Section VI

Guidance/guidelines by source category: Source categories in Part III of Annex C

Part III Source category (f): Specific chemical production processes releasing chemicals listed in Annex C

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List of Abbreviations

2,4-D	2,4-Dichlorophenoxyacetic acid
1,2-DCBz	1,2-Dichlorobenzene
1,4-DCBz	1,4-Dichlorobenzene
2,4-DCBP	Bis(2,4)-dichlorobenzoylperoxide
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
1,2,4-TCBz	1,2,4-Trichlorobenzene
ABS	Acrylonitrile Butadiene Styrene
BAT	Best available techniques
BAT-AEL	BAT-Associated Emission Level(s)
BATc	BAT conclusions (EU)
BEP	Best environmental practices
BREFs	Best Available Techniques Reference Documents (EU)
CAK BATc	(EU) BAT conclusions for the production of chlor-alkali
CNP	Chloronitrofen
CO	Carbon monoxid
CO2	Carbon dioxid
CWW BATc	(EU) BAT conclusions for common waste water and waste gas treatment/management systems in the chemical sector
EDC	Ethylene dichloride
GEF	Global Environment Facility
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HCl	Hydrogen chloride
IED	Industrial Emissions Directive (EU)
IPCS	International Programme on Chemical Safety
LVOC BATc	BAT conclusions for the production of large volume organic chemicals (EU)
METI	Japanese Ministry of Economy, Trade and Industry
OFC BATc	(EU) BAT conclusions for the manufacture of organic fine chemicals
PCB	Polychlorinated biphenyls
PCBz	Polychlorninated benzenes
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
PCN	Polychlorinated naphthalenes
PCNB	Pentachloronitrobenzene, quintozene
PCP	Pentachlorophenol
PeCB	Pentachlorobenzene
POPs	Persistent organic pollutants
psig	Pounds per square inch gauge (unit of measurement for pressure, USA)
PVC	Poly(vinyl chloride)
TCPA	Tetrachlorophthalic acid
UPOPs	Unintentional produced POPs
US EPA	United States Environmental Protection Agency
VCM	Vinyl chloride monomer
WCC	World Chlorine Council
WGC BATc	(EU) BAT conclusions on industrial emissions, for common waste gas management and treatment systems in the chemical sector

VI.F Specific chemical production processes releasing chemicals listed in Annex C

Summary

This section focuses on processes for the manufacture of industrial chemicals that are known to form unintentional persistent organic pollutants (UPOPs) listed in Annex C of the Stockholm Convention. Most of the processes described share common steps, including chlorination of organic or inorganic raw materials. Primary measures to avoid or reduce the formation of unintentional POPs are substitution of chemicals associated with the formation of unintentional POPs, alternative synthesis routes or modification of synthesis parameters like temperature, solvent or pH. For certain products, BAT manufacturing processes that reduce formation of unintentional POPs are presented. Secondary measures to eliminate the unintentional POPs formed in the production from the product, are distillation and crystallization. The separated unintentional POPs included in the high-molecular-weight side product fractions require environmentally sound management and destruction and can be destroyed in BAT waste incinerators or other BAT technologies defined herein.

Efficient separation and destruction of chlorinated organic side products, which may include persistent organic pollutants, is key to BAT applicable to these processes, as is the associated guidance for any incorporated incineration processes. Hydrogen chloride generated in the processes can be recycle in some processes or sold as secondary HCl possibly after refining. A range of performance standards associated with best available techniques are provided relevant to the individual processes.

1. Introduction to chemical processes and unintentional POP formation

1.1 Introduction to chemical processes including chlorination

1. This section focuses on processes for the manufacture of industrial chemicals that could theoretically give rise to chemicals listed in Annex C of the Stockholm Convention. Chlorination processes are used in the synthesis of hundreds of industrial and specialty chemicals (Wiley Interscience 2000; Stringer and Johnston 2001; UNEP 2013a; UNEP 2015; American Chemical Council 2017). Releases, including historic releases, from these industries and chemicals significantly contribute to the environmental contamination with unintentional POPs (Weber *et al.* 2008; UNEP 2013b; UNEP 2022a) including ongoing contamination of the food web (Weber *et al.* 2018; Petrlik *et al.* 2022). Chlorine chemistry may also be used in processes where the final product contains no chlorine atoms but generate unintentional POPs including PCDD/PCDF as in the case of production of caprolactam via the cyclohexane photonitrosation method (Kawamoto and Weber 2021) or certain pesticides (Holt *et al.* 2010). Under BAT/BEP conditions of operation, however, the emission of chemicals listed in Annex C from these processes and their concentrations in the products can be significantly reduced (UNEP 2013a; US EPA 2001) but the resulting waste containing the unintentional POPs requires environmentally sound management or disposal (UNEP 2023a).

2. Many of the general principles developed here – including more efficient use of raw materials and minimization of by-products and waste – are principles that support both better economic and environmental performance, consistent with modern principles of what is called green chemistry and engineering. They can also be applied to the much larger number of manufacturing processes used to produce a wide range of fine (low-volume specialty) chemicals, including pesticides, colorants (pigments and dyes), and pharmaceuticals. Production of such chemicals can depend on the unique properties of chlorine that make it a valuable synthetic tool.

3. Annex I to this section contains a list of some of the processes for the manufacture of industrial chemicals that can lead to the creation of chemicals listed in Annex C (Wiley Interscience 2000; UNEP 2013a; UNEP 2015). It is beyond the scope of this section to define best

available techniques and best environmental practices for each of these processes individually; rather, the processes will be examined for what they have in common and how those common practices can be addressed to reduce the formation, and particularly the release, of chemicals listed in Annex C of the Stockholm Convention.

4. Most of the organic processes involve a hydrocarbon, saturated or unsaturated, treated with elemental chlorine and in most processes also a catalyst. Reactions can be electrophilic additions to olefins, chlorination of aromatics, Friedel-Crafts-type electrophilic substitution of aromatic ring systems, or homolytic cleavage of carbon-hydrogen bonds with subsequent formation of the aliphatic chloride. In many cases chlorine atoms are present in the final product; on the other hand, in some processes (addition of an alcohol or amine to phosgene to produce, for example, polycarbonate and polyurethane plastics) no chlorine atoms are present in the final product. In addition, most of the processes involve generation of hydrogen chloride (HCl) as a co-product/by-product, via dehydrohalogenation or free radical reaction of chlorine with aliphatic hydrogen (Figures 1 and 2) and the resulting HCl can be contaminated with PCDD/PCDF and other UPOPs at different levels (Wang *et al.* 2014; UNEP 2015).
Additionally, inorganic chemicals are produced by chlorination such as iron chloride by direct chlorination of scrap or titanium dioxide which is produced with elemental chlorine and coke at high temperatures (see Section 2.3).

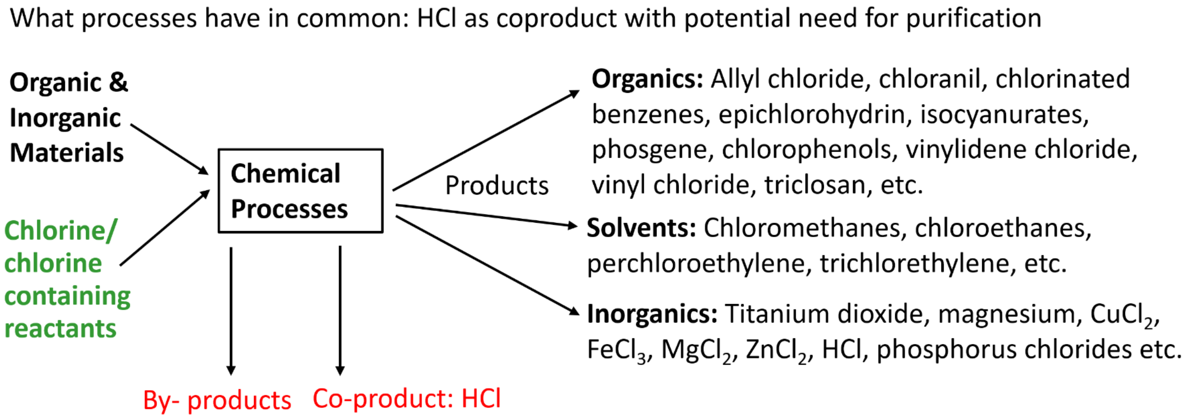
5. Crude products of these reactions vary in overall yield and purity as well as unintentional POPs content, and as with virtually all industrial chemical processes, purification of the final product is required prior to sale or further internal use.

6. Purification can involve separation of a mixture of saleable products – in many cases a spectrum of useful products results from a single reaction treatment – or separation of saleable products from the inevitable formation of high-molecular-weight by-products. For most organics and some inorganics that purification step involves distillation.

7. Generally, high-molecular-weight by-products containing the largest share of unintentional POPs are not saleable as themselves. In some cases, they are thermally oxidized, with HCl, carbon monoxide (CO) and carbon dioxide (CO_2) as products of this oxidation. HCl is recovered and reused as an integral part of the process (Figure 1). In other cases, they are viewed as wastes to be destroyed, usually by hazardous waste incineration, though HCl recycling is common.

8. Also, other processes where elemental chlorine is formed can be a source for PCDD/PCDF as documented for the soil digestion by aqua regia and production of reactive chlorine resulting in high PCDD/PCDF formation and release (Xie *et al.* 2023). This finding highlights that processes where elemental chlorine is formed or used should be assessed more systematically.

Figure 1. General process overview



1.2 Formation of unintentional POPs in the chemical industry

9. All unintentional POPs can be formed in chemical processes depending on the molecular structures involved. In the thermal *de novo* formation all aromatic unintentional POPs are formed and it is suggested by the UNEP toolkit that PCDD/PCDF are used as indicators for inventory development (UNEP 2013a). However, for chemical production processes, the formation of individual POPs can be quite specific as seen. For example, in the formation of polychlorinated biphenyls (PCB) in the production of certain pigments where, due to the structure of intermediates and educts, specifically unintentional PCB (Hu and Hornbuckle 2010; Anezaki and Nakano 2014; Anezaki *et al.* 2015; Anh *et al.* 2021) or hexachlorobenzene (HCB) (Government of Japan 2006) are formed. In other chemical processes like chlorinated solvent production high levels of HCB, hexachlorobutadiene (HCBD), PCB and polychlorinated naphthalenes (PCN) are formed (UNEP 2022a). Therefore, for chemical productions PCDD/PCDF cannot be used as lead parameter for other chemicals listed in Annex C but the formation mechanisms need to be understood to evaluate processes for unintentional POPs formation and monitor the relevant unintentional POPs when implementing BAT/BEP.

