters that incorporate a catalytic coating
- treatment of collected dusts in high-temperature furnaces to destroy dioxins and to recover metals.

Fume generation in all furnaces is required to be minimised by effective furnace control, although this alone is likely to give sufficient abatement to be considered to meet BAT for only copper or cupro-nickel alloys.

¹⁰ www.epa.state.oh.us/dapc/mact/frame1.html.

The emission concentrations associated with the above techniques range from <0.1 to 0.5 ng/Nm³ I-TEQ depending on the feed, the smelting or melting process, and the techniques or combination of techniques that are used for PCDD and PCDF removal.

An EC BAT document for smitheries and foundries is under development (European Commission, 2003). The proposed BAT in relation to PCDD and PCDF formation focuses on the primary and secondary controls. Primary measures to prevent PCDD and PCDF formation include:

- providing a secondary chamber, interlocked with the primary chamber such that the primary chamber cannot be used until the afterburner is up to temperature, and ensuring a residence time of 2 seconds with an oxygen level of >6%
- continuous temperature monitoring and control in the secondary chamber (T >850°C)
- maintaining the particulate matter concentration at a level <20 mg/m³
- providing quick quenching of the off-gases through the *de novo* synthesis range of 250–650°C
- preventing or minimising the build-up of dust along the cooling trajectory of the flue gas, especially in the heat exchanger (e.g. using vertical heat exchanger tubes, efficient internal cleaning, high-temperature de-dusting).

Abatement measures that may be considered are activated carbon injection with high-efficiency fabric filtration, and catalytic oxidation.

The EC BAT reference document for ferrous metal processing (European Commission, 2001a) addresses re-heating and heat treatment furnaces. It focuses on thermal efficiency and good combustion. It does not specifically address PCDD and PCDF emissions.

8.4 United Kingdom best practice

The UK Environment Agency also promulgates technical guidance documents for Integrated Pollution Control (IPC) and Local Authority Air Pollution Control, which are being revised to reflect the requirements of the IPPC directive.

Under the UK regulatory regime smaller, potentially less polluting processes are designated as Part B processes and control over air emissions is the responsibility of the local authorities. The relevant Local Authority Process Guidance Control (LAPC) Process Guidance Notes available from, which are used to assist in the development of legally binding plant-specific authorisations for the metallurgical industry, are currently being reviewed. These guidelines relate to Part B processes. Part A processes (i.e. larger operations) are dealt with on a case-by-case basis through the licensing process.

The following guidance notes relevant to this study are available from the Environment Agency's website (www.environment-agency.gov.uk). All are Draft Process Guidance Notes for Technical Working Group Consultation issued in December 2002, but are comprehensive in relation to PCDD and PCDF from small secondary-metal-processing operations.

- *PG 2/1 Furnaces for the Extraction of Non-Ferrous Metal from Scrap* (UK Environment Agency, 2002c) – covers the extraction of non-ferrous metals from scrap (i.e. refining operations to cleanse, reduce or remove unwanted materials); primarily covers recycling facilities physically treating mixed scrap.

- *PG 2/3 Electrical, Crucible and Reverberatory Furnaces* (UK Environment Agency, 2002b) – covers furnaces in which iron and steel or ferrous alloys are melted and refined, held or poured.
- *PG 2/5 Hot and Cold Blast Cupolas and Rotary Furnaces*(UK Environment Agency, 2002d) – covers furnaces in which iron and steel or ferrous alloys are melted and refined, held or poured.
- *PG 2/6a Processes for Melting and Producing Aluminium and Aluminium Alloys* (UK Environment Agency, 2002e) – covers aluminium foundries melting and producing aluminium and alloys from aluminium ingots or clean returned scrap with limited refining.
- *PG 2/8 Copper and Copper Alloy Processes* (UK Environment Agency, 2002a) – for melting and producing copper and its alloys with limited refining; covers the main alloys of copper including brass, bronze and gunmetal.

The BAT for secondary metal recovery from guidance note PG 2/1 are summarised in Table 20.

Table 20: BAT for non-ferrous metal recovery (PG 2/1)

Source of PCDD and PCDF	Substance contributing to formation	Control technique
Charging the furnace	Products of incomplete combustion	Afterburner temperature should be maintained at > 850°C
Stack emissions from the furnace	Products of incomplete combustion and metal oxides	Use of afterburner and dry filtration plant to minimise emissions
Fluxes	Chloride and fluoride	Minimise flux use to the extent practicable; dry filtration plant where necessary to abate particulate matter

Under PG 2/1 (UK Environment Agency, 2002c), scrap metal facilities will be required to have an afterburner. The afterburner is to burn any products of incomplete combustion that may arise from the primary melter as a result of incorrect fuel-to-air ratios, overloading, or incorrect operating temperatures.

