

Appendix

GUIDANCE DOCUMENT ON BEST AVAILABLE TECHNIQUES TO CONTROL EMISSIONS OF PERSISTENT ORGANIC POLLUTANTS FROM MAJOR STATIONARY SOURCES

I. INTRODUCTION

1. The purpose of this document is to provide guidance to the Parties to the Convention in identifying control options and best available techniques for reducing emissions of persistent organic pollutants (POPs) from major stationary sources with a view to implementing the obligations of the Protocol on POPs. In particular, it provides guidance to the Parties on reducing their total annual emissions of the substances listed in annex III to the Protocol, in line with the basic obligations set out in article 3 to the Protocol and on meeting the emission limit values for dioxins and furans (PCDD/F) as set out in Annex IV to the Protocol.

2. The document describes control techniques for reducing emissions of dioxins and furans (PCDD/F) as well as of polycyclic aromatic hydrocarbons (PAHs) from major stationary sources. The techniques described may also be used for reducing other POPs. For the information on control options and techniques to reduce emissions of POPs as well as on their performance and costs, the guidance document refers to the best available techniques (BAT) as described in the European Union BAT Reference Documents (EU BREFs) and to other relevant sources.

II. DEFINITIONS

3. In this guidance document:

(a) "Protocol" means the Protocol on Persistent Organic Pollutants adopted in Aarhus on 24 June 1998;

(b) "Parties" means, unless the context otherwise requires, the Parties to the Protocol;

(c) "Persistent organic pollutants" (POPs) are organic substances that: (i) possess toxic characteristics; (ii) are persistent; (iii) bioaccumulate; (iv) are prone to long-range transboundary atmospheric transport and deposition; and (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources;

(d) "Substance" means a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment; or (b) forming a mixture normally marketed as a single article;

(e) "Emission" means the release of a substance from a point or diffuse source into the atmosphere;

(f) "Polycyclic aromatic hydrocarbons"(PAHs): For the purposes of emission inventories, the following four indicator compounds shall be used: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene;

(g) "Polychlorinated dibenzo-p-dioxins/furans" (PCDD/F) are tricyclic, aromatic compounds formed by two benzene rings which are connected by two oxygen atoms in PCDD and by one oxygen atom in PCDF and the hydrogen atoms of which may be replaced by up to eight chlorine atoms;

(h) "Stationary source" means any fixed building, structure, facility, installation, or equipment that emits or may emit any persistent organic pollutant directly or indirectly into the atmosphere;

(i) "Major stationary source category" means any stationary source category listed in annex VIII to the Protocol;

(j) "Best available techniques" (BAT) means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and their impact on the environment as a whole:

(i) 'Techniques' includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

(ii) 'Available' techniques means those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the territory of the Party in question, as long as they are reasonably accessible to the operator;

(iii) 'Best' means most effective in achieving a high general level of protection of the environment as a whole;

III. GENERAL APPROACHES TO CONTROLLING EMISSIONS OF PERSISTENT ORGANIC POLLUTANTS

4. There are several approaches to the control or prevention of POPs emissions from stationary sources. These include the replacement of relevant feed materials, process modifications (including maintenance and operational control) and retrofitting existing plants. The following list provides a general indication of available measures, which may be implemented either separately or in combination:

- (a) Replacement of feed materials which are POPs or where there is a direct link between the composition of the raw-materials and POPs emissions from the source;
- (b) Best environmental practices such as good housekeeping, preventive maintenance programmes, or process changes such as closed systems (for instance in cokeries or use of inert electrodes for electrolysis);
- (c) Modification of process design to ensure complete combustion, thus preventing the formation of persistent organic pollutants, through the control of parameters such as incineration temperature or residence time;
- (d) Methods for flue-gas cleaning such as thermal or catalytic incineration or oxidation, dust precipitation, adsorption;
- (e) Treatment of residuals, wastes and sewage sludge by, for example, thermal treatment or rendering them inert.

5. The emission levels given for different measures in tables 1, 2, 4, 5, 6, 8, and 9 are generally case-specific. The figures or ranges give the emission levels as a percentage of the emission limit values using conventional techniques.

6. Cost-efficiency considerations may be based on total costs per year per unit of abatement (including capital and operational costs). POPs emission reduction costs should also be considered within the framework of the overall process economics, e.g. the impact of control measures and costs of production. Cost-efficiency considerations should take into account that the measures to reduce emissions of POPs also will reduce emissions of other pollutants such as heavy metals or acidifying agents. The cost-efficiency of measures should be established in relation to the effects on all pollutants, and not be based on reduction of only the amount of POPs. Given the many influencing factors, investment and operating cost figures are highly case-specific.

IV. CONTROL TECHNIQUES FOR THE REDUCTION OF EMISSIONS OF DIOXINS AND FURANS

A. Waste incineration

7. Waste incineration includes municipal waste, hazardous waste, medical waste, non-hazardous industrial waste and sewage sludge incineration.

8. The main control measures for PCDD/F emissions from waste incineration facilities are:

- (a) Primary measures regarding incinerated wastes;
- (b) Primary measures regarding process techniques;

(c) Measures to control physical parameters of the combustion process and waste gases (e.g. temperature stages, cooling rate, oxygen content, etc.);

(d) Cleaning of the flue gas;

(e) Treatment of residuals from the cleaning process.

9. The environmentally sound design and operation of waste incinerators requires the use of both best available techniques and best environmental practices (which are to some extent overlapping). Primary measures for municipal or hazardous waste incineration are not sufficient. It is most effective to modify the incineration process and to install secondary measures for flue gas cleaning. Best environmental practices for waste management can be useful primary measures. These practices are focused on environmentally sound waste management for instance waste minimization; recycling; waste inspection; removal of ferrous and non-ferrous metals; proper waste handling, storage and pre-treatment; minimizing storage times; and proper waste loading.

10. Primary measures involving management of feed material by reducing halogenated substances and replacing them by non-halogenated substances are not technically effective appropriate for municipal or hazardous waste incineration.