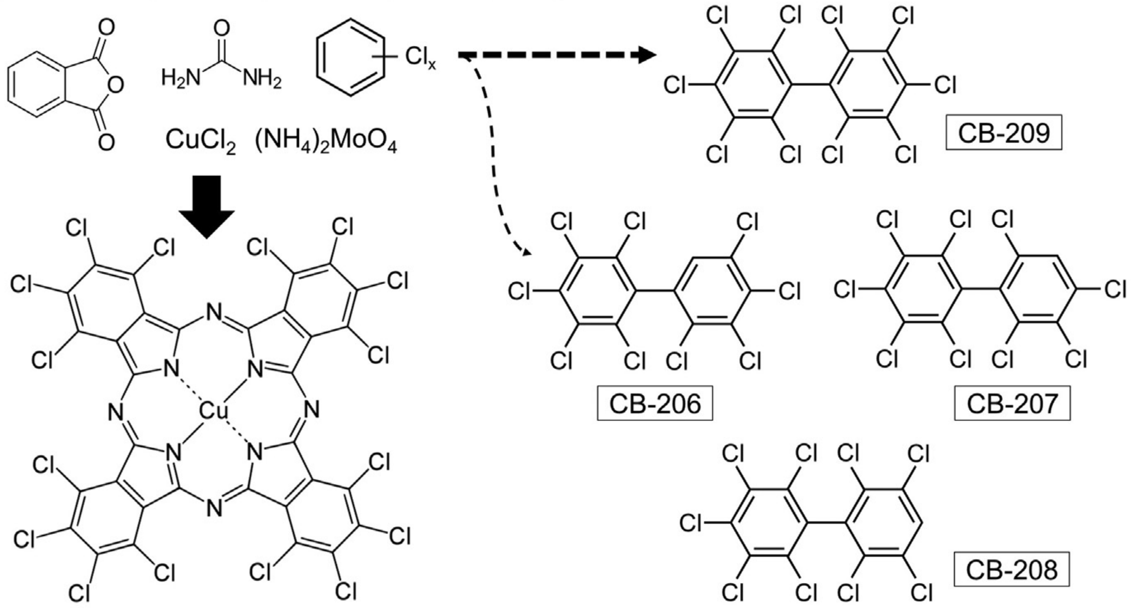
Formation of PCDD/PCDF, PCB and other unintentional POPs due to precursor quality of the chemical product

10. The most well-known examples of high PCDD/PCDF levels in organochlorine chemicals are those where the products are precursors of PCDD/PCDF, such as 2,4,5-trichlorophenol, pentachlorophenol (PCP) and PCBs contributing tonnes of TEQ to environmental burden (Weber *et al.* 2008; Götz *et al.* 2013). With global total yearly emission of all sources estimated to be 100 kg TEQ/year around 2016 (Wang *et al.* 2016). Production processes for these chemicals have a very high potential for the formation of PCDD/PCDF and major products are listed in the Toolkit (UNEP 2013a).

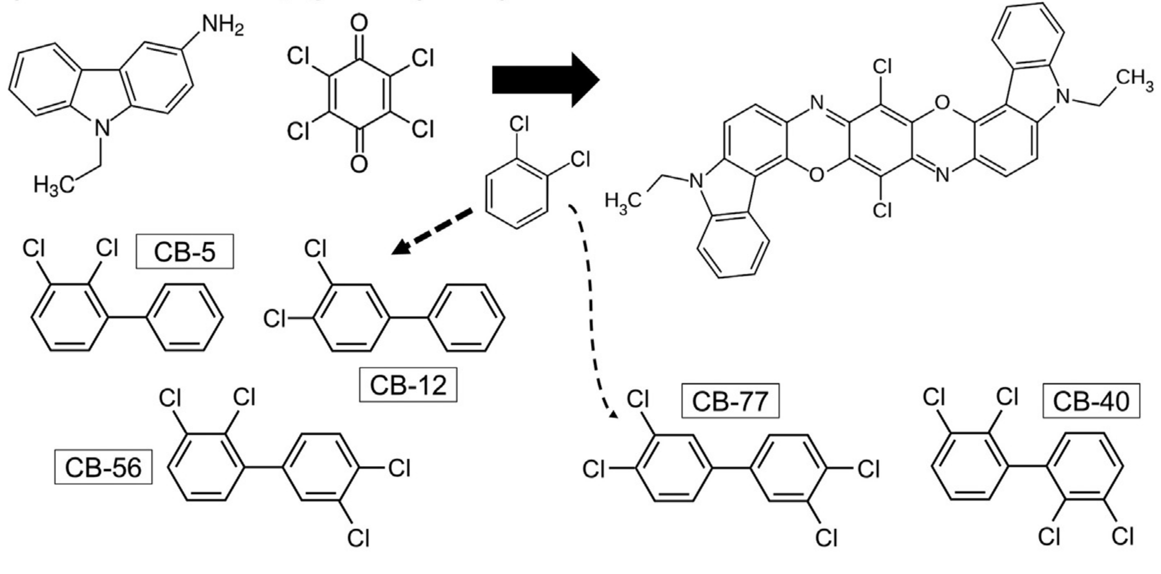
11. Certain chemicals have a specific formation potential for unintentional PCBs with the PCB precursor chlorobenzene as solvent in the production of phthalocyanine green pigment (PG7) and dioxazine violet pigment (PV23) (Figure 2) or the PCB precursors 3,3′-dichlorobenzidine in the production of disazo yellow pigment (PY13) or 2,2′,5,5′-tetrachlorobenzidine (Hu and Hornbuckle 2010; Anezaki and Nakano 2014; Anezaki, *et al.* 2015; Anh *et al.* 2021) (Figure 2).

Figure 2. Some formation pathways of unintentionally produced PCBs in selected organic pigments (Hu and Hornbuckle, 2010; Anezaki and Nakano, 2014; Anezaki, *et al.* 2015; Rodenburg *et al.* 2015; Hunger and Schmidt 2018; Anh *et al.* 2021)

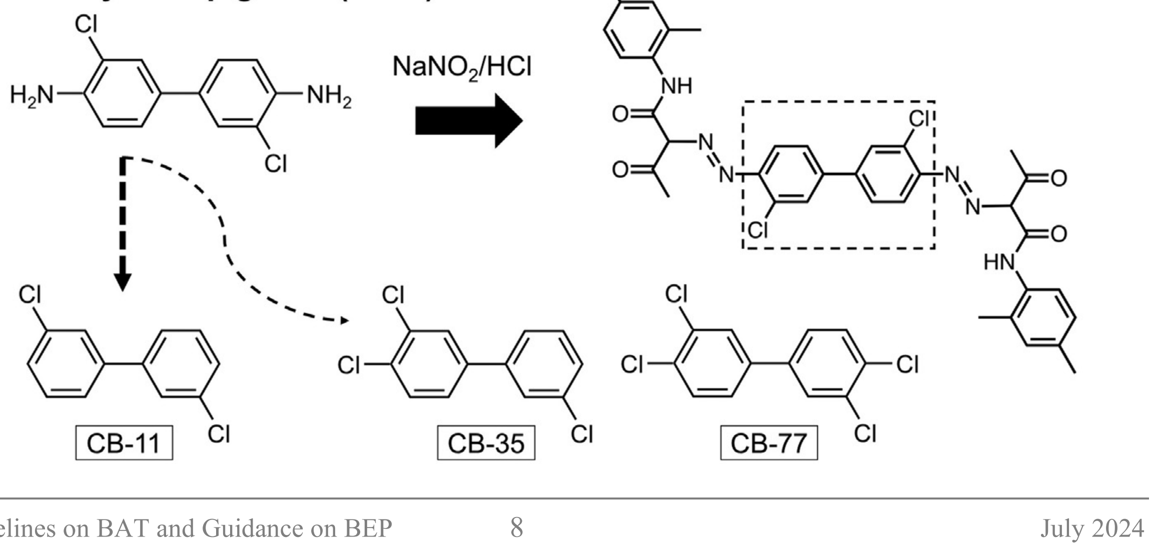
(a) Phthalocyanine green pigment (PG7)



(b) Dioxazine violet pigment (PV23)



(c) Disazo yellow pigment (PY13)



12. PCBs are also specifically unintentionally formed in the production of silicone rubber when bis(2,4)-dichlorobenzoylperoxide (2,4-DCBP) is used as catalyst and cross-linking agent with specific formation and release of PCB-47, PCB-51 and PCB-68 (Herkert *et al.* 2018; Hombrecher *et al.* 2021; Kaifie *et al.* 2022).

13. Some chemicals also have specific formation potential for HCB such as the pesticides dacthal and pentachloronitrobenzene (Mumma *et al.* 1975). Also, in the synthesis of tetrachlorophthalic acid (TCPA), a major chemical for the synthesis of a range of pigments such as chlorinated phthalocyanines (Figure 2(a) and 2(c)) or azo red and yellow, unintentional HCB is formed in a 50 to 3000 mg/kg range (Government of Japan 2006).

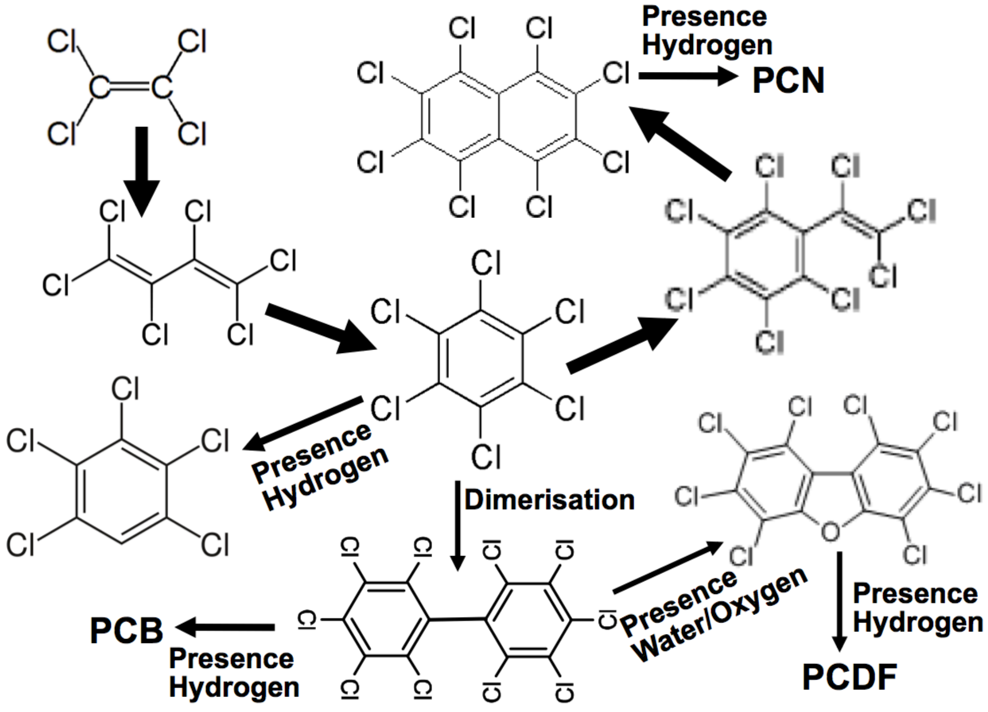
Formation of unintentional POPs due to chlorination of polycyclic aromatic hydrocarbons (PAHs)