The general techniques to minimise PCDD and PCDF emissions identified in the guidance notes are feedstock control, good combustion and abatement of particulate matter. The specific requirements relating to PCDD and PCDF minimisation are as follows:

If feedstock, fluxes or fuel contains chloride or fluoride (e.g. engine oil, plastic, grease, synthetic materials, potassium aluminium fluoride)

THEN:

1. *Is secondary chamber (after burner) interlocked with primary chamber such that the primary chamber cannot be used until the after burner is up to temperature?*
2. *Is the temperature in the secondary chamber continuously monitored?*
3. *Is the temperature in the secondary chamber maintained at >850°C?*
4. *Is the secondary chamber designed to achieve a residence time of at least two seconds?*
5. *Is the secondary chamber designed to achieve an oxygen level within the combustion chamber of >6%?*
6. *Is there a continuous indicative monitor for particulate matter?*

7. *Is the particulate matter concentration maintained at less than 20 mg per cubic metre?*

If the answer is NO to any of the above questions (1–7) then there is an annual monitoring requirement for dioxins and a limit of 1.0 ng/m³.¹¹

Furthermore, where gases from the secondary chamber are filtered or scrubbed prior to emission in order to achieve the emission limit for particulate matter of 20 mg/m³, then the gases should be cooled quickly (quick quench, within about two seconds) through the de novo synthesis zone of 650 to 250°C.

8.5 Canada

The Canadian Council of Ministers for the Environment (CCME, 2003) has promulgated a Canada-Wide Standard (CWS) for PCDD and PCDF for steel manufacturing in electric arc furnaces, which includes the recovery of steel resources (i.e. secondary metals processing as defined in this study).

The CWS applicable for new and existing furnaces is as follows:¹²

New and modified furnaces

Dioxin and furans emissions shall be less than 100 pg ITEQ/Rm³ from any new or modified steel manufacturing EAF.

Existing furnaces

Phase 1 Dioxin and furans emissions shall be less than 150 pg ITEQ/Rm³ at all existing steel manufacturing EAFs by 2006.

Phase 2 Dioxin and furans emissions shall be less than 100 pg ITEQ/Rm³ at all existing steel manufacturing EAFs by 2010.

¹¹ The reference conditions are specified as 273K, 101.3 kPa; the oxygen and water references should be those corresponding to the normal operating conditions of the process concerned.

¹² Rm³ is the volume at 25°C, 101.3 kPa, dry gas basis and operating O₂ levels.

9 Dioxin Control Options in New Zealand

9.1 Characteristics of the New Zealand industry

Key findings from the survey and test programme are as follows.

- Eleven of 14 large and medium sites have fabric filtration (80%) compared to only 10 of 68 for small-to-medium and small sites (15%). Overall, the rate of control appears low at just over 25% in terms of the number of sites, but in terms of metal melted over 80% is controlled by fabric filtration.
- Five of the 82 (6%) sites have afterburners, which represents 12% in terms of total metal melted.
- Raw materials were reported as comprising generally clean/internally generated scrap or ingots for the majority of sites; most contaminated scrap is processed at a few large sites.
- There is a high level of use of electrical induction furnaces and crucibles, which are generally externally heated with gas or electricity.
- Only two or three sites have thermal scrap pre-treatment processes (pyrolysis, combustion, drying).
- Large sources are responsible for the great majority of the production (71%) and the emissions.
- There are a very small number of sites with relatively high discharges of PCDD and PCDF.
- Emissions factors compare well with emission factors for Europe for highly controlled sites.

9.2 The need for further controls in New Zealand

Given that this study has characterised the New Zealand secondary metal industry as a relatively low emitter of PCDD and PCDF compared to findings for other countries, further controls do not appear to be warranted.

Reductions for the principal emission sources could be considered. Control of PCDD and PCDF is complex - it is not simply a matter of clean scrap, fabric filtration and afterburning, but also involves process control, particularly combustion control. It may be necessary to consider reductions via both primary and secondary measures. Primary measures prevent the formation of PCDD and PCDF and secondary measures prevent the compounds from entering the environment.

Primary measures include:

- selection of clean scrap
- substitution of process raw materials
- improving combustion conditions
- avoiding slow pre-heat of raw materials under conditions that can result in formation of PCDD and PCDF emissions
- quenching the off gases from 500°C to below 200°C

- inhibition of formation by urea or strong basic raw materials (Buekens, 2002).

Secondary measures to remove PCDD and PCDF include:

- the use of afterburners to destroy organic pollutants
- high-efficiency fabric filtration
- catalytic filtration systems which destroy PCDD and PCDF
- adsorption on active carbon or coke
- dry scrubbing with lime and active carbon followed by fabric filtration
- rapid quench to minimise *de novo* formation (650–200°C).