11. The modification of process techniques to optimize combustion conditions is an important and effective measure for the reduction of PCDD/F emissions (usually 850° C or higher, assessment of oxygen supply depending on the heating value and consistency of the wastes, sufficient residence time – above 850° C for more than 2 seconds -- and turbulence of the gas, avoidance of cold gas regions in the incinerator, etc.). Fluidized bed incinerators keep a lower temperature than 850°C with adequate emission results. For existing incinerators this would normally involve redesigning and/or replacing a plant – an option which may not be economically viable in all countries. The carbon content in ashes should be minimized.

12. If hazardous wastes with a content of more than 1% of halogenated organic substances, expressed as chlorine, are incinerated, the temperature has to be raised to 1,100° C for at least two seconds.

13. Flue gas measures. The following measures are possibilities for lowering reasonably effectively the PCDD/F content in the flue gas. The de novo synthesis takes place at about 250 to 450° C. These measures are a prerequisite for further reductions to achieve the desired levels at the end of the pipe:

(a) Quenching the flue gases (very effective and relatively inexpensive);

(b) Using low-temperature electric discharge systems;

(c) Avoiding fly ash deposition in the flue gas exhaust system.

14. Methods for cleaning the flue gas are:

- (a) Conventional dust separators for the reduction of particle-bound PCDD/F, e.g. electrostatic precipitators (ESP) or fabric filters (bag houses);
- (b) Oxidising organohalogens through selective catalytic reduction (SCR);
- (c) Adsorption with activated charcoal or coke in fixed or fluidized systems;
- (d) Different types of adsorption methods and optimized scrubbing systems with mixtures of activated charcoal, open hearth coal, lime and limestone solutions in fixed bed, moving bed and fluidized bed reactors. The collection efficiency for gaseous PCDD/F can be improved with the use of a suitable pre-coat layer of activated coke on the surface of a bag filter;
- (e) Destruction using catalytic filter bags; and
- (f) Catalytic combustion methods using different types of catalysts (i.e. Pt/A₂O₃ or copper-chromite catalysts with different promoters to stabilize the surface area and to reduce ageing of the catalysts).

15. The methods mentioned above are capable of reaching emission levels below 0.1 ng TEQ/m³ PCDD/F in the flue gas. However, in systems using activated charcoal or coke adsorbers/filters care must be taken to ensure that fugitive carbon dust does not increase PCDD/F emissions downstream. Also, it should be noted that adsorbers and dedusting installations prior to catalysts (SCR technique) yield PCDD/F-laden residues, which need to be reprocessed or require proper disposal.

16. A comparison between the different measures to reduce PCDD/F in flue gas is very complex. The resulting matrix includes a wide range of industrial plants with different capacities and configuration. Cost parameters include the reduction measures for minimizing other pollutants as well, such as heavy metals (particle-bound or not particle-bound). A direct relation for the reduction in PCDD/F emissions alone cannot, therefore, be isolated in most cases. A summary of the available data for the various control measures is given in table 1.

17. Medical waste incinerators may be a major source of PCDD/F in many countries. Specific medical wastes such as human anatomical parts, infected waste, needles, blood, plasma and cytostatica are treated as a special form of hazardous waste, while other medical wastes are frequently incinerated on-site in a batch operation. Incinerators operating with batch systems can meet the same requirements for PCDD/F reduction as other waste incinerators.

18. Parties may wish to consider adopting policies to encourage the incineration of municipal and medical waste in large regional facilities rather than in smaller ones. This approach may make the application of BAT more cost-effective.

19. The treatment of residuals from the flue-gas cleaning process. Unlike incinerator ashes, these residuals contain relatively high concentrations of heavy metals, organic pollutants

(including PCDD/F), chlorides and sulphides. Their method of disposal, therefore, has to be well controlled. Wet scrubber systems in particular produce large quantities of acidic, contaminated liquid waste. Some special treatment methods exist. They include:

- (a) The catalytic treatment of fabric filter dusts under conditions of low temperatures and lack of oxygen;
- (b) The scrubbing of fabric filter dusts by the 3-R process (extraction of heavy metals by acids and combustion for destruction of organic matter);
- (c) The vitrification of fabric filter dusts;
- (d) Further methods of immobilization.

Table 1: Comparison of different flue-gas cleaning measures and process modifications in waste incineration plants to reduce PCDD/F emissions

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Primary measures by modification of feed materials:			
- Elimination of precursors and chlorine-containing feed materials; and - Management of waste streams.	Resulting emission level not quantified; seems not to be linearly dependent on the amount of the feed material.		Pre-sorting of feed material not sufficient; only parts could be collected; other chlorine-containing material, for instance kitchen salt, paper, etc., cannot be avoided. For hazardous chemical waste this is not desirable. Useful primary measure and feasible in special cases (for instance, waste oils, electrical components, etc.) with the possible added benefit of recycling of the materials.
<u>Modification of process technology:</u>			
- Optimized combustion			Retrofitting of the whole process needed.

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
conditions;			
<ul style="list-style-type: none">- Avoidance of temperatures below 850° C and cold regions in flue gas;- Sufficient oxygen content; control of oxygen input depending on the heating value and consistency of feed material; and- Sufficient residence time and turbulence; (i.e.) more than 2 seconds residence time at above 850° C and for Cl (chlorine) content in the feedstock above 1 % (m/m) (<i>at</i>) above 1,100° C.			

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
<u>Flue gas measures:</u> Avoiding particle deposition by:			
- Soot cleaners, mechanical rappers, sonic or steam soot blowers.			Steam soot blowing can increase PCDD/F formation rates.
- Dust removal;	< 10	Medium	Removal of PCDD/F adsorbed onto particles. Removal methods of particles in hot flue gas streams used only in pilot plants.
- Fabric filters;	1-0.1	Higher	Use at temperatures < 250° C.
- Cyclones; and	Low efficiency	Medium	
- Electrostatic precipitation.	Medium efficiency		Formation of PCDD/F risk if used in the range 450-200 °C
Gas quenching.			
High-performance adsorption unit with added activated charcoal particles (electrodynamic venturi).			