14. PCNs and PCBs are produced by chlorination of naphthalene and biphenyl respectively. In some production processes involving chlorination, the presence of PAHs leads to the formation of PCDFs, PCBs, and PCNs by chlorination. Also, HCB and pentachlorobenzene (PeCB) are formed during chlorination and oxidative degradation of polycyclic aromatic compounds (PAHs and soot) and degradation of the larger aromatic structures (Weber *et al.* 2001). The chloralkali production using graphite electrodes is the most well-known industrial process with large formation and release of PCDFs in kg TEQ scale from single production (Otto *et al.* 2006; Yamamoto *et al.* 2018). This process also results in high release of PCNs, HCB, PeCB, HCBD and the formation of chlorinated PAHs (Takasuga *et al.* 2020). This formation route is also relevant for the production of organochlorine chemicals, e.g., unintentional PCNs are present in commercial PCB mixtures at levels between 2 mg/kg to 1300 mg/kg due to naphthalene impurities in biphenyl educt (Yamashita *et al.* 2000; Huang *et al.* 2015a). Unintentional PCNs and PCBs can be present in 100 mg/kg in chlorinated paraffins formed from the naphthalene and biphenyl present as impurities in paraffin (Takasuga *et al.* 2012a, b).

Condensation reaction of smaller organochlorines to unintentional POPs

15. Unintentional POPs are formed in some processes when smaller organochlorine chemicals undergo condensation reactions and build-up of aromatic compounds including unintentional POPs. Perhaps the most well-known processes in this regard are the productions of chlorinated solvents such as tetrachloroethylene, trichloroethylene and ethylene dichloride which were known to contain high levels of HCB (Jacoff *et al.* 1986; Weber *et al.* 2011a) and HCBD (Mumma and Lawless 1975; UNEP 2022a). A first total screening of unintentional POPs in the production of chlorinated methanes in China revealed the formation of high levels of PCN and PCB, leading to estimated total releases of 563 g TEQ/year from PCNs and 32 g TEQ/year from PCDD/PCDF for 2010 (Zhang *et al.* 2015). The simplified formation mechanism of unintentional POPs in the production of perchloroethylene or tetrachloromethane are shown in Figure 3.

Figure 3. Formation of unintentionally POPs in the production of perchloroethylene (Weber *et al.* 2011a); for unintentional product distribution in TCM production see Zhang *et al.* (2015)



Formation of PCDD/PCDF and other UPOPs from unintentionally formed precursors

16. In some processes neither the products nor intermediates are PCDD/PCDF precursors but nevertheless PCDD/PCDF are formed. The abovementioned formation of aromatic compounds due to condensation reactions of smaller molecules is one example of the formation of chlorinated aromatic precursors (e.g. chlorobenzenes) which, by further dimerization, can form unintentional PCB and PCDF (Figure 3; Weber *et al.* 2011a; Zhang *et al.* 2015). Also, the formation of PCDD/PCDF in phthalocyanines which do not contain direct precursors but, during their production, precursors are formed at elevated reaction temperatures with formation of PCDD/PCDF which can be minimized by temperature control and purified raw material (Brychcy and Wagner 1998).

Chemicals forming unintentional POPs from degradation in use and in the environment

17. Some chlorinated organics form unintentional POPs when they degrade during use or in the environment. The high octachlorodibenzo-p-dioxin (OCDD) levels detected in the environment in the 1990s were explained by photochemical formation of OCDD from PCP in the atmosphere (Baker and Hites 2000). OCDD is also formed from PCP in sewage sludge and composting (Munoz *et al.* 2018) partly facilitated by enzymes (Klimm *et al.* 1998) but also formed from PCP on clay at ambient temperature (Gu *et al.* 2008). The formation of UPOPs has also been described for quintozene (pentachloronitrobenzene; PCNB) which forms ~3% pentachlorobenzene when degrading in the environment (Beck and Hansen 1974; Kamal *et al.* 1983) and was therefore a major release source of PeCB (UNEP 2010). Furthermore, the pesticide quintozene can form PCDD/PCDF under sunlight during use (Holt *et al.* 2010). Also 2,4-Dichlorophenoxyacetic acid (2,4-D) and triclosan form additional PCDD/PCDF under sunlight which are however mainly low chlorinated congeners not fully substituted in the 2,3,7,8-position and therefore do not possess the particular dioxin-toxicity (Holt *et al.* 2010; Halden *et al.* 2017). Such formation of UPOPs (and other hazardous degradation products) should be considered in the life cycle assessment of chemicals.

1.3 Use of BAT/BEP in the chemical industry

18. The BAT/BEP for the reduction of unintentional POPs defined in this document is only one aspect of chemical production. Other BAT/BEP considerations exist in the chemical industry,

such as an integrated approach to control releases. BAT/BEP for the chemical industry has been defined in different countries or regions. For example, the European Union developed best available techniques reference documents (BREFs) under the Industrial Emissions Directive (IED, 2010/75/EU) which is the main instrument regulating pollutant emission from industrial installations. The BAT conclusions (BATc) contained are adopted by the European Commission as Implementing Decision. The IED requires that these BATc are the reference for setting permit conditions.

19. Several of the BREFs/BATc are relevant to the application of BAT to processes using chlorination: for example, the BREF/BATc relating to large volume organic chemical processes (LVOC, European Commission 2017), the BREF/BATc common waste gas management and treatment systems in the chemical sector (WGC, European Commission 2023), the BREF/BATc production of chlor-alkali (CAK, European Commission 2014), the BREF/BATc Common Waste Water and Waste Gas Treatment/Management in the Chemical Sector (CWW, European Commission 2016), the BREF Organic Fine Chemicals (OFC, European Commission 2006), the BREF Production of Speciality Inorganic Chemicals (SIC, European Commission 2007a) and the BREF Manufacture of Large Volume Inorganic Chemicals. Solids and Others (LVIC-S, European Commission 2007b). These BREFs and BAT conclusions have open access (https://eippcb.jrc.ec.europa.eu/reference).

1.4 Major basic process steps in chemical production

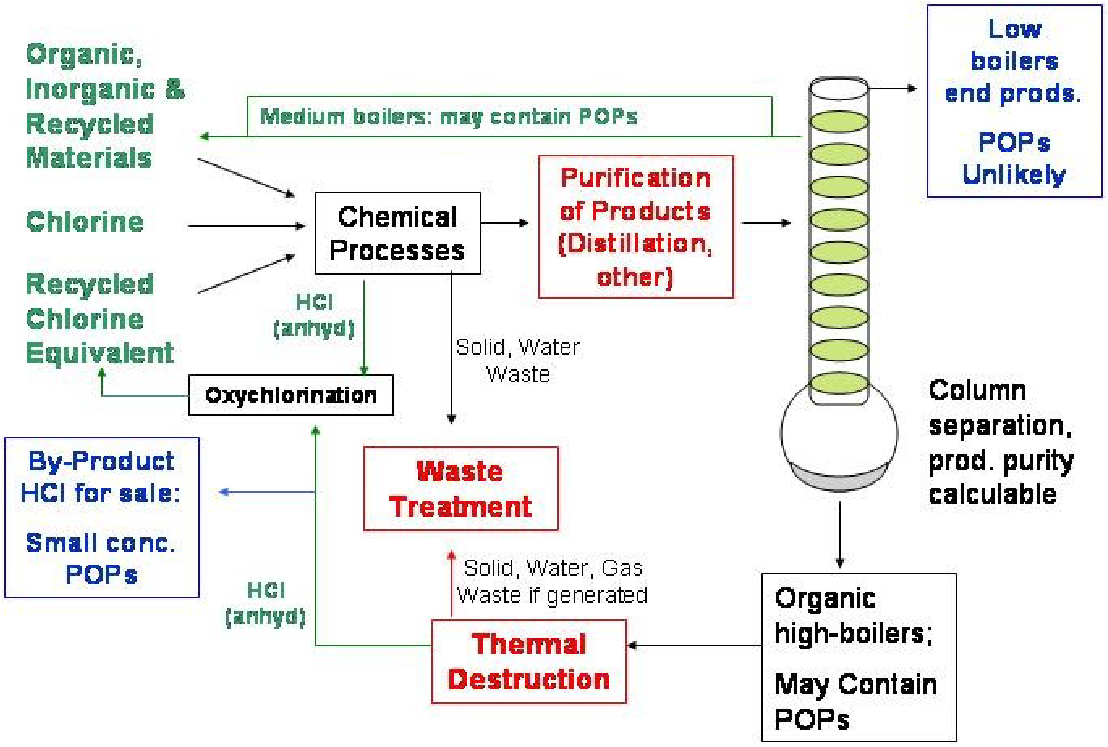
1.4.1 What chemical processes have in common

20. Figure 4 generically summarizes many of the major processes, including chlorination of organic or inorganic raw materials, purification of the products, separation of streams for recycle (HCl, medium boilers), destruction of by-products (organic high boilers) and sale of products (low boilers, HCl, end products). Major processes and product groups are described in Chapter 2.

21. A number of factors influence the amount of PCDD/PCDF and other UPOPs that may be formed in a given manufacturing process. The likelihood of PCDD/PCDF generation in chemical processes to manufacture chlorine-containing materials generally decreases in the order chlorophenols > chlorobenzenes > aliphatic chlorides > inorganic chlorides (Fiedler *et al.* 2000). Production conditions which can affect the rate of formation include temperature, pH, catalyst, and reaction kinetics (US EPA 1997).

22. Total PCDD/PCDF production will be affected both by propensity (ease) of formation and volume throughput, so a large-volume process such as chlorine production may give a larger mass flow than a high-concentration/higher-yielding but smaller-volume process.