Therefore, given the complexity, potential range of control options and relatively small number of significant sources, the most effective approach to further reductions of PCDD and PCDF emissions from New Zealand's secondary metals industry may be by addressing individual sites on a case-by-case basis. The logical forum for this is through the resource consent process as administered by regional councils. However, it is important for regional decision-makers to recognise the national and global significance of PCDD and PCDF emissions and not just focus on the potential effects on local environments.

Appendix A: Metals Industry Survey Form

Metallurgical Industry Survey – air emissions study

Company name: Contact numbers:.....

Contact person: Email:

1. Melting methods (please copy the form and complete separately for each individual process on-site).

	tick	Production quantity (range)		
		daily (kg)	annual (t)	
electric induction				<i>If unable to specify precisely, please indicate general furnace capacities as follows:</i> "Small" – ≤1,000 kg/day "Small-medium" – 1,000 to 5,000 kg/day "Medium" – 5,000 to 20,000 kg/day "Large" – >20,000 kg/day
arc furnace				
resistance furnace				
cupola				
rotary				
tilting rotary				
reverberatory				
oil/gas fired crucible				
other (specify)				
.....				

2a. Ferrous metals cast

	tick	daily (kg)	annual (t)	
Irons				Specify metal treatment/flux used, e.g. magnesium, O ₂ , lancing, lime, fluorspar, other
Steels				

2b. Non-ferrous metals cast

	tick	daily (kg)	annual (t)	
Aluminium				Specify metal treatment/flux used, e.g. NaCl, chlorine, nitrogen, other additives
Copper-based				
Zinc				
Lead				
Other (specify)				

3. Is the operation batch or continuous?

	tick		
Batch	<input type="checkbox"/>	Approximate time for a batch/melt cycle	_____ hours
Semi-continuous	<input type="checkbox"/>	Size of batch/melt cycle	_____ kg (metals cast)
Continuous	<input type="checkbox"/>		

4. What air pollution control equipment is in place on the furnace?

	tick	<i>If associated with more than one process or furnace specify</i>
Water scrubber	<input type="checkbox"/>	_____
Bag filter	<input type="checkbox"/>	_____ Is lime added to the bag filter? Yes/No
Cyclone	<input type="checkbox"/>	_____
Afterburner	<input type="checkbox"/>	_____
None	<input type="checkbox"/>	_____
Other (specify)	<input type="checkbox"/>	_____

.....

5. Heat recovery or gas quenching on fume extraction? Yes / No

6. Has any emission testing been carried out on the furnace air emissions? Yes / No

7. Any sample ports in main discharge vent? Yes / No
 Reasonable access? Yes / No

8. (Optional) If testing has been carried out, what contaminants have been tested?
 (e.g. particulate matter, metals, dioxins)

.....

Would you make the data available to the study? Yes / No
 (Note confidentiality of your site could be agreed)

9. Condition of input materials used

tick	Metal input quality
<input type="checkbox"/>	clean – internally generated returns or ingots from elsewhere
<input type="checkbox"/>	contaminated with cutting oil (specify if type known) _____
<input type="checkbox"/>	contaminated with paint
<input type="checkbox"/>	contaminated with plastics
<input type="checkbox"/>	mixed
<input type="checkbox"/>	other (specify) _____

10. Is pretreatment or precleaning of scrap used? (Specify)

11. Method of ventilation from furnaces or melters

Is furnace hooded and directly ventilated?

Yes / No

Estimated potential fume capture efficiency over the furnace	tick	
		100%
		75%
		50%
		<50%

12. What form of general workspace ventilation is used?

tick	
	natural
	forced (separate from furnace/s)
	forced (combined with furnace/s)