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Selective catalytic reduction (SCR).		High investment and low operating costs	NOx reduction if ammonia (NH ₃) is added; high space demand, spent catalysts and residues of activated carbon (AC) or lignite coke (ALC) may be disposed of, catalysts can be reprocessed by manufacturers in most cases, AC and ALC can be combusted under strictly controlled conditions.
Different types of wet and dry adsorption methods with mixtures of activated charcoal, open-hearth coke, lime and limestone solutions in fixed bed, moving bed and fluidized bed reactors:			
Fixed bed reactor, adsorption with activated charcoal or open-hearth coke; and	< 2 (0.1 ng TEQ/m ³)	High in-vestment, medium operating costs	Removal of residuals, high demand of space.
Entrained flow or circulating fluidized bed reactor with added activated coke/lime or limestone solutions and	< 10 (0.1 ng TEQ/m ³)	Low in-vestment, medium operating costs	Removal of residuals.

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
subsequent fabric filter.			
Destruction using catalytic filter bags	<0.5 (0.1 ng TEQ/m ³)	High investment	
Use of carbon impregnated materials of PCDD/F adsorption in the wet scrubbers	30	Low investment	Only applicable to wet scrubbers especially if there is evidence of dioxin built up. Can be used in combination with subsequent dioxin management options

a/ Remaining emission compared to unreduced mode.

B. Thermal processes in the metallurgical industry

20. Specific processes in the metallurgical industry may be important remaining sources of PCDD/F emissions. These are:

- (a) Primary iron and steel industry (e.g., sinter plants, iron pelletizing);
- (b) Secondary iron and steel industry; and
- (c) Primary and secondary non-ferrous metal industry (production of copper).

PCDD/F emission control measures for the metallurgical industries are summarized in table 2.

21. Metal production and treatment plants with PCDD/F emissions can meet a maximum emission concentration <0.1 – 0.5 ng TEQ/m³ (if waste gas volume flow > 5000 m³/h) using control measures. EU BREFs describe for non-ferrous metallurgy, iron and steel production, (sinter plants and electric arc furnaces), that BAT associated emission levels are <0.1 – 0.5 ng TEQ/m³.

Table 2: Options for emission reduction of PCDD/F from thermal processes in the metallurgical industry

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Sinter plants			
<u>Primary measures:</u>			
- Optimization/encapsulation of sinter conveying belts;		Low	Not 100% achievable
- Waste gas recirculation e.g. emission optimized sintering (EOS) reducing waste gas flow by ca. 35% (reduced costs of further secondary measures by the reduced waste gas flow), cap. 1 million Nm ³ /h;	40	Medium	
<u>Secondary measures:</u>			
- Addition of limestone/activated carbon mixtures. Followed by dust separation preferably by fabric filters;	High efficiency (0.1 – 0.5 ng TEQ/m ³)	Medium	
- High-performance scrubbers - existing installation: AIRFINE (Voest Alpine Stahl Linz) since 1993 for 600 000 Nm ³ /h; second installation in use since 1997 in the Netherlands (Corus plant IJmuiden).	High efficiency emission reduction to 0.2-0.4 ng TEQ/m ³	Medium	0.1 ng TEQ/m ³ could be reached with higher energy demand; no existing installation
Non-ferrous production (e.g. copper)			
<u>Primary measures:</u>			
- Pre-sorting of scrap, avoidance of feed material like plastics and PVC-contaminated scrap, stripping of coatings and use of chlorine-free insulating materials		Low	

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
<u>Secondary measures:</u>			
- Quenching the hot waste gases	High efficiency	Low	
- Use of oxygen or of oxygen-enriched air in firing, oxygen injection in the shaft kiln (providing complete combustion and minimization of waste gas volume)	5 - 7 (1.5-2 TEQ/m ³)		
- Fixed bed reactor or fluidized jet stream reactor by adsorption with activated charcoal or open-hearth coal dust; Single- and multi-stage fabric filter with injection of limestone/activated carbon upstream of the filter.	(0.1 ng TEQ/m ³)	High	
- Catalytic oxidation	(0.1 ng TEQ/m ³)	High	
- Reduction of residence time in the critical region of temperature in the waste gas system			
Iron and steel production			
<u>Primary measures:</u>			
- Cleaning of the scrap from oil prior to charging of production vessels		Low	[Cleaning solvents have to be used. – deleted]
- Elimination of organic tramp materials such as oils, emulsions, greases, paint and plastics from feedstock cleaning		Low	
- Lowering of the specific high waste gas volumes; but maximum capture of potentially		Medium	

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
PCDD/F contaminated waste gases is desirable.			
<u>Secondary measures:</u>			
- Separate collection and treatment of emissions from loading and discharging		Low	
- Fabric filtre in combination with coke injection	< 1	Medium	
- Use of an optimal temperature profile during cool-down of waste gas	(<0.1 ng TEQ/m ³)		
- Use of a combustion chamber for treatment of the waste gas			
Secondary aluminium production			
<u>Primary measures:</u>			
- Avoidance of halogenated material (hexachloroethane);		Low	
- Avoidance of chlorine-containing lubricants (for instance chlorinated paraffins)		Low	
- Clean-up and sorting of dirty scrap charges, e.g. by swarf decoating and drying, swim-sink separation techniques and whirling stream deposition			
<u>Secondary measures:</u>			
- Single- and multi-stage fabric filter with added activation of limestone/ activated carbon upstream of the filter	< 1 (0.1 ng TEQ/m ³)	Medium/ high	
- Minimization and separate		Medium/	

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
removal and purification of differently contaminated waste gas flows		high	
- Avoidance of particulate deposition from the waste gas and promotion of rapid passing of the critical temperature range		Medium/ high	
- Improved pretreatment of aluminium scrap shredders by using swim-sink separation techniques and grading through whirling stream deposition		Medium/ high	

^{a/} Remaining emission compared to unreduced mode.