Figure 4. Block diagram of generic organic process



1.4.2 Direct chlorination

23. Free radical addition of chlorine to aliphatic hydrocarbons, typically methane, and direct electrophilic addition of a halogen to an alkene are well known from basic organic chemistry. As utilized in industry, the former is catalysed by light and the latter is typically a low-temperature operation catalysed by ferric chloride ($FeCl_3$) (Process Economics Program 2000). In the former, a free radical mechanism is desired. On the other hand, in the latter, unproductive side reactions result from free radicals, which can be inhibited with low concentrations of oxygen.

24. There is little if any potential for formation of by-product persistent organic pollutants in direct chlorination processes of pure aliphatic hydrocarbons but when aromatic impurities are present then unintentional POPs such as PCNs, PCBs and PCDD/PCDF are formed as documented for the SCCP production (Section 2.7.1; Takasuga *et al.* 2012a; Takasuga *et al.* 2012b; Xie *et al.* 2023). Aromatic feedstocks can also be chlorinated directly under mediation of a Lewis acid catalyst. The presence of aromatic chlorides as products of the process results in the generation of unintentional POPs (see examples in Chapter 2).

1.4.3 Main product isolation

25. Another common facet of these processes is the need to purify products that will either be sold or used in subsequent process steps. In virtually all cases, organic reaction products will be distilled. Fractional distillation separates streams of desired products and also separates desired products from unwanted high-molecular-weight materials called heavy ends or tars. If formation of unintentional POPs is observed in the distillation process, then inhibitors might be added before distillation (European Commission 2017 p. 111).

26. Distillation is a standard engineering unit operation. It is based on sequential vaporization and condensation of liquid in a column, which typically includes packing or trays in order to

maximize its internal surface area. Vapour that reaches the top of the column is enriched in the lowest-boiling material present in the distillation mixture.

27. Design and operation of distillation units are well understood, both in separations theory and in practice. For non-azeotroping materials with widely separated boiling points – for example, vinyl chloride and PCDD/PCDF – virtually complete separations can be accomplished in a well-designed and operated column (Luyben and Chien 2011).

28. Desired materials are isolated and transported as liquids. For materials with boiling points above ambient temperature (e.g. ethylene dichloride), closed but not pressurized containers are used. For materials with boiling point below ambient temperature (e.g. vinyl chloride, chlorine), pressurized containers are used.

29. Some product isolations will not lend themselves to distillation. In principle, similarly useful and rigorous techniques (e.g. recrystallization) may be devised for specific materials. To the extent that those practices can demonstrate a similar result, such as isolation of by-products into a separate stream, these may, in some circumstances, also qualify as best available techniques.

1.4.4 Recovery of co-product hydrogen chloride

30. Hydrogen chloride (HCl) is generated as by-product in about 40 manufacturing processes (Glauser *et al.* 2009). HCl is handled in one or more of the following ways. It can simply be neutralized and discharged as salt (sodium chloride). However, in some processes HCl can constitute a large amount of the effective use of input chlorine, so neutralization and discharge carries with it a large cost in the loss of potential raw material. HCl can be recovered, hydrated and then sold as the commercial product hydrochloric/muriatic acid or used for pH adjustment in chloralkali cells. Thus, there is some recycling of HCl electrolytically to chlorine.

31. Secondary HCl/muriatic acid, arising as a co-product/by-product of chemical production can contain PCDD/PCDF and other unintentional POPs (Section 2.8.1).

32. HCl can also be dried, oxidized catalytically and, in the presence of organic raw material, reacted as elemental chlorine to generate more of the desired product. The process by which this is accomplished is called oxychlorination and constitutes a means of in-process recovery of a valuable chlorine feedstock.

1.4.5 Destruction of production wastes and recovery of hydrogen chloride

33. Undesired materials, including heavy ends, are usually destroyed in thermal processes at high temperature, with or without oxygen. Figure 5 shows a prototypical heavy ends destruction train with HCl recovery.

34. Environmentally sound management of by-product and waste streams from chemical operations is critical to preventing the release of chemicals listed in Annex C to the environment. This management includes both effective and high-performance destruction of waste within a process and effective end-of-pipe methods to prevent release. Such destruction and end-of-pipe systems for the chemical and other industries are usually well defined by regulation, and should be monitored closely by operators and authorities. For example, the European Union Directive on Industrial Emission (IED) requires in Chapter IV special provisions for waste incineration plants and waste co-incineration plants with regard to operation conditions and PCDD/PCDF formation: “If hazardous waste with a content of more than 1 % of halogenated organic substances, expressed as chlorine, is incinerated or co-incinerated, the temperature required to comply with the first and second subparagraphs shall be at least 1100°C.” Furthermore, in the SIC-BREF, in the LVOC BATc and the WGC BATc ‘fast-quenching’ is described for waste gas treatment or incineration of chlorinated compounds to avoid reformation of dioxins and furans (de-novo

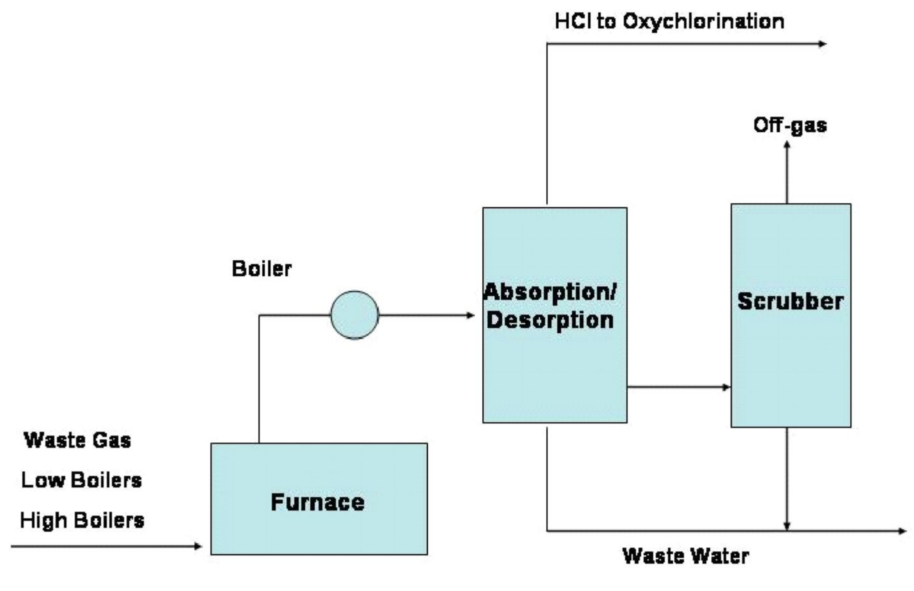
synthesis) (European Commission 2007a, 2017, 2023). The LVOC BATc and the WGC BATc furthermore state the injection of activated carbon as technique to remove PCDD/PCDF in waste gas streams. These best available techniques also apply to end of pipe waste gas treatment techniques.

35. Air, water and solid emissions from these processes can be analysed for chemicals listed in Annex C and treated appropriately. Further information is available in the European Union BREFs on large volume organic chemical processes (LVOC) and on Common Waste Gas Management and Treatment Systems in the Chemical Sector (WGC). A basic review of the technology of air, water and solids treatment is found in the cross-cutting considerations section (III.C) of the present guidelines.

36. In general, best available techniques for airstreams can involve recovery and recycling of HCl, combustion of trace volatiles, scrubbing of incinerator output streams with water, alkaline solutions or dry alkali, and addition of activated carbon and baghouses for removal of particulate. These may be used alone or in combination. Treatment of water streams can involve stripping and recovery (condensation or absorption) of volatile materials from water.

37. Subsequent biological purification of water streams with removal of solids is done in a dedicated water treatment system. Best available techniques for both streams will be considered in the granting of permits for facilities combusting heavy ends.

Figure 5. By-product destruction



2. Potential sources and major processes of chemicals listed in Annex C

2.1 Conditions facilitating the formation of unintentional POPs in chemical production

38. Central to formation of the basic structure of PCDD, PCDF, PCB, PCN and HCB/PeCB is the presence or generation of aromatic compounds (Section 1.2). Those materials must, at some point, be chlorinated. For a wide range of chemical processes, aromatic compounds and conditions for chlorination are present, in particular processes that produce chlorinated aromatic compounds like chlorophenols, chlorobenzenes and related compounds or processes that utilize, alone or together, elemental chlorine or other oxidative conditions which facilitate chlorination

with the presence of organic materials (Table 1). Further conditions favouring the formation of unintentional POPs are elevated temperature, alkaline conditions and the presence of free radicals (UNEP 2013a; Section 1.2).

39. Combustion and waste gas treatment is a likely source of formation of unintentional POPs and the levels formed and released depend on the technology employed in combustion processes which are described in Section V.A "Waste Incineration" for minimizing and controlling releases.

40. Many national inventories of emission for PCDD/PCDF often focus on thermal sources like incineration, metal industry and open burning (UNEP 2013a; Wang *et al.* 2016). A few inventories have quantified the historic releases of PCDD/PCDF from particular pesticides and pesticide production revealing that single pesticide productions have disposed PCDD/PCDF of up to 800 kg TEQ and therefore a multifold of total global PCDD/PCDF release of approx. 100 kg TEQ/a (Wang *et al.* 2016). This highlights the need to destroy production waste from organochlorine productions and evaluate the disposal (Weber *et al.* 2008)

41. The contribution of unintentional PCB in the atmosphere is increasing and accounting for several percent and up to 85% of total PCB with marker congeners of unintentional PCBs from chemical production such as PCB-11, PCB-68, and PCB-209 (Mastin *et al.* 2022; Figure 2). Therefore, unintentional PCB formation from chemical production (Figure 2; Table 1 and 3) is a major contributor to environmental PCB contamination and needs to be better controlled and reduced in chemicals and products.

42. Also, for PCNs, major formation of unintentional PCNs stems from chemical production with e.g. formation of 427 kg PCNs/year including 563 g TEQ/year from chlorinated methane in China alone (Zhang *et al.* 2015). For HCB, some inventories of HCB as a by-product exist (Mumma *et al.* 1975; Bailey 2001; Barber, Sweetman and Jones 2005; Barber *et al.* 2005). The worldwide peak production and releases of HCB in high income countries occurred in the late 1970s and early 1980s. Production was about 10,000 tonnes per year from 1978 to 1981 of which 80% is believed to have been in Europe (Rippen and Frank 1986). A major input to the environment was its use as a pesticide, mainly as a fungicide for seeds of onions and sorghum and for crops such as wheat, barley, oats and rye, and as a fungicide to control bunt in wheat. After HCB pesticidal use stopped, the major formation and release became chemical (Table 1) and thermal processes.