Appendix B: Survey Results

Table A1: Metal type, air pollution control and raw material quality

Foundry size	Metals processed				Air pollution control	Estimated fume capture (%)	Raw material quality
	Al and Al alloys	Ferrous	Cu and Cu alloys	Other			
Large							
L1	Y		Y		Bag filter	90+	Clean
L2	Y		Y		Bag filter	90+	Mixed
L3	Y				Bag filter	Unknown	Clean
L4			Y	Y	Bag filter	75–100	Clean
L5		Y			Bag filter	75	Clean
L6	Y				Bag filter	Unknown	Clean
Medium							
M1				Y	Unknown		Unknown
M2				Y	Bag filter	100	Unknown
M3	Y	Y			None		Clean
M4	Y	Y	Y		Bag filter	Unknown	Unknown
M5			Y	Y	Bag filter	100	Mixed
					Bag filter (arc)	75	
M6		Y			None (induction)		Clean
M7	Y	Y			None		Clean
M8	Y	Y	Y		Bag filter	Unknown	Unknown
Small–medium							
SM1	Y	Y	Y		None		Unknown
SM2		Y	Y		Unknown		Unknown
SM3		Y			Bag filter	Unknown	Unknown
SM4			Y		Bag filter	Unknown	Clean
SM5			Y		Cyclone	100	Clean
SM6	Y	Y			Bag filter (induction)	75	
					None (crucible)		Mixed
SM7				Y	Bag filter	75–100	Mixed
SM8			Y		Bag filter	75–100	Clean
SM9		Y			None		Clean
SM10	Y				None		Clean
SM11				Y	None		Unknown
SM12		Y			Water scrubber	Unknown	Unknown
SM13		Y			None		Unknown
SM14		Y			None		Unknown
SM15		Y	Y		None		Clean
SM16	Y				None		Unknown
SM17	Y		Y	Y	Bag filter	<50	Clean
					Bag filter (arc)	75	Clean
SM18		Y			None (induction)		
Small							
S1	Y	Y	Y		None		Mixed
S2	Y		Y	Y	None		Mixed
S3	Y	Y	Y		None		Unknown
S4	Y		Y	Y	None		Clean
S5	Y		Y		Afterburner	Unknown	Clean
S6	Y				None		Clean
S7		Y			None		Unknown
S8	Y	Y			Bag filter		Unknown
S9		Y			Water scrubber	100	Clean
S10	Y		Y		Bag filter	75	Clean
S11	Y	Y	Y		Afterburner	>50	Unknown
S12	Y		Y		None		Clean
S13	Y		Y		None		Clean
S14			Y		Filter	75	Clean
S15	Y		Y		Water scrubber	100	Mixed
					Afterburner		
S16	Y	Y	Y	Y	Bag filter	<50	Clean
S17	Y			Y	None		Unknown
S18				Y	None		Mixed
S19	Y		Y	Y	None		Unknown
S20	Y				None		Clean
S21				Y	None		Clean
S22	Y		Y		Cyclone	75	Clean
S23	Y			Y	None		Unknown
S24		Y	Y		None		Clean
S25	Y		Y		None		Unknown
S26	Y		Y		None		Clean
S27	Y	Y	Y		None		Unknown
S28	Y		Y	Y	None		Unknown
S29	Y		Y		None		Clean
S30	Y		Y	Y	None		Clean

Table A2: Furnace type and air pollution control for aluminium production

Foundry size	Type of furnace								Air pollution control
	Induction	Resistance	Rotary	Reveratory	Tilting rotary/ crucible	Oil/gas-fired crucible	Oil/fuel oven	Other	
L1	Y		Y	Y					Bag filter
L2	Y					Y			Bag filter
L3								Remelt (gas)	Bag filter
L6				Y					Bag filter
M3	Y								None
M4	Y								Bag filter
M7		Y							None
M8	Y								None
SM1	Y								None
SM6						Y			Bag filter – ducted hood – crucible
SM10						Y			None
SM16	Y								None
SM17						Y			Bag filter
S1	Y								None
S2						Y			None
S3	Y								None
S4		Y							None
S5						Y			Afterburner
S6					Y	Y			None
S8				Y					
S10	Y								Bag filter
S11	Y								Afterburner
S12								Electric, diesel and gas-fired furnaces	None
S13								Diesel-fired furnace	None
S15							Y		Bag filter – induction
S16	Y	Y				Y			Bag filter
S17								Open (diesel)	None
S19						Y			None
S20						Y			None
S22		Y							Cyclone
S23								Pit	None
S25								Diesel-fired furnace	None
S26	Y					Y			None
S27	Y					Y			None
S28						Y			None
S29						Y			None
S30	Y								None
S31						Y			None
S34								Gas-fired furnace	
S39						Y			None
S41						Y			None
S42						Y			None
S43						Y			None
S44								Unknown	
S45						Y			None
S46								Pit (diesel)	None
S47						Y			None
S48						Y			None
Total	15	4	1	3	1	22	1	9	13

Table A3: Furnace type and air pollution control for ferrous metal production

Foundry size	Type of furnace						Air pollution control
	Induction	Arc	Resistance	Cupola	Oil/gas-fired crucible	Other	
L5	Y						Bag filter
M3	Y						None
M4	Y	Y					Bag filter
M6	Y	Y					Bagfilter – arc None – induction
M7	Y						None
M8	Y						Bag filter – ferrous
SM1	Y						None
SM2						Unknown	
SM3	Y	Y					Bag filter – arc Bag filter – induction
SM6	Y						Ducted hood – crucible
SM9	Y						None
SM12				Y			Water scrubber
SM13	Y						None
SM14		Y					None
SM15	Y						None
SM18	Y	Y					Bag filter – arc Induction – none
S1	Y						None
S7	Y						None
S8							
S9				Y			Water scrubber
S11	Y						Afterburner
S16	Y		Y		Y		Bag filter
S24	Y						None
S27	Y				Y		
S36					Y		None
S37	Y						None
S48					Y		None
Total	20	5	1	2	4	1	11