1. Sinter plants

22. Measurements at sinter plants in the iron and steel industry have generally shown PCDD/F emissions in the range of 0.4 to 4 ng TEQ/m³. A single measurement at one plant without any control measures showed an emission concentration of 43 ng TEQ/m³.

23. Halogenated compounds may result in the formation of PCDD/F if they enter sinter plants in the feed materials (coke breeze, salt content in the ore) and in added recycled material (e.g. millscale, blast furnace top gas dust, filter dusts and sludges from waste water treatment). However, similarly to waste incineration, there is no clear link between the chlorine content of the feed materials and emissions of PCDD/F. An appropriate measure may be the avoidance of contaminated residual material and de-oiling or degreasing of millscale prior to its introduction into the sinter plant.

24. The most effective PCDD/F emission reduction can be achieved using a combination of different secondary measures, as follows:

(a) Recirculating waste gas significantly reduces PCDD/F emissions. Furthermore, the waste gas flow is reduced significantly, thereby reducing the cost of installing any additional end-of-pipe control systems;

(b) Installing fabric filters (in combination with electrostatic precipitators in some cases) or electrostatic precipitators with the injection of activated carbon/open-hearth coal/limestone mixtures into the waste gas;

(c) Scrubbing methods have been developed which include pre-quenching of the waste gas, leaching by high-performance scrubbing and separation by drip deposition.

Emissions of 0.2 to 0.4 ng TEQ/m³ can be achieved. By adding suitable adsorption agents like lignite coal cokes/coal slack, an emission concentration of 0.1 ng TEQ/m³ can be reached;

(d) Advanced electrostatic precipitators (ESPs) are available (e.g moving electrode ESP, ESP pulse system, high voltage operation of ESP).

2. Primary and secondary production of copper

25. Existing plants for the primary and secondary production of copper can achieve a PCDD/F emission level of a few picograms to 2 ng TEQ/m³ after flue-gas cleaning. A single copper shaft furnace emitted up to 29 ng TEQ/m³ PCDD/F before optimization of the aggregates. Generally, there is a wide range of PCDD/F emission values from these plants because of the large differences in raw materials used in differing aggregates and processes.

26. Generally, the following measures are suitable for reducing PCDD/F emissions:

(a) Pre-sorting scrap;

(b) Pretreating scrap, for example stripping of plastic or PVC coatings, pretreating cable scrap using only cold/mechanical methods;

(c) Quenching hot waste gases (providing utilization of heat), to reduce residence time in the critical region of temperature in the waste gas system;

(d) Using oxygen or oxygen-enriched air in firing, or oxygen injection in the shaft kiln (providing complete combustion and minimization of waste gas volume);

(e) Adsorption in a fixed bed reactor or fluidized jet stream reactor with activated charcoal or open-hearth coal dust, injection of activated carbon in combination with a fabric filter; and

(f) Catalytic oxidation.

3. Production of steel

27. PCDD/F emissions from converter steelworks for steel production and from hot blast cupola furnaces, electric furnaces and electric arc furnaces for the melting of cast iron may be significantly lower than 0.1 ng TEQ/m³. Cold-air furnaces and rotary tube furnaces (melting of cast iron) have higher PCDD/F emissions.

28. Electric arc furnaces used in secondary steel production can achieve an emission concentration value of 0.1 ng TEQ/m³ if the following measures are used:

(a) Separate collection of emissions from loading and discharging; [and – ~~deleted~~]

- (b) Use of a fabric filter or an electrostatic precipitator in combination with coke injection;
- (c) Use of an optimal temperature profile during cool-down of waste gas; and
- (d) Use of combustion chamber for treatment of the waste gas.

29. A possibility to further reduce PCDD/F emissions is the injection of activated carbon upstream of the fabric filter.

30. The feedstock to electric arc furnaces often contains oils, emulsions or greases. General primary measures for PCDD/F reduction can be sorting, de-oiling and de-coating of scraps, which may contain plastics, rubber, paints, pigments and vulcanizing additives.

4. Smelting plants in the secondary aluminium industry

31. PCDD/F emissions from smelting plants in the secondary aluminium industry are in the range of approximately 0.1 to 14 ng TEQ/m³. These levels depend on the type of smelting aggregates, materials used and waste gas purification techniques employed.

32. In summary, single- and multi-stage fabric filters with the addition of limestone/activated carbon/open-hearth coal upstream of the filter meet the emission concentration of 0.1 ng TEQ/m³, with reduction efficiencies of 99%.

33. The following measures can also be considered:

- (a) Minimizing and separately removing and purifying differently contaminated waste gas flows;
- (b) Avoiding waste gas particle deposition;
- (c) Rapidly passing the critical temperature range;
- (d) Improving the pre-sorting of scrap aluminium from shredders by using swim-sink separation techniques and grading through whirling stream deposition; and
- (e) Improving the pre-cleaning of scrap aluminium by swarf decoating and swarf drying.

34. Options (d) and (e) are important because it is unlikely that modern fluxless smelting techniques (which avoid halide salt fluxes) will be able to handle the low-grade scrap that can be used in rotary kilns.

35. Discussions are continuing under the Convention for the Protection of the Marine Environment of the North-east Atlantic regarding the revision of an earlier recommendation to phase out the use of hexachloroethane in the aluminium industry.

36. The melt can be treated using state-of-the-art technology, for example with nitrogen/chlorine mixtures in the ratio of between 9:1 and 8:2, gas injection equipment for fine dispersion and nitrogen pre- and post-flushing and vacuum degreasing. For nitrogen/chlorine mixtures, a PCDD/F emission concentration of about 0.03 ng TEQ/m³ was measured (as compared to values of > 1 ng TEQ/m³ for treatment with chlorine only). Chlorine is required for the removal of magnesium and other undesired components.