Table 1: Unintentional POPs formation potential of processes and chemicals productions known to produce unintentional POPs (Formation potential of individual UPOPs in the process: H: high; M: medium; L: low; ND: no data; X: likely not relevant) (UNEP 2013a; UNEP 2015)

	PCDD/PCDF	**PCB**	**PCN**	**HCB/PeCB**	**HCBD**
Chloralkali (Graphite)	H	M	H	H	M
Chloralkali (Modern proc.)	L	ND	ND	ND	ND
Oxychlorination	H	ND	ND	H	H
Secondary HCl*	L – H	ND	ND	ND	ND
TiO2 (chlorine)	H	H	ND	ND	ND
Magnesium (chlorine)	H	H	H	H	ND
Magnesium (reduction process)	L	L	M	M	ND
FeCl3 (chlorine)	L-H	ND	ND	H	ND
FeCl3 (HCl*)	L-M	ND	ND	ND	ND
Chloromethanes, chloroethanes	L	H	H	H	H
PCP	H	ND	ND	H	X
2,4,5-T	H	ND	ND	ND	X

	PCDD/PCDF	PCB	PCN	HCB/PeCB	HCBD
2,4-D	L-H	ND	ND	ND	X
Triclosan	L-H	ND	ND	ND	X
PCNB; quintozene	H	H	ND	H	X
CNP	M-H	ND	ND	ND	X
Dacthal	L	ND	ND	H	X
p-Chloranil	H	M	ND	M	X
Chlorobenzenes	L-M	H	ND	L-H	X
TCPA	ND	ND	ND	M-H	X
Various TCPA-derived pigments	ND	ND	ND	L-M	X
Phthalocyanine Green	H	M-H	M-H	H	ND
Copper Phthalocyanine	L	L-M	ND	ND	ND
Dioxazine pigments	L-M	L-M	ND	ND	ND
Disazo Yellow pigment 13	X	M	L-M	X	X
Various chlorine-substituted organic colorants (e.g. Table 3)	ND	L-H	ND	L-M	ND
SCCP	L	L-M	L-M	ND	ND
Silicone via chlorosilanes	ND	M	M	M-H	ND
Silicone rubber (with 2,4-DCBP)	ND	H	X	X	X

*The content of the individual UPOPs depends on the production process in which the HCl is generated

2.2 Chlorine and sodium/potassium hydroxide production

43. Production of chlorine (Cl_2; CAS 7782-50-5) is the first step in producing chemicals and consumer goods that contain chlorine, as well as those for which some form of chlorine is used during their production. Chlorine and either sodium or potassium hydroxide are produced by electrolysis of aqueous solutions of sodium or potassium chloride respectively. There are several technologies associated with this process, and while a full treatment of the process is beyond the scope of this guidance, an overview is provided in other documents (Wiley Interscience 2000; Stringer and Johnston 2001; European Commission 2014).

44. The use of graphite electrodes in this process is known to be a major source of chemicals listed in Annex C in the past (CAK BREF, European Commission 2014; Yamamoto *et al.* 2018). Many chlor-alkali sites wich produced chlorine for several decades and up to 130 years are contaminated with PCDD/PCDF, PCNs, PCB, HCB and HCBD as documented by peer reviewed studies (Rappe *et al.* 1991; Otto *et al.* 2006; Takasuga *et al.* 2020) and information have been compiled (e.g. Stringer and Johnston 2001; Weber *et al.* 2008; CAK BREF European Commission 2014). Also other persistent halogenated organic compounds and polycyclic aromatic hydrocarbons (PAHs). The graphite electrodes are generally considered obsolete in modern facilities (see Section 3.2.1 below). In addition, the mercury cell technology resulted in large mercury pollution at production sites and are assessed in the frame of the Minamata Convention (Crook and Mousavi 2016; UNEP 2019a).

45. The major technologies used today are the membrane and the diaphragm technology (Section 3.2.1). In these BAT processes, PCDD/PCDF are also formed and have been measured in releases but at lower levels (US EPA 2004; Dyke and Amendola 2007; UNEP 2013a). A full mechanistic understanding of formation is lacking; however, it is believed that contact of elemental chlorine with preformed furan-like structures in organic gaskets and seals could be a source (Section 2.9).

46. Additionally, electrolytic diaphragm and membrane technologies are also used industrially to recover chlorine from hydrochloric acid solutions, producing hydrogen (but no caustic alkali) as a co-product but at much lower production scale (S&P Global Inc 2023). Furthermore, electrolysis of fused chloride salts (Downs process) also enables chlorine to be produced as a by-product of the manufacture of metallic sodium or magnesium (S&P Global Inc 2023). No data are available on the generation of unintentional POPs in these processes.

47. Global production of chlorine was 99.3 million tonnes in 2022 (Statista 2023). Its use distribution, on a worldwide basis, was estimated for 2022 as follows (S&P Global Inc 2023):

- More than 33% is used in the EDC/VCM/PVC production chain – production of ethylene dichloride (EDC), which is used to make vinyl chloride (VCM) that is polymerized to produce polyvinyl chloride (PVC);
- Other organic chemical markets (propylene oxide, epichlorohydrin, TDI, MDI, polycarbonate and chlorinated intermediates) accounted for more than 25% of chlorine consumption
- 20% is used to produce other organic derivatives;
- 10% is used in the production of inorganic chemicals and pulp and paper; and
- The remaining 10% is used in a variety of processes including water treatment.

2.3 Oxychlorination process

2.3.1 Background of oxychlorination process

48. In oxychlorination, an organic such as ethylene reacts with dry HCl and either air or pure oxygen in a heterogeneous catalytic reaction (Figure 6 and Figure **7**). An example is the reaction involving HCl, oxygen and ethylene to form ethylene dichloride and water.

$$C_2H_4 + 2HCl + ½O_2 \longrightarrow C_2H_4Cl_2 + H_2O$$

49. While there are many different commercial oxychlorination processes, in each case the reaction is carried out in the vapour phase over a modified Deacon catalyst. Unlike the Deacon process (which uses air or oxygen to oxidize HCl to chlorine and water under heat and catalysis) oxychlorination of ethylene occurs readily at temperatures well below those required for HCl oxidation. The catalyst typically contains cupric chloride ($CuCl_2$) as the primary active ingredient, impregnated on a porous support such as alumina, and may also contain numerous other additives.

50. The presence of heat, elemental chlorine, copper chloride catalyst and organic material makes the oxychlorination process a potential source of chemicals listed in Annex C, especially PCDD/PCDF and HCB. Aromatics may be generated in high-temperature processes and may also be present in feed materials, including HCl or air. Conditions in an oxychlorination reactor are in some ways similar to conditions in the areas of an incinerator downstream of the combustion zone, but may or may not contain similar amounts of soot-like elemental carbon or polycyclic aromatic hydrocarbons, which may contribute to *de novo* formation of PCDF (Lenoir *et al.* 2001; Process Economics Program 2000). Chemicals listed in Annex C created in this process, however, can be virtually completely removed from product and isolated in high-boiling materials (heavy ends) as a result of the distillation process.

51. Some chemicals listed in Annex C will adhere to catalyst particles. In the case of fixed bed systems, they can be a part of the spent catalyst that is removed from service. This material can be treated thermally to destroy adsorbed organics or placed in a secure landfill. In reactors, fluidized bed catalyst particles undergo size attrition and can become entrained in the vapour stream. These particles eventually show up in solid waste or in the biological solids removed at the end of water treatment.

52. The oxychlorination reaction generates heat and thus requires cooling for temperature control, which is essential for efficient production of ethylene dichloride. While there is an effective minimum temperature for the reactions, excessively high reactor temperatures lead to

more by-products, mainly through increased ethylene oxidation to carbon oxides and increased ethylene dichloride cracking. Cracking of ethylene dichloride yields vinyl chloride monomer and subsequent oxychlorination and cracking steps can lead progressively to higher-molecular-weight by-products with higher levels of chlorine substitution and is therefore prone to UPOPs formation. Excessive temperatures (>300 °C) can also deactivate the catalyst through increased sublimation of $CuCl_2$. There is a strong commercial incentive to avoid those reaction conditions (overheating) that have the potential to lead to the production of polychlorinated byproducts.

53. There are two types of catalyst systems used in oxychlorination: fixed bed and fluid bed. Both can be considered best available techniques as also acknowledged in the European BREF for the production of Large Volume Organic Chemicals (LVOC) (European Commission 2017).

54. Furthermore, the LVOC BREF addresses specifically POPs in the waste gases of EDC and VCM processes. The waste gases include halogenated compounds (e.g. PCDD/PCDF), HCl and, in some cases, chlorine. There are also emissions to air from storage and fugitive releases of VOCs and halogenated compounds. There is normally a shared end-of-pipe vent treatment unit to abate emissions. Thus, waste gas streams may be a major source of POPs. Attention has to be drawn to the reformation of PCDD/PCDF in the waste gas abatement system, which can be avoided by best available techniques (e.g. rapid waste gas cooling after post combustion). Use of certain feedstocks in an oxychlorination process may lead to higher formation of persistent organic pollutants. For example, oxychlorination of heavy ends in a vinyl chloride plant can give considerable yields of PCDD/PCDF (UK Environment Agency 1997).