Table A4: Furnace type and air pollution control for copper production

Foundry size	Type of furnace						Air pollution control
	Induction	Resistance	Tilting rotary/crucible	Oil/gas-fired crucible	Oil/fuel oven	Other	
L1			Y				Bag filter
L2	Y						Bag filter
L4	Y		Y				Bag filter
M4	Y						Bag filter
M5	Y						Bag filter
M8	Y						None
SM1	Y						None
SM2						Unknown	
SM4	Y						Bag filter
SM5	Y						Cyclone
SM8	Y						Bag filter
SM15	Y						None
SM17				Y			Bag filter
S1	Y						None
S2				Y			none
S3	Y						none
S4				Y			None
S5				Y			Afterburner
S10	Y						Bag filter
S11	Y						Afterburner
S12						Electric, diesel and gas-fired furnaces	None
S13						Diesel-fired furnaces	None
S14				Y			Fabric filter
S15					Y		Water scrubber
S16	Y	Y		Y			Afterburner
S18				Y			Bag filter
S22				Y			None
S24	Y						Cyclone
S25						Diesel-fired furnace	None
S26	Y			Y			None
S27	Y			Y			None
S28				Y			None
S29				Y			None
S30	Y						None
S31				Y			None
S32				Y			None
S33	Y						Baghouse
S34						Gas-fired furnace	
S35				Y			None
S38						Unknown	
S42				Y			None
S43				Y			None
S45				Y			None
S48				Y			None
S50				Y			None
Total	20	1	2	20	1	6	16

Table A5: Furnace type and air pollution control for other metals production

Foundry size	Type of furnace					Air pollution control
	Induction	Resistance	Rotary	Oil/gas-fired crucible	Other	
M1						
M2			Y			Bag filter
M5					Diesel-fired furnace	Bag filter
SM7				Y		Bag filter
SM11				Y		None
SM17				Y		Bag filter
S2				Y		None
S4				Y		None
S16	Y	Y		Y		Bag filter
S17					Open (diesel)	None
S18				Y		None
S19				Y		None
S21				Y		None
S23					Pit	None
S28				Y		None
S30	Y					None
S32				Y		None
S40	Y					Filter extractor
S48				Y		None
S49	Y					Afterburner
Total	4	1	1	12	3	8

Appendix C: PCDD and PCDF Emission Test Results

Table A6: PCDD and PCDF emission concentration (ng/m³)

Sample no.	Sample type	Concentration (ng/m ³)					
		Total I-TEQ			Total WHO-TEQ		
		Excluding LOD	Half LOD	Including LOD	Excluding LOD	Half LOD	Including LOD
S1	Gaseous + particulate	0.012	0.014	0.015	0.014	0.016	0.018
S2	Gaseous + particulate	0.022	0.024	0.025	0.024	0.026	0.027
S3	Gaseous + particulate	0.020	0.021	0.022	0.020	0.021	0.023
S4	Gaseous + particulate	0.00000	0.00049	0.00098	0.00000	0.00059	0.0012
S5	Gaseous + particulate	0.00000	0.0010	0.0020	0.00000	0.0011	0.0022
S6	Gaseous + particulate	0.00024	0.0019	0.0036	0.00023	0.0018	0.0033
S7	Gaseous + particulate	0.0060	0.0090	0.012	0.0040	0.0070	0.011
S8	Gaseous + particulate	0.00011	0.0013	0.0025	0.00010	0.0014	0.0027
S9	Gaseous + particulate	0.00004	0.0016	0.0032	0.00004	0.0018	0.0035
S10	Gaseous + particulate	0.00007	0.0011	0.0022	0.00007	0.0012	0.00024
S11	Gaseous + particulate	0.10	0.10	0.10	0.11	0.11	0.11
S12	Gaseous + particulate	0.57	0.57	0.57	0.61	0.61	0.61
S13	Particulate	0.0033	0.0046	0.0059	0.0033	0.0048	0.0063
S14	Gaseous	0.00031	0.0020	0.0036	0.00031	0.0021	0.0039
S13 + S14	Gaseous + particulate	0.0036	0.0066	0.0095	0.0036	0.0069	0.010
S15	Gaseous + particulate	0.00024	0.0019	0.0037	0.00024	0.0022	0.0041
S16	Particulate	0.0083	0.012	0.015	0.0083	0.012	0.016
S17	Gaseous	0.0021	0.0030	0.0040	0.0020	0.0034	0.0047
S16 + S17	Gaseous + particulate	0.010	0.015	0.019	0.010	0.016	0.021
S18	Particulate	7.3	7.3	7.3	7.7	7.7	7.7
S19	Gaseous	0.59	0.59	0.59	0.64	0.64	0.64
S18 + S19	Gaseous + particulate	7.9	7.9	7.9	8.4	8.4	8.4
S20	Gaseous + particulate	0.0033	0.0037	0.0042	0.0036	0.0040	0.0044
S21	Gaseous + particulate	0.0065	0.0076	0.0087	0.0065	0.0079	0.0093
S22	Gaseous + particulate	0.059	0.059	0.059	0.067	0.067	0.067
S23	Gaseous + particulate	0.0024	0.0040	0.0056	0.0024	0.0043	0.0061
S24	Gaseous + particulate	0.0079	0.0079	0.0079	0.0093	0.0093	0.0093
S25	Gaseous + particulate	0.00045	0.0012	0.0019	0.00045	0.0013	0.0022
S26 + S27	Gaseous + particulate furnace and casting	0.00003	0.00004	0.00004	0.00003	0.00004	0.00004
S28 + S29 + S30	Gaseous + particulate furnace and casting	0.00035	0.00036	0.00037	0.00037	0.00038	0.00039