C. Combustion of fossil fuels in utility and industrial boilers

37. In the combustion of fossil fuels in utility and industrial boilers (>50 MW thermal capacity), improved energy efficiency and energy conservation will result in a decline in the emissions of all pollutants because of reduced fuel requirements. This will also result in a reduction in PCDD/F emissions. It would not be cost-effective to remove chlorine from coal or oil, but in any case the trend towards gas-fired stations will help to reduce PCDD/F emissions from this sector.

38. The feasibility of fuel switching is dominated by local circumstances. The use of coal or biomass rich organohalogen compounds or halogenated compounds should be avoided where possible in installations that are not equipped with emission abatement technologies. The waste should only be combusted in installations equipped with proper emission abatement technologies. Fuel switch from waste, coal, or biomass containing organohalogen compounds to natural gas will reduce the formation of organohalogen compounds in the off-gases. This can result in a significant decrease of PCDD/F emissions from small installations that are not equipped with emission abatement technologies.

39. Fossil fired utility boilers in power plants may use fuels based on biomass together with fossil fuels to reduce emissions of greenhouse gases.

40. The burning of biomass containing high levels of organohalogen compounds or halogenated compounds should only be performed in installations equipped with proper emission abatement techniques.

41. Fuel switch from waste, coal, or biomass containing organohalogen compounds to natural gas will reduce the formation of organohalogen compounds in the off-gases. This can result in a significant decrease of PCDD/F emissions from small installations that are not equipped with emission abatement technologies.

42. The feasibility of fuel switching is dominated by local circumstances.

43. It should be noted that PCDD/F emissions could increase significantly if waste material (sewage sludge, waste oil, rubber wastes, etc.) is added to the fuel. The combustion of wastes for energy supply should be undertaken only in installations using waste gas purification systems with highly efficient PCDD/F reduction (described in section A above).

44. The application of techniques to reduce emissions of nitrogen oxides, sulphur dioxide and particulates from the flue gas can also remove PCDD/F emissions. When using these techniques, PCDD/F removal efficiencies will vary from plant to plant. Research is ongoing to develop PCDD/F removal techniques, but until such techniques are available on an industrial scale, no best available technique is identified for the specific purpose of PCDD/F removal.

45. Emissions of PCDD/F from industrial boilers are generally low and emission levels associated from the sector can be below 0.1 ng TEQ/m^3

D. Residential combustion

46. Residential combustion appliances can have a noticeable contribution to total emissions of PCDD/F. This contribution is less significant when approved fuels are properly used. In addition, large regional differences in emissions can occur due to the type and quality of fuel, geographical appliance density and usage. In addition, large regional differences in emissions can occur due to the type and quality of fuel, geographical appliance density and usage.

47. Domestic fireplaces have a worse burn-out rate for hydrocarbons in fuels and waste gases than large combustion installations. This is especially true if they use solid fuels such as wood and coal, with PCDD/F emission concentrations in the range of 0.1 to 0.7 ng TEQ/m^3 .

48. Burning packing material added to solid fuels increases PCDD/F emissions. Even though it is prohibited in some countries, the burning of rubbish and packing material may occur in private households. Due to increasing disposal charges, it must be recognized that household waste materials are being burned in domestic firing installations. The use of wood with the addition of waste packing material can lead to an increase in PCDD/F emissions from 0.06 ng TEQ/m^3 (exclusively wood) to 8 ng TEQ/m^3 (relative to 11% oxygen by volume). These results have been confirmed by investigations in several countries in which up to 114 ng TEQ/m^3 (with respect to 13% oxygen by volume) was measured in waste gases from residential combustion appliances burning waste materials.

49. The emissions from residential combustion appliances can be reduced by restricting the input materials to good-quality fuel and avoiding the burning of waste, halogenated plastics and other materials. Public information programmes for the purchasers/operators of residential combustion appliances can be effective in achieving this goal.

E. Firing installations for wood (<50 MW capacity)

50. Measurement results for wood-firing installations indicate that PCDD/F emissions above 0.1 ng TEQ/m^3 occur in waste gases especially during unfavourable burn-out conditions and/or when the substances burned have a higher content of chlorinated compounds than normal untreated wood. An indication of poor firing is the total carbon concentration in the waste gas. Correlations have been found between CO emissions, burn-out quality and PCDD/F emissions.

51. Table 3 summarizes some emission concentrations and factors for wood-firing installations.

Table 3: Quantity-related emission concentrations and factors for wood-firing installations

Fuel	Emission concentration (ng TEQ/m ³)	Emission factor (ng TEQ/kg)	Emission factor (ng/GJ)
Natural wood (beech tree)	0.02 - 0.10	0.23 - 1.3	12 - 70
Natural wood chips from forests	0.07 - 0.21	0.79 - 2.6	43 - 140
Chipboard	0.02 - 0.08	0.29 - 0.9	16 - 50
Urban waste wood	2.7 - 14.4	26 - 173	1400 - 9400
Residential waste	114	3230	
Charcoal	0.03		

52. The combustion of urban waste wood (demolition wood) in moving grates leads to relatively high PCDD/F emissions, compared to non-waste wood sources. A primary measure for emission reduction is to avoid the use of treated waste wood in wood-firing installations. Combustion of treated wood should be undertaken only in installations with the appropriate flue-gas cleaning to minimize PCDD/F emissions.

53. Biomass fuels can have a high chloride content e.g. straw, or wood from a saline environment, which can lead to an increased formation of PCDD/F when these biomass are incinerated as fuel. Fuel switch to fuels with a low-chlorine content for dedicated combustion plants firing biomass will have a large impact on PCDD/F emissions.

54. If needed installations firing biomass can be equipped with abatement techniques to reduce emissions of particulate matter, like fabric filters or electrostatic precipitators; this will reduce emission of PCDD/F significantly.

55. Post combustion abatement technologies might be economically viable or feasible on plant biomass above 0.5 MW, and then could be limited to simple cyclone type abatement. For smaller plant fuel quality and burner design may have greater influence on emissions.

V. CONTROL TECHNIQUES FOR THE REDUCTION OF PAH EMISSIONS

A. Coke production

56. During coke production, PAHs are released into the ambient air mainly:

(a) When the oven is charged through the charging holes;

(b) By leakages from the oven door, the ascension pipes and the charging hole lids;

and

- (c) During coke pushing and coke cooling.