Figure 6. C_1 and C_2 processes

(Wiley Interscience 2000)

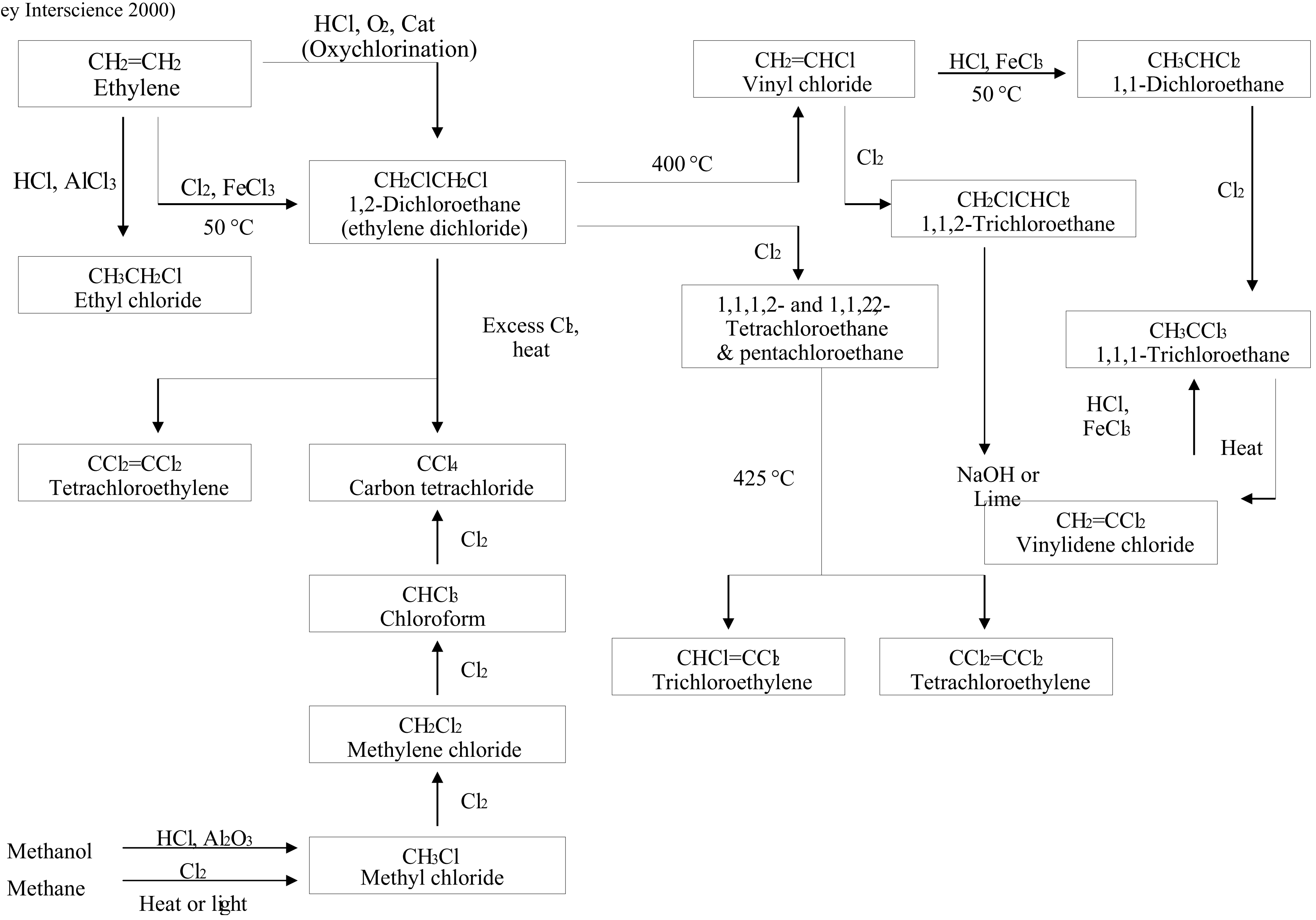
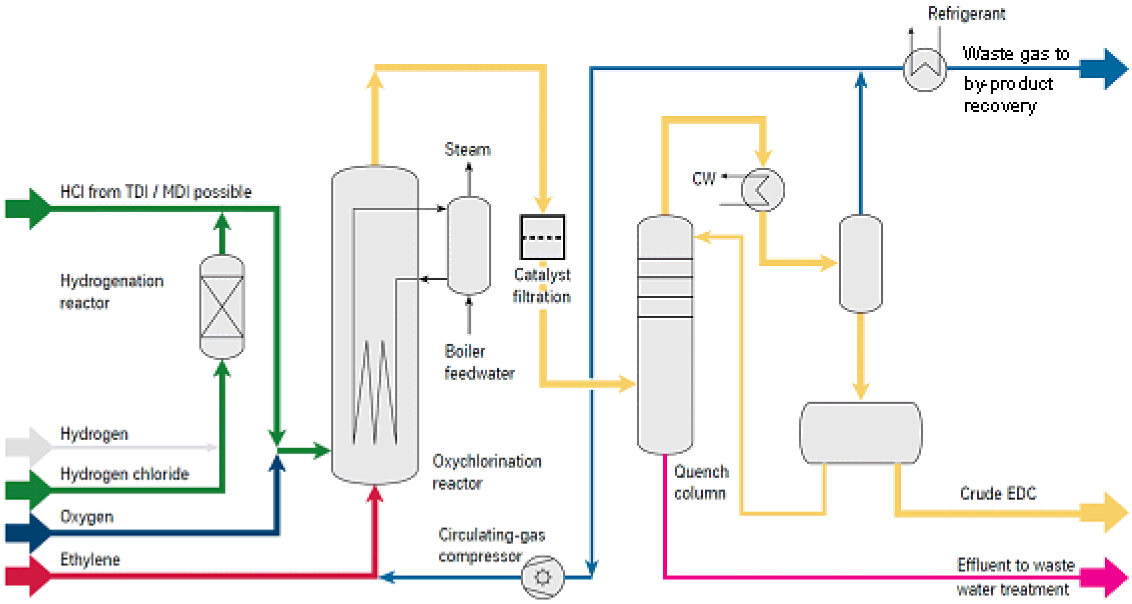


Figure 7. Oxychlorination flow diagram



Source: https://www.westlakevinnolit.com/en/licensing/edc-oxychlorination-process, Westlake GmbH & Co. KG

2.3.2 Fixed bed oxychlorination

55. Fixed bed reactors resemble multitube heat exchangers, with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of the catalyst within the tubes is important to ensure uniform pressure drop, flow and residence time through each tube. Reaction heat is removed by generating steam on the shell side of the reactor, or by flowing some other heat transfer fluid through it.

56. Temperature control in these reactions is important. The tendency to develop hot spots in a fixed bed can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in proportions that vary along the length of the tubes, so that there is low catalyst activity at the inlet, but the activity steadily increases to a maximum at the outlet.

57. Alternatively, tubes can be packed with catalyst formulated to have an activity gradient along the length of the tubes. Multiple reactors in series can also be used in fixed bed oxychlorination, providing a similar activity gradient. Using pure oxygen as feed instead of air permits lower temperature and therefore lowers the formation of chlorinated by-products; however, this must be balanced against the cost of energy expended in producing pure oxygen. Staging the air or oxygen feed and grading the catalyst activity flattens the temperature profile and allows improved temperature control (Process Economics Program 2000).

2.3.3 Fluid bed oxychlorination

58. Fluid bed oxychlorination reactors are typically vertical cylindrical vessels equipped with a support grid and feed sparger system designed to provide good fluidization and feed distribution. They contain internal cooling coils for heat removal and use either internal or external cyclones to minimize catalyst carry-over. Fluidization of the catalyst assures close contact between feed and

product vapours, catalyst and heat transfer surfaces, and results in a uniform temperature within the reactor. Reaction heat is removed by generating steam within the cooling coils or by passing some other heat transfer medium through them.

59. Operating temperature of 220 °C – 245 °C and gauge pressure of 150–500 kPa are typical for oxychlorination with a fluid bed reactor. Fixed bed oxychlorination generally operates at higher temperatures (230 °C – 300 °C) and gauge pressures of 150–1,400 kPa. Chlorinated by-products of ethylene oxychlorination typically include 1,1,2-trichloroethane, chloroform, carbon tetrachloride, ethyl chloride, chloral, 2-chloroethanol, all of the chloroethylene congeners, and higher-boiling compounds (Process Economics Program 2000).

2.4 Chlorinated solvents

2.4.1 Production of chlorinated aliphatic solvent

60. Because the process to generate trichloroethylene, perchloroethylene and carbon tetrachloride involves chlorination, oxychlorination and pyrolysis, by-products will include chemicals listed in Annex C including high levels of hexachlorobutadiene (HCBD), HCB, PCBs and PCNs (Mumma and Lawless 1975; Zhang *et al.* 2015; UNEP 2022a). These materials can be separated from the final product by distillation and isolated in a fraction known as heavy ends (Section 4.2). In the past, heavy end materials were commonly landfilled even in high income countries (Weber *et al.* 2011b). Since the 1970s these wastes are destroyed in high income countries using hazardous waste incineration, or other thermal destruction with recovery and reuse of HCl (Papp 1996; European Commission 2017). There is also the proposal to recycle production waste of EDC/VCM production to various products (Kurta *et al.* 2013), however, the fate of unintentional POPs in these wastes and the related products was not considered.

61. There are examples of large extant stocks and legacies in landfills of HCB and HCBD-containing material resulting from early solvent manufacture or more recent poor manufacturing practice without ESM of waste (Weber *et al.* 2011a; Weber *et al.* 2011b; UNEP 2013b). For low-income countries where destruction capacities are lacking, the landfilling of such waste might still continue with risk of pollution and long term releases and the need for developing and implementing ESM (Weber *et al.* 2011b; UNEP 2023a).

2.4.2 Production and use of chlorinated aromatic solvents

62. Chlorinated benzenes are important solvents or educts in the synthesis of pigments and other chemicals. One source of unintentional POPs (in particular PCBs and PCDD/PCDF) in certain pigment and pesticide production is the use of chlorinated aromatic solvents or educts (e.g. chlorobenzene, dichlorobenzene). For example, the PCBs in phthalocyanines including the non-chlorinated phthalocyanine stem from the use of chlorinated solvents (UNEP 2015). The PCB-content of phthalocyanines was due to the use of chlorinated aromatic solvents like dichlorobenzene and trichlorobenzene (Kerner and Maissen 1980; Anliker 1981; Heindl and Hutzinger 1986) and was often above regulation limit in the EU (50 mg/kg) or the limit in the United States (25 mg/kg) (Brychcy and Wagner 1998). Also, PCDD/PCDF levels in phthalocyanines were sometimes above German chemical regulation limits (Brychcy and Wagner 1998). There are two options for the presence of PCB and PCDD/PCDF from chlorobenzene solvents:

- They are already present in the chlorobenzene solvent.
- They are newly formed in the production of phthalocyanines

63. Both pathways are found in practice. Chlorobenzenes used as solvents can contain PCB and PCDD/PCDFs (German Environmental Agency 1985; Liu *et al.* 2004; Liu *et al.* 2023). PCBs can also be formed by the condensation of chlorobenzenes used as solvents during condition of phthalocyanine synthesis reaching temperature of 190 - 210°C (Brychcy and Wagner 1998). E.g. PCBs are formed when heating of 1,2,4-trichlorobenzene (used as solvent) at 200°C in the presence of copper chloride. These reaction conditions also resulted in the formation of PCDD/PCDF in ppt/ppb-range (Heindl and Hutzinger 1989). When decreasing the temperature, PCDD/PCDFs are still formed at 180°C, but were not detected at 160°C and below (Heindl and Hutzinger 1989). This study demonstrates the importance of detailed assessment on temperature effects and metal effects on PCDD/PCDF formation when using chlorinated benzenes as solvents or reaction products.