Table A7: PCDD and PCDF emission rate (ng/h)

Sample no.	Sample type	Emission rate (ng/h)					
		Total I-TEQ			Total WHO-TEQ		
		Excluding LOD	Half LOD	Including LOD	Excluding LOD	Half LOD	Including LOD
S1	Gaseous + particulate	280	323	366	331	373	415
S2	Gaseous + particulate	586	632	677	645	690	736
S3	Gaseous + particulate	186	196	207	189	200	211
S4	Gaseous + particulate	0.0	5.0	10	0.0	6.0	12
S5	Gaseous + particulate	0.0	25	51	0.0	27	55
S6	Gaseous + particulate	8.3	67	127	8.2	62	117
S7	Gaseous + particulate	195	303	412	132	251	370
S8	Gaseous + particulate	0.22	2.4	4.5	0.20	2.5	4.8
S9	Gaseous + particulate	0.03	2.8	5.6	0.03	3.1	6.2
S10	Gaseous + particulate	0.25	4.2	8.2	0.25	4.7	9.2
S11	Gaseous + particulate	6,017	6,026	6,036	6,605	6,613	6,620
S12	Gaseous + particulate	33,969	33,971	33,974	36,801	36,802	36,802
S13	Particulate	10	14	18	10	15	19
S14	Gaseous	0.94	5.9	11	0.94	6.4	12
S13 + S14	Gaseous + particulate	11	20	29	11	21	31
S15	Gaseous + particulate	0.74	6.1	11	0.07	6.7	13
S16	Particulate	49	68	88	48	74	94
S17	Gaseous	12	18	23	12	20	27
S16 + S17	Gaseous + particulate	61	86	112	60	94	122
S18	Particulate	40,805	40,805	40,805	43,228	43,228	43,228
S19	Gaseous	3,322	3,322	3,322	3,572	3,572	3,572
S18 + S19	Gaseous + particulate	44,127	44,127	44,127	46,800	46,800	46,800
S20	Gaseous + particulate	38	43	48	41	46	51
S21	Gaseous + particulate	142	165	189	142	172	203
S22	Gaseous + particulate	1,220	1,225	1,229	1,388	1,393	1,397
S23	Gaseous + particulate	50	83	116	50	89	128
S24	Gaseous + particulate	30	30	30	35	35	35
S25	Gaseous + particulate	1.5	3.9	6.4	1.5	4.4	7.3
S26 + S27	Gaseous + particulate	1.3	1.4	1.6	1.3	1.5	1.7
S28 + S29 + S30	Gaseous + particulate	14	15	15	15	15	16

Table A8: PCDD and PCDF emission per tonne of metal (ng/tonne)

Sample no.	Sample type	Emission rate per tonne of metal (ng/tonne)					
		Total I-TEQ			Total WHO-TEQ		
		Excluding LOD	Half LOD	Including LOD	Excluding LOD	Half LOD	Including LOD
S1	Gaseous + particulate	260	300	339	307	346	385
S2	Gaseous + particulate	544	586	628	598	640	682
S3	Gaseous + particulate	186	196	207	189	200	211
S4	Gaseous + particulate	0.0	3.7	7.3	0.0	4.4	8.8
S5	Gaseous + particulate	0.0	59	118	0.0	64	127
S6	Gaseous + particulate	3.7	30	56	3.6	28	52
S7	Gaseous + particulate	87	135	183	59	111	164
S8	Gaseous + particulate	0.49	5.3	10	0.45	5.6	10.8
S9	Gaseous + particulate	0.20	17	33	0.20	18	36
S10	Gaseous + particulate	0.16	2.7	5.3	0.16	3.0	5.9
S11	Gaseous + particulate	4,938	4,945	4,953	5,421	5,427	5,433
S12	Gaseous + particulate	17,245	17,246	17,247	18,683	18,683	18,683
S13	Particulate	21	29	37	21	30	39
S14	Gaseous	2.0	12	23	2.0	13	25
S13 + S14	Gaseous + particulate	23	41	59	23	43	64
S15	Gaseous + particulate	2.1	17	33	2.1	19	37
S16	Particulate	41	57	73	40	60	79
S17	Gaseous	10	15	20	10	16	23
S16 + S17	Gaseous + particulate	51	72	93	50	76	101
S18	Particulate	82,413	82,413	82,413	87,308	87,308	87,308
S19	Gaseous	6,710	6,710	6,710	7,214	7,214	7,214
S18 + S19	Gaseous + particulate	89,123	89,123	89,123	94,522	94,522	94,522
S20	Gaseous + particulate	71	80	90	77	86	95
S21	Gaseous + particulate	142	166	190	142	173	204
S22	Gaseous + particulate	535	537	539	608	610	612
S23	Gaseous + particulate	32	53	74	32	57	81
S24	Gaseous + particulate	45	45	45	53	53	53
S25	Gaseous + particulate	2.2	5.8	9.4	2.22	6.50	10.80
S26 + S27	Gaseous + particulate	9.4	11	12	10	11	12
S28 + S29 + S30	Gaseous + particulate	154	158	162	160	165	170