57. Benzo(a)pyrene (BaP) concentration varies substantially between the individual sources in a coke battery. The highest BaP concentrations are found on the top of the battery and in the immediate vicinity of the doors.

58. PAHs from coke production can be reduced by retrofitting or reducing the coke consumption in iron and steel production, by replacing part of the coke with high value coal or waste oil etc. This might entail the closure and replacement of old coke batteries and the general reduction in coke production, for instance by injecting high-value coal in steel production.

59. A PAH reduction strategy for coke batteries should include the following technical measures:

- (a) Charging the coke ovens:
- (i) Particulate matter emission reduction when charging the coal from the bunker into the charging cars;
 - (ii) Closed systems for coal transfer when coal pre-heating is used;
 - (iii) Extraction of filling gases and subsequent treatment, either by passing the gases into the adjacent oven or by passing via a collecting main to an incinerator and a subsequent dedusting device. In some cases the extracted filling gases may be burned on the charging cars, but the environmental performance and safety of these charging-car-based systems is less satisfactory. Sufficient suction should be generated by steam or water injection in the ascension pipes;
- (b) Emissions at charging hole lids during coking operation should be avoided by:
- (i) Using charging hole lids with highly efficient sealing;
 - (ii) Luting the charging hole lids with clay (or equally effective material) after each charging operation;
 - (iii) Cleaning the charging hole lids and frames before closing the charging hole;
 - (iv) Keeping oven ceilings free from coal residuals;
- (c) Ascension pipe lids should be equipped with water seals to avoid gas and tar emissions, and the proper operation of the seals should be maintained by regular cleaning;
- (d) Coke oven machinery for operating the coke oven doors should be equipped with systems for cleaning the seals' surfaces on the oven door frames and oven doors;

(e) Coke oven doors:

(i) Highly effective seals should be used (e.g. spring-loaded membrane doors);

(ii) Seals on the oven doors and door frames should be cleaned thoroughly at every handling operation;

(iii) Doors should be designed in a manner that allows the installation of particulate matter (PM) extraction systems with connection to a dedusting device (via a collecting main) during pushing operations;

(f) The coke transfer machine should be equipped with an integrated hood, stationary duct and stationary gas cleaning system (preferably a fabric filter);

(g) Low-emission procedures should be applied for coke cooling, e.g. dry coke cooling. The replacement of a wet quenching process by dry coke cooling should be preferred, so long as the generation of wastewater is avoided by using a closed circulation system. The dusts generated when dry quenched coke is handled should be reduced.

60. A coke-making process referred to as “non-recovery coke-making” emits significantly less PAHs than the more conventional by-product recovery process. This is because the ovens operate under negative pressure, thereby eliminating leaks to the atmosphere from the coke oven doors. During coking, the raw coke oven gas is removed from the ovens by a natural draught, which maintains a negative pressure in the ovens. These ovens are not designed to recover the chemical by-products from raw coke oven gas. Instead, the off-gases from the coking process (including PAHs) are burned efficiently at high temperatures and with long residence times. The waste heat from this incineration is used to provide the energy for coking, and excess heat may be used to generate steam. The economics of this type of coking operation may require a cogeneration unit to produce electricity from the excess steam. Currently, there is only one non-recovery coke plant operating in the United States, and one is in operation in Australia. The process is basically a horizontal sole-flue non-recovery coke oven with an incineration chamber adjoining two ovens. The process provides for alternate charging and coking schedules between the two ovens. Thus, one oven is always providing the incineration chamber with coke gases. The coke gas combustion in the incineration chamber provides the necessary heat source. The incineration chamber design provides the necessary dwell time (approximately 1 second) and high temperatures (minimum of 900° C).

61. An effective monitoring programme for leakages from coke oven door seals, ascension pipes and charging hole lids should be operated. This implies the monitoring and recording of leakages and immediate repair or maintenance. A significant reduction of diffuse emissions can thus be achieved.

62. Retrofitting existing coke batteries to facilitate condensation of flue gases from all sources (with heat recovery) results in a PAHs reduction of 86% to more than 90% in air (without regard to waste water treatment). Investment costs can be amortized in five years, taking into account recovered energy, heated water, gas for synthesis and saved cooling water.

63. Increasing coke oven volumes results in a decrease in the total number of ovens, oven door openings (amount of pushed ovens per day), number of seals in a coke battery and consequently PAH emissions. Productivity increases in the same way by decreasing operating and personnel costs.

64. Dry coke cooling systems require a higher investment cost than wet methods. Higher operating costs can be compensated for by heat recovery in a process of pre-heating the coke. The energy efficiency of a combined dry coke cooling/coal pre-heating system rises from 38 to 65%. Coal pre-heating boosts productivity by 30%. This can be raised to 40% because the coking process is more homogeneous.

65. All tanks and installations for the storage and treatment of coal tar and coal tar products must be equipped with an efficient vapour recovery return and/or vapour destruction system. The operating costs of vapour destruction systems can be reduced in an autothermal after-burning mode if the concentration of the carbon compounds in the waste is high enough.

66. Table 4 summarizes PAHs emission reduction measures in coke production plants.

Table 4: PAH emission control for coke production

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Retrofitting of old plants with condensation of emitted flue gases from all sources includes the following measures:	Total < 10 (without waste water)	High	Emissions to waste water by wet quenching are very high. This method should be applied only if the waste is reused in a closed cycle.
- Evacuation and after-burning of the filling gases during charging of ovens or passing the gases into the adjacent oven as far as possible;	5	(Amortization of investment costs, taking into account energy recovery, heated water, gas for synthesis and saved cooling water, may be 5 years.)	
- Emissions at charging hole lids should be avoided as far as possible, e.g. by special hole lid construction and highly effective sealing methods. Coke oven doors with highly	< 5		

effective sealings should be used. Cleaning of charging hole lids and frames before closing the charging hole;			
- Waste gases from pushing operations should be collected and fed to a dedusting device;	< 5	Higher investment costs than for wet cooling (but lower costs by preheating of coke and use of waste heat.)	
- Quenching during coke cooling by wet methods only if properly applied without waste water.			
Low emission procedures for coke cooling, e.g. dry coke cooling.	No emissions into water	Higher investment costs than for wet cooling (but lower costs by preheating of coke and use of waste heat.)	
Increasing the use of high-volume ovens to lower the number of openings and the surface of sealing areas.	Considerable	Investment about 10% higher than conventional plants	In most cases total retrofitting or the installation of a new cokery is needed.

a/ Remaining emission compared to unreduced mode.