2.5 Pesticides associated with unintentional POPs

64. Pesticides like PCP, 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T), 2,4-D, chloronitrofen (CNP), and pentachloronitrobenzene (PCNB; quintozene) were responsible for major PCDD/PCDF contamination of the environment in the past (Masunaga et al. 2001; Weber *et al.* 2008; Holt *et al.* 2010; UNEP 2013a; UNEP 2015). Also, recent findings of elevated PCDD/PCDF in human milk in the Marshall Islands and eggs in Serbia with a distinct congener pattern indicate that PCDD/PCDF from 2,4-D related pesticides were responsible for the elevated contamination (Petrlik *et al.* 2022; Malisch *et al.* 2023).

65. Levels of PCDD/PCDF for the same pesticide can differ several orders of magnitude as e.g. discovered for 2,4-D (UNEP 2013a) caused by differences in synthesis routes and production conditions.

66. Facilities utilizing products manufactured in the processes should also examine the need for secondary measures of their own, especially waste disposal practices using BAT. For many pesticides potential PCDD/PCDF contamination is suspected (Table 7 in Annex II) but for a range of these pesticides an assessment is missing and more monitoring is needed (see Section 2.10).

2.5.1 Modified production of pentachlorophenol and sodium pentachlorophenate

67. Three routes to pentachlorophenol are known commercially: chlorination of phenol by chlorine over a catalyst, hydrolysis of HCB with sodium hydroxide and thermolysis of HCB. The most common route was the chlorination of phenol by chlorine. Sodium pentachlorophenate can be produced via hydrolysis of HCB or, more commonly, by treatment of pentachlorophenol by sodium hydroxide.

68. For both products, careful control of reaction conditions (e.g. temperature, chlorine feed rate and purity of catalyst) leads to significant reductions of PCDD/PCDF contaminants. In the United States, emission of these materials was reduced from about 3–4 mg I-TEQ/kg in the mid- to late 1980s to about 1 mg I-TEQ/kg since 1988 (US EPA 2001). In Japan, PCP produced in the 1960s contained 6.6 mg I-TEQ/kg while products from 1970s contained less than 0.1 mg I-TEQ/kg (Masunaga *et al.* 2001). Emission factors of the remaining products are not known.

2.5.2 Production of pentachloronitrobenzene (PCNB; quintozene)

69. PCNB can be produced by either the chlorination of nitrobenzene/chloronitrobenzene or the nitration of chlorinated benzenes (IPCS 1984). Today the production via nitrobenzene or chloronitrobenzene seems preferred (Huang *et al.* 2015b). Chlorosulfonic acid is used as solvent and nitrobenzene or monochloronitrobenzene is used as the raw material. Iodine is used as catalyst. After heating to 60–100 °C, the chlorine gas is introduced while stirring the mixture.

After the chlorination is completed, the mixture is reduced and filtered (Huang *et al.* 2015b). PCDD/PCDF and in particular dl-PCB levels were above the regulatory limits of Japan for pesticides (Huang *et al.* 2015b)[1] and the use of PCNB in Australia was considered a major PCDD/PCDF release source (Holt *et al.* 2010). The PCDD/PCDF levels in the formulation were higher compared to the raw PCNB purchased from the producers indicating that milling processes in the formulation of the pesticide might have increased PCDD/PCDF levels (Huang *et al.* 2015b).

2.6 Pigments and dyes containing unintentional POPs

70. A range of pigments are known to form and contain unintentional POPs and have been listed in the UNEP Toolkit with emission factors for PCDD/PCDF, and for PCBs where data were available (UNEP 2013a). Two examples are described below. For more information see Table 1 and Table 3.

2.6.1 Chloranil

71. Chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4dione) is the precursor for production of dioxazine pigments and dyes. It is also used as an intermediate in pharmaceutical products such as diuretics and antisterone (Liu *et al.* 2012). When prepared by chlorination of phenol or aniline via elemental chlorine, significant amounts of PCDD/PCDF are generated as by-products (UNEP 2013a; Table 2). Also, the production of chloranil via hydroquinone generated extreme high concentrations of PCDD/PCDF (and of PCB, HCB and PeCB) (Liu *et al.* 2012; Table 2). The differences in the levels of the products of the hydroquinone route were due to the refining and recrystallization of the cleaner products with the more sensitive use for pharmaceutical production (Liu *et al.* 2012; see Section 4.3).

Table 2: PCDD/PCDF emission factors for *p*-Chloranil production (UNEP 2013a)

***p*-Chloranil Production**	**Emission Factors (µg TEQ/t product)**
Direct chlorination of phenol	400,000
Chlorination of hydroquinone with minimal purification	1,500,000
Chlorination of hydroquinone with moderate purification	26,000
Chlorination of hydroquinone with advanced purification	150

2.6.2 PCB in pigments

72. A wide range of pigments and dyes contain unintentional PCBs. This can be caused by chlorobenzenes as solvents (see Section 2.4) or the presence of a PCB precursor in the production of the pigments (Hu and Hornbuckle 2010; Anezaki and Nakano 2014; Anezaki, *et al.* 2015; Anh *et al.* 2021). The PCB levels in pigments and dyes were found above national regulatory limits of e.g. the 50 mg/kg limit for PCB in products in Japan (Table 3; METI 2013).

Table 3: Pigment batches monitored by the Japanese Ministry of Economy and Trade exceeding 50 mg/kg* limit for import or use in Japan (METI 2013)

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[1] The use was restricted in Australia, Canada, the European Union, and New Zealand and currently the US EPA is considering restriction (US EPA 2022).

Name of Pigment	Name of Product	Amount of PCB (ppm)
Pigment Red -2 (CAS: 6041-94-7)	ZA-855 Red	37～58 ppm
	PERMANENT RED G-87	52 ppm
	FAST RED F2R (PR-2) POWDER	61 ppm
Pigment Red -112 (CAS: 6535-46-2)	ZA-862 Red	16～121 ppm
	Permanent Red GY	
Pigment Yellow -12 (CAS: 6358-85-6)	Pigment Yellow 1207	1,500 ppm
	Disazo Yellow G 178－4	110 ppm
Pigment Yellow -13 (CAS: 5102-83-0)	DISAZO YELLOW 3GR-M	220 ppm
	DISAZO YELLOW 3GR-M-5	
Pigment Yellow -14 (CAS: 5408-75-7)	SUIMEI YELLOW GGNB	810 ppm
Pigment Yellow -17 (CAS: 4531-49-1)	SUIMEI YELLOW 7G	700 ppm
	SUIMEI YELLOW 7GKT	1000 ppm
Pigment Yellow -55 (CAS: 6358-37-8)	SUIMEI YELLOW DRO-10	1,500 ppm
	SYMULER Fast Yellow 4539	
Pigment Yellow -81 (CAS: 22094-93-5)	SUIMEI YELLOW F10G	79 ppm
Pigment Yellow -83 (CAS: 5567-15-7)	SUMIKAPRINT FAST YELLOW HR-M	52～280 ppm
	SUMITONE FAST YELLOW HR-M-5	
	SUMIKAPRINT FAST YELLOW HR-T-2	
	SUMIKAPRINT FAST YELLOW HR	
	PY-2GN	
	SUIMEI YELLOW ERT	2,000 ppm
	SUIMEI YELLOW 5RT	
	Permanent Yellow HR-1183-2	59 ppm
Pigment Yellow -165 (CAS: 5102-83-0)	FAST YELLOW F5G	208 ppm
Pigment Orange -13 (CAS: 3520-72-7)	Orange BO-01	1,000 ppm
Pigment Orange -34 (CAS: 15793-73-4)	SUIMEI PYRAZOLONE ORANGE GR-N	190 ppm

*Please note that pigments might have lower PCB concentrations depending on production parameters. The analytical interferences by corresponding chlorobenzidines need to be controlled and excluded.

2.7 Other aliphatic chemicals

73. In addition to the aliphatic processes of the EDC and solvent production listed with emission factors for PCDD/PCDF (UNEP 2013a), other productions of aliphatic chemicals involving chlorination can also be formed and can release PCDD/PCDF and other unintentional POPs.

2.7.1 Chlorinated paraffins

74. Chlorinated paraffins are the most produced semivolatile organochlorines with a yearly production of more than 1 megaton (Mt) (Chen *et al.* 2022). Unintentional POPs detected in chlorinated paraffins were PCDD/PCDF, PCB and PCNs (Takasuga *et al.* 2012a; Takasuga *et al.* 2012b; He *et al.* 2023). The pattern of the PCBs and PCNs indicated that biphenyl and naphthalene were present in the reaction mixture and PCBs and PCNs were then formed by

chlorination in parallel to the synthesis of chlorinated paraffins at levels up to 100 mg/kg. It was estimated that approximately 100 tonnes unintentional PCB might be formed per year from the production of the approximately 1 million tonnes of chlorinated paraffins (Takasuga *et al.* 2012b). Also, the presence PCDF and PCDD have been detected in CP mixtures but at lower levels compared to PCNs and PCBs (Takasuga *et al.* 2012a; Takasuga *et al.* 2012b; He *et al.* 2023). Dibenzofuran, biphenyl and phenolic structures were detected in paraffin educts as likely precursors for PCDD/PCDF (He *et al.* 2023).

75. BAT/BEP for the production of chlorinated paraffins with unintentional POPs below UTC content are the use of clean paraffin mixtures with low content of PAHs, dibenzofuran, and phenolic compounds which does not result in formation of UPOP content above UTC limits.

2.7.2 Caprolactam (2-Azacycloheptanone) production from cyclohexane

76. In caprolactam production, formation of PCDD/PCDFs in the cyclohexane photonitrosation process has been reported with release to the aquatic environment above Japanese regulatory limit of 10 pg TEQ/L (Kawamoto and Weber 2021). The air emission of this caprolactam production route of 0.00035 µg TEQ/t was reported in the Japanese national inventory (Iwata *et al.* 2008). Also, unintentional PCB and HCB are formed and emitted with an HCB air emission factor of 3.2 µg /t of caprolactam and a PCB air emission factor of 8.1 µg /t have been reported in the Japanese inventory (Iwata *et al.* 2008).

77. Unintentional POPs can be eliminated by substitution of caprolactam production via other synthesis routes (see Section 3.2.5).