Units and Abbreviations

g	Gram
µg	Microgram (10 ⁻⁶ g)
ng	Nanogram (10 ⁻⁹ g)
m	Metre
m ³	Cubic metre
Nm ³	Normal cubic metre of dry gas at 0°C and 101.3 kPa
ppmv	Parts per million on a volume basis
pg	Picogram (10 ⁻¹² g)
ACC	Accident Compensation Corporation
BAT	Best available technique
CARB	California Air Resources Board
CCME	Canadian Council of Ministers for the Environment
CO	Carbon monoxide
EAF	Electric arc furnace
EC	European Commission
EPA	Environmental Protection Agency
HAPs	Hazardous air pollutants
HMIP	Her Majesty's Inspectorate of Pollution
HRMS	High-resolution mass spectrometer
IPPC	Integrated Pollution and Prevention Control
I-TEQ	International Toxic Equivalent
LOD	Limit of detection
MACT	Maximum achievable control technology
NESHAP	National Emission Standards for Hazardous Air Pollutants
N-TEQ	Nordic Toxic Equivalent
PCDD	Polychlorinated dibenzo-para-dioxins
PCDF	Polychlorinated dibenzofurans
PG	Process guidance
POPs	Persistent organic pollutants
PPC	Pollution and Prevention Control
PUF	Polyurethane foam
US EPA	United States Environmental Protection Agency
UNEP	United Nations Environment Programme
WHO-TEQ	World Health Organisation Toxic Equivalent

References

- Auckland Regional Council. 2001. *Proposed Auckland Regional Plan: Air Land and Water*. Auckland Regional Council, Auckland.
- Buekens A. 2002. *Studies on dioxin formation in metallurgical processes*. Paper presented at the Chloride Metallurgy 2002: Practice and Theory of Chloride/Metal Interaction conference, Montreal, Canada.
- Buekens A, Stiegliz L, Hell K, et al. 2001. Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. *Chemosphere* 42: 729–35.
- California Air Resources Board. 1990. *Method 428 Determination of Polychlorinated Dibenzo-P-Dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyle Emissions from Stationary Sources*. Californian Environmental Protection Agency, Engineering and Laboratory Branch Monitoring and Laboratory Division www.arb.ca.gov/testmeth/vol3/m_428.pdf.
- CCME (Canadian Council of Ministers for the Environment). 2003. *Canada-Wide Standards for Dioxins and Furans: Steel Manufacturing Electric Arc Furnaces*. Ministry for the Environment, Ontario, Canada.
- Charles E Napier Ltd. 2000. *Background Technical Discussion Paper on the Release and Control of Dioxins/Furans from the Steel Sector* (draft September 2000). Ottawa, Canada.
- Coutinho M, Rodrigues R, Düwel U, et al. 2001. *The DG ENV Dioxin Emission Inventory – Stage II: Characterisation of the emissions of secondary aluminium and copper production plants and a hospital waste incinerator in Portugal*. VDI-BERICHT, 1585: 161–6.
- Environment Canada. 2001. *Release Inventory Report*. Environment Canada, Quebec.
- European Commission. 2001a. *IPCC Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry*. <http://www.jrc.es/pub/english.cgi/0/733169>.
- European Commission. 2001b. *IPCC Reference Document on Best Available Techniques in the Non-ferrous Metals Industries*. <http://www.jrc.es/pub/english.cgi/0/733169>.
- European Commission. 2003. *IPCC Draft Reference Document on Best Available Techniques in the Smitheries and Foundries Industry*. <http://www.jrc.es/pub/english.cgi/0/733169>.
- Farrell F, Hitchens D, Lindblom J, et al. 2001. *The Impact of Best Available Technologies on the Competitiveness of the European Non-ferrous Metals Industry*. Institute for Prospective Technological Studies, Seville.
- Her Majesty's Inspectorate of Pollution. 1995. *A Review of Dioxin Emissions in the UK*. (DOE/HMIP/RR/95/004). Department of the Environment, London.
- Kutz FW, Barnes DG, Bottimore DP, et al. 1990. The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. *Chemosphere* 20: 751–7.
- Ministry for the Environment. 2000. *New Zealand Inventory of Dioxin Emissions to Air, Land and Water, and Reservoir Sources*. Ministry for the Environment, Wellington, New Zealand.
- Ministry for the Environment. 2001. *An Action Plan for Reducing Discharges of Dioxin to Air*. Ministry for the Environment, Wellington, New Zealand.
- Nakamura T. 2000. An Issue on Dioxin Emissions in Metal Production Industries. *Current Advance in Materials Processes* 13(4): 992.
- Newby MR. 2001. *Report on the Growth Potential of the New Zealand Foundry Industry for Industry New Zealand*. Scientific & Industrial Services, Auckland.
- New Zealand Metal Casting Industry Association. 1995. *New Zealand Foundry Industry Directory*. New Zealand Metal Casting Industry Association, Wellington.