B. Anode production

67. PAH emissions from anode production have to be dealt with in a similar fashion as those from coke production.

68. The following secondary measures for emission reduction of PAH-contaminated dust are used:

- (a) Electrostatic tar precipitation;
- (b) Combination of a conventional electrostatic tar filter with a wet electrostatic filter as a more efficient technical measure;
- (c) Thermal after-burning of the waste gases; and
- (d) Dry scrubbing with limestone/petroleum coke or aluminum oxide (Al₂O₃).

69. The operating costs in thermal after-burning can be reduced in an autothermal after-burning mode if the concentration of carbon compounds in the waste gas is high enough. Table 5 summarizes PAHs emission control measures for anode production.

Table 5: PAHs emission control for anode production

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Modernization of old plants by reducing diffuse emissions with the following measures:	3–10	High	
- Reduction of leakages;			
- Installation of flexible sealants at the oven doors;			
- Evacuation of filling gases and subsequent treatment, either by passing the gases into the adjacent oven or by passing the gases via a collecting main to an incinerator and a subsequent dedusting device on the ground;			
- Operating and coke oven cooling systems; and			
- Evacuation and purification of particulate emissions from coke.			
Established technologies for anode production in the Netherlands:	45–50		Implemented in the Netherlands in 1990. Scrubbing with limestone or petroleum cokes is effective for reducing PAH; with aluminium not know.
- New kiln with dry scrubber (with limestone/petroleum cokes or with aluminium)			
- Effluent recycling in paste unit.			

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
BAT:			
- Electrostatic dust precipitation; and	2–5		Regular cleaning of tar is needed.
- Thermal after-burning.	15	Lower operating costs in an autothermal mode.	Operating in autothermal mode only if the concentration of PAH in the waste gas is high.

a/ Remaining emission compared to unreduced mode.

C. Aluminium industry

70. Aluminium is produced from aluminium oxide (Al_2O_3) by electrolysis in pots (cells) electrically connected in series. Pots are classified as prebake or Soederberg pots, according to the type of the anode.

71. Prebake pots have anodes consisting of calcined (baked) carbon blocks, which are replaced after partial consumption. Soederberg anodes are baked in the cell, with a mixture of petroleum coke and coal tar pitch acting as a binder.

72. Very high PAH emissions are released from the Soederberg process. Primary abatement measures include modernization of existing plants and optimization of the processes, which could reduce PAH emissions by 70–90%. An emission level of 0.015 kg B(a)P/ton of Al could be reached. Replacing the existing Soederberg cells by prebaked ones would require major reconstruction of the existing process, but would nearly eliminate the PAH emissions. The capital costs of such replacements are very high.

73. Table 6 summarizes PAHs emission control measures for aluminium production.

Table 6: PAH emission control for aluminium production using the Soederberg process

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Replacement of Soederberg electrodes by: - Prebaked electrodes (avoidance of pitch binders); - Inert anodes.	3–30	Higher costs for electrodes about US\$ 800 million	Soederberg electrodes are cheaper than prebaked ones, because no anode baking plant is needed. Research is in progress, but expectations are low. Efficient operation and monitoring of emission are

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
			essential parts of emission control. Poor performance could cause significant diffuse emissions.
Closed prebake systems with point feeding of alumina and efficient process control, hoods covering the entire pot and allowing efficient collection of air pollutants.	1–5		
Soederberg pot with vertical contact bolts and waste gas collection systems.	> 10	Retrofit of Soederberg technology by encapsulation and modified feeding point: US\$ 50,000 – 100,000 per furnace	Diffuse emissions occur during feeding, crust breaking and lifting of iron contact bolts to a higher position
Sumitomo technology (anode briquettes for VSS process).		Low - Medium	
Gas cleaning:			
- Electrostatic tar filters;	2–5	Low	High rate of sparking and electrical arcing;
- Combination of conventional electrostatic tar filters with electrostatic wet gas cleaning;	> 1	Medium	Wet gas-cleaning generates waste water.
- Thermal after-burning.			
Pitch use with higher melting point (HSS + VSS)	High	Medium Low - medium	
Use of dry scrubbing in existing HSS + VSS plants.		Medium - high	

^{a/} Remaining emission compared to unreduced mode.

74. According to the European Union reference document (BREF) on non-ferrous metal, the achievable level for PAHs (total – OSPAR11) is $< 200 \mu\text{g} / \text{m}^3$.

D. Residential combustion

75. PAHs emissions from residential combustion can be detected from stoves or open fireplaces especially when wood or coal is used. Households could be a significant source of PAHs emissions. This is the result of the use of fireplaces and small firing installations burning solid fuels in households. In some countries the usual fuel for stoves is coal. Coal-burning stoves emit less PAHs than wood-burning ones, because of their higher combustion temperatures and more consistent fuel quality.

76. Furthermore, combustion systems with optimized operation characteristics (e.g. burning rate) effectively control PAHs emissions from residential combustion. Optimized combustion conditions include optimized combustion chamber design and optimized supply of air. There are several techniques which optimize combustion conditions and reduce emissions. There is a significant difference in emissions between different techniques. A modern wood-fired boiler with a water accumulation tank, representing BAT, reduces the emission by more than 90% compared to an outdated boiler without a water accumulation tank. A modern boiler has three different zones: a fireplace for the gasification of wood, a gas combustion zone with ceramics or other material which allow temperatures of some $1,000^\circ \text{C}$, and a convection zone. The convection part where the water absorbs the heat should be sufficiently long and effective so that the gas temperature can be reduced from $1,000^\circ \text{C}$ to 250°C or less. There are also several techniques to supplement old and outdated boilers, for example with water accumulation tanks, ceramic inserts and pellet burners.