- Öberg T, Allhammar G. 1989. Chlorinated aromatics from metallurgical industries: process factors influencing production and emission. *Chemosphere* 19(1–6): 711–16.
- Otago Regional Council. 2003. *Regional Plan: Air*. Otago Regional Council, Dunedin.
- Quass U, Fermann M, Bröker G. 2000. *The European Dioxin Emission Inventory Stage II*. http://europa.eu.int/comm/environment/dioxin/stage2/volume_1.pdf.
- Tysklind M, Söderström G, Rappe C, et al. 1989. PCDD and PCDF emissions from a scrap metal melting process at a steel mill. *Chemosphere* 19(1–6): 705–10.
- UK Environment Agency. 2002a. *Copper and Copper Alloy Processes*. (Process guidance note, draft). UK Environment Agency, Bristol.
- UK Environment Agency. 2002b. *Electrical, Crucible and Reverberatory Furnaces*. (Process guidance note, draft). <http://www.environment-agency.gov.uk/business/lapc>.
- UK Environment Agency. 2002c. *Furnaces for the Extraction of Non-Ferrous Metal from Scrap*. (Process guidance note, draft). UK Environment Agency, Bristol.
- UK Environment Agency. 2002d. *Hot and Cold Blast Cupolas and Rotary Furnaces*. (Process guidance note, draft). UK Environment Agency, Bristol.
- UK Environment Agency. 2002e. *Processes for Melting and Producing Aluminium and Aluminium Alloys*. (Process guidance note, draft). UK Environment Agency, Bristol.
- UNEP (United Nations Environment Programme). 1999. *Dioxin and Furan Inventories, National and Regional Emissions of PCDD/PCDF*. United Nations Environment Programme, Geneva.
- UNEP (United Nations Environment Programme). 2001a. *Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases* (Draft). United Nations Environment Programme, Geneva. Available at: <http://www.chem.unep.ch/pops/pdf/toolkit/toolkit.pdf>.
- UNEP (United Nations Environment Programme). 2001b. *Stockholm Convention on Persistent Organic Pollutants (POPs) Text and Annexes*. United Nations Environment Programme, Geneva.
- US EPA (United States Environmental Protection Agency). 1997. *Locating and Estimating Air Emissions from Sources of Dioxins and Furans* Office of Air Quality Planning and Standards, Office of Air and Radiation, US EPA, Washington, DC.
- US EPA (United States Environmental Protection Agency). 2000. *Draft Dioxin Reassessment*. National Centre for Environmental Assessment, US EPA, Washington, DC. Available at: <http://cfpub.epa.gov/ncea/cfm/ap42/ch12/final/c12s09.cfm>.
- US EPA (United States Environmental Protection Agency). 2000. National Emission Standards for Hazardous Air Pollutants for Secondary Aluminium Production: Final Rule. *Federal Register* 65(57: Pt II; 40 CFR Pt 63). Office of the Federal Register, National Archives and Records Administration, Washington DC.
- US EPA (United States Environmental Protection Agency). 2002. National Emission Standards from Iron and Steel Foundries: Proposed Rule. *Federal Register* 67(246: Pt II; 40 CFR Pt 63). Office of the Federal Register, National Archives and Records Administration, Washington DC.
- Van den Berg M, Birnbaum L, Bosveld ATC, et al. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* 106: 775–92.
- Working Group of the Subcommittee Air/Technology of the Federal Government/Federal States Immission Control Committee. 1996. *Determination of Requirements to Limit Emissions of Dioxins and Furan*. Umweltbundesamt, Berlin, Germany.