77. Optimized burning rates are accompanied by low emissions of carbon monoxide (CO), total hydrocarbons (THCs) and PAHs. Setting limits (type approval regulations) on the emission of CO and THCs also affects the emission of PAHs. Low emission of CO and THCs results in low emission of PAHs. Since measuring PAH is far more expensive than measuring CO, it is more cost-effective to set a limit value for CO and THCs. For example four CEN¹ standards (EN 303-5; EN 13.229; EN 13.240 and EN 12.809) have been published for coal- and wood-fired appliances up to 300 kW (see table 7). These standards set maximum values for CO and THCs and PM.

78. Emissions from residential wood combustion stoves and boilers can be reduced by the following primary measures:

- (a) By public information and awareness programmes regarding:
 - (i) The proper operation of stoves and boilers;

¹ European Committee for Standardization.

- (ii) The use of untreated wood only;
 - (iii) Fuel preparation procedures and the correct seasoning of wood for moisture content;
- (b) By establishing a programme to promote the replacement of the oldest existing boilers and stoves by modern stoves and boilers.

79. Emissions of PAH from residential wood combustion in new stoves and boilers can be reduced by the following secondary measures:

- (a) Reducing the emissions of PM by equipping stoves and boilers with abatement techniques aimed at reducing emissions of dust;
- (b) Equipping stoves and boilers with abatement techniques aimed at oxidising PAH.
 - (i) Possible abatement techniques that control the emissions of particulate matter are electrostatic precipitators, ceramic filters, fabric filters using metal filament fabric or retrofitting of an afterburner. The costs and environmental benefits of the use of these techniques on small stoves and boilers have to be evaluated;
 - (ii) Possible abatement techniques that will burn the PAHs are partly re-circulation of the stack gases or catalytic converters that will oxidise the PAHs. The costs and environmental benefits of the use of these techniques on small stoves and boilers has to be evaluated;

80. More general measures for PAH emission reduction are those related to the development of centralized systems for households and energy conservation such as improved thermal insulation to reduce energy consumption.

81. The feasibility of fuel switching is dominated by local circumstances. Emission of PAHs from domestic heating systems can be reduced by switching the fuels from wood or coal to natural gas.

82. Information is summarized in table 7.

Table 7: PAHs emission control for residential combustions

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
Use of dried coal and wood (dried wood is wood stored for at least 18–24 months).	High effectiveness		
Use of dried coal.	High		

Management options	Emission level (%) ^{a/}	Estimated costs	Management risks
	effectiveness		
Design of heating systems for solid fuels to provide optimized complete burning conditions: - Gasification zone; - Combustion with ceramics; - Effective convection zone.	55	Medium	Negotiations have to be held with stove manufacturers to introduce an approval scheme for stoves.
Water accumulation tank. (manually fed installations only)	High effectiveness	Medium	
Technical instructions for efficient operation.	30–40	Low	Might be achieved also by vigorous public education, combined with practical instructions and stove type regulation.
Public information programme concerning the use of wood-burning stoves.			
Secondary measures to reduces emissions of particulates or to burn PAHs	<5 %	Medium to high	Costs are relative to size of the installation and re-use of heat produced

a/ Remaining emission compared to unreduced mode.

E. Wood preservation installations

83. Wood preservation with PAH-containing coal-tar products may be a major source of PAH emissions to the air. Emissions may occur during the impregnation process itself as well as during storage, handling and use of the impregnated wood in the open air.

84. The most widely used PAH-containing coal-tar products are carbolineum and creosote. Both are coal tar distillates containing PAHs for the protection of timber (wood) against biological attack.

85. PAH emissions from wood preservation, installations and storage facilities may be reduced using several approaches, implemented either separately or in combination, such as:

(a) Requirements on storage conditions to prevent pollution of soil and surface water by leached PAH and contaminated rainwater (e.g. storage sites impermeable to rainwater, roof cover, reuse of contaminated water for the impregnation process, quality demands for the material produced);

(b) Measures to reduce atmospheric emissions at impregnation plants (e.g. the hot wood should be cooled down from 90° C to 30° C at least before transport to storage sites. However, an alternative method using pressure steam under vacuum conditions to impregnate the wood with creosote should be highlighted as BAT);

(c) The optimum loading of wood preservative, which gives adequate protection to the treated wood product in situ, can be regarded as a BAT as this will reduce the demand for replacements, thereby reducing emissions from the wood preservation installations;

(d) Using wood preservation products with a lower content of those PAHs that are POPs:

(i) Possibly using modified creosote which is taken to be a distillation fraction boiling between 270° C and 355° C, which reduces both the emissions of the more volatile PAHs and the heavier, more toxic PAHs;

(ii) Discouraging the use of carbolineum would also reduce PAH emissions;

(e) Evaluating and then using, as appropriate, alternatives, such as those in table 9, that minimize reliance on PAH-based products.

86. Burning of impregnated wood gives rise to PAHs emissions and other harmful substances. If burning does take place, it should be done in installations with adequate abatement techniques.

Table 8: Possible alternatives to wood preservation involving PAH-based products

Management options	Management risks
Use of alternative materials for application in construction:	Other environmental problems have to be evaluated such as:
- Sustainably produced hardwood (riverbanks, fences, gates);	- Availability of suitably produced wood;
- Plastics (horticulture posts);	- Emissions caused by the production and disposal of plastics, especially PVC.
- Concrete (railway sleepers);	
- Replacement of artificial constructions by	

Management options	Management risks
natural ones (such as riverbanks, fences, etc.);	
- Use of untreated wood.	
There are several alternative wood-preserving techniques in development which do not include impregnation with PAH-based products.	