2.8 Inorganic chemical production

78. Chlorine is used in generating inorganics whether it remains in the final product (NaOCl, ClO_2, HCl, $FeCl_3$, $AlCl_3$, $ZnCl_2$, etc.) or is simply used in the process (TiO_2, Mg, Si). These inorganic compounds may be used either stoichiometrically (NaOCl, ClO_2) or as catalysts ($FeCl_3$, $AlCl_3$, $ZnCl_2$, etc.). There are two inorganic chemical manufacturing processes identified with known high production of chemicals listed in Annex C: chloride process manufacture of titanium dioxide (TiO_2) by certain manufacturers and production of anhydrous magnesium chloride ($MgCl_2$), an intermediate in the manufacture of magnesium metal, which have contaminated entire Fjords in Norway and rivers and related flood plains in Germany and the US with 100 kg of TEQ of PCDD/PCDF and high unintentional PCBs release (Knutzen und Oehme 1989; Praipipat *et al.* 2013; Förstner *et al.* 2016).

79. Other metal carbochlorination processes for purification of ore may involve similar conditions.

2.8.1 Hydrochloric acid

80. Hydrochloric acid is produced as primary HCl or recovered as secondary HCl from a wide range of chemical processes (see Section 1.4.4). Primary HCl is produced by reaction of hydrogen and chlorine or by reaction of metal chlorides (Hisham and Bommaraju 1995). The HCl samples produced by direct synthesis from chlorine did not contain measurable concentration of PCDD/PCDF (Wang *et al.* 2014).

81. Most HCl is produced as a secondary product (muriatic acid) of about 40 manufacturing processes, so emission factors are related to those processes (UNEP 2015; S&P Global Inc. 2022). The levels vary depending on the type of processes they originate, the operation of the respective process and whether the HCl has been refined.

82. In the secondary HCl product of two EDC/VCM/PVC facilities in the U.S., PCDD/PCDF concentrations of 20.8 and 28.1 pg I-TEQ/L were measured in samples of sales-grade aqueous hydrochloric acid (Carroll *et al.* 1997) indicating that the HCl has been refined. The secondary HCl from the production of chlorinated paraffins (n=2) had an average concentration of PCDD/PCDF of 8950 pg/L (Wang *et al.* 2014). For HCl from other chlorinated organic compounds in the chlor-alkali industry (n=8) the PCDD/PCDF were 780 pg/L (Wang *et al.* 2014). Furthermore 8 HCl samples from printed circuit etching processes were measured with average PCDD/PCDF amount of 82.9 ng/L (1260 pg TEQ/L) and maximum values of 540 ng/L (20,600 pg TEQ/L). The origin and respective processes of these 8 HCl samples was not clarified in this study (Wang *et al.* 2014).

83. Considering that HCl is partly used in the food and feed industry and PCDD/PCDF contaminated HCl has resulted in food contamination (Hoogenboom *et al.* 2007).

84. Different methods for purification of HCl are available and have been patented including distillation or removal of impurities by adsorptive resins or activated carbon (Allen 1947; Stultz *et al.* 1992; Cronin *et al.* 1994).

2.8.2 Titanium dioxide, chlorine process

85. There are two processes for manufacture of titanium dioxide (TiO_2): the chloride process and the sulphate process (see Section 3.2.7). In both processes, a mineral feedstock is used to extract pure TiO_2. Nevertheless, there are fundamental differences in the process routes and the potential emissions of chemicals listed in Annex C. TiO_2 ore, such as rutile or ilmenite – containing other metal oxides – is chlorinated under high temperature with the use of coke to produce titanium tetrachloride ($TiCl_4$), a stable, distillable liquid. Other metal halides are removed after cooling. $TiCl_4$ is then purified and oxidized with O_2, liberating chlorine, which is recycled in the process. This oxidation process is carried out between 900 – 2000 °C, in either a plasma arc furnace or in a toluene fired furnace, using oxygen injection (European Commission 2007b). A generalized overview of the chloride process is shown in Figure 8.

86. The presence of coke, chlorine, metals and elevated temperature in chlorination stage of the chloride route result in PCDD/PCDF and other unintentional POPs. PCDD/PCDF concentrations in residues from $TiCl_4/TiO_2$ production facilities were reported as follows: wastewater treatment solids, 402 ng TEQ/kg; chloride solids/waste acid, 812 ng TEQ/L; filter press solids, 2,615 ng TEQ/kg (US EPA 2001; UNEP 2013a).

87. Also, high releases of unintentional PCBs are documented with contamination of a river (Heine and Pavlick 2019). In 2014, Titanium Metals Corporation agreed to pay a record $13.75 million civil penalty[1] and perform an extensive investigation and cleanup stemming primarily from the unauthorized manufacture and disposal of unintentional PCBs at its manufacturing facility (US EPA 2014; US EPA 2023). An initial study of TiO_2 pigments has shown that PCDD/PCDFs and PCB can be transferred to a smaller extent to the pigment products (Ctistis *et al.* 2016). The emission from the chlorination process into the atmosphere contains also traces of chlorine, $TiCl_4$, HCl, CO and COS, even after the $TiCl_4$ condensation. $TiCl_4$, chlorine and HCl are adsorbed in a multistage system by aqueous scrubbers (remove HCl, $TiCl_4$) followed by caustic scrubbers (chlorine). The wash liquors are recycled in the process or recovered and partly sold as pure hydrochloric acid (28%).

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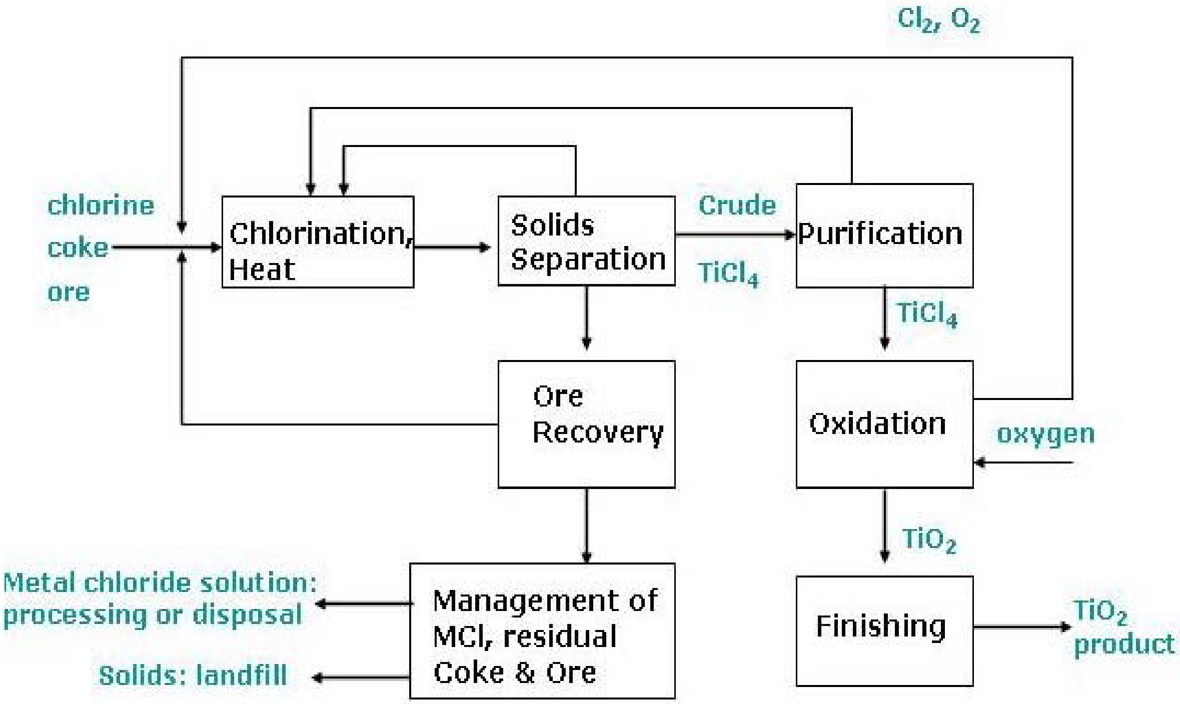
[1] Titanium Metals Corporation has unlawfully manufactured PCBs as a by-product of its titanium manufacturing process, without an exclusion from TSCA's ban (US EPA 2014; US EPA 2023).

88. Typical waste generated by the chloride process includes wastewaters from chlorinator coke and ore solids recovery, reaction scrubbers, chemical tank storage scrubbers, product finishing operations and wastewater treatment solids decantation. Waste solids from the chlorination stage, which consist of metal chlorides, coke and some ores, are neutralised in a chalk or lime slurry. The metals are precipitated and stabilised, and the filter cake might be landfilled, while the aqueous filtrate is discharged to the appropriate aqueous environment. Alternatively, the waste solids can also be treated by a special process to convert them into by-product hydrochloric acid and oxides. The conversion process involves roasting the chlorides in air to form HCl and leaving the oxides and unreacted coke as a solid residue. It allows for the chlorine content of the wastes to be utilised as hydrochloric acid (see Section 2.8.1). In the situation where the acid is sold, excess acid is usually neutralized (European Commission 2007b). If the residual coke is used for energy production, the potential content of PCDD/PCDF and other unintentional POPs must be considered. Liquid emissions from the process are treated in a variety of ways. They can be an integral part of the gas and solids treatment systems, which normally has the effect of neutralising residual acidity and precipitating soluble metal chlorides. A significant proportion of the effluent can originate from the finishing section of the plant. This liquid consists of slightly alkaline solutions of alkali metal sulphates and chlorides together with suspended solids (TiO_2), which result from the coating process (European Commission 2007b).

Figure 8. Chloride process for manufacturing titanium dioxide



2.8.3 Magnesium production, chlorine process

89. The production of magnesium from ores is partly based on electrolysis of magnesium chloride ($MgCl_2$). $MgCl_2$ can be produced by the reaction of magnesium oxide (MgO) and coke with elemental chlorine at 700–800 °C. Large amounts of PCDD/PCDF can be released from such $MgCl_2$ productions. 50 to 100 kg TEQ were emitted into water from an individual factory and contaminated a Fjord (Knutsen & Oehme 1989). Details on this process and releases from it as well as BAT/BEP are presented in section VI.B (iii) of the present guidelines (magnesium production) and are not elaborated here. An alternative production process of magnesium without chlorine is described in Section 3.2.9.

2.8.4 Ferric chloride ($FeCl_3$)

90. Ferric chloride ($FeCl_3$) treatment is used for water treatment including drinking water, e.g. to help to remove arsenic from drinking water (UNEP 2015). For the manufacture of $FeCl_3$ a stream of chlorine is passed over iron scrap at 650°C (Heindl and Hutzinger 1986).

91. Only a few data of PCDD/PCDF and other unintentional POPs are published for $FeCl_3$. High levels of UPOPs were detected in the $FeCl_3$ product including HCB (4 g/t) and PCBs (0.8 g/t) and highly chlorinated PCDF (∑PCDF 0.042 g/t) (Heindl and Hutzinger 1986).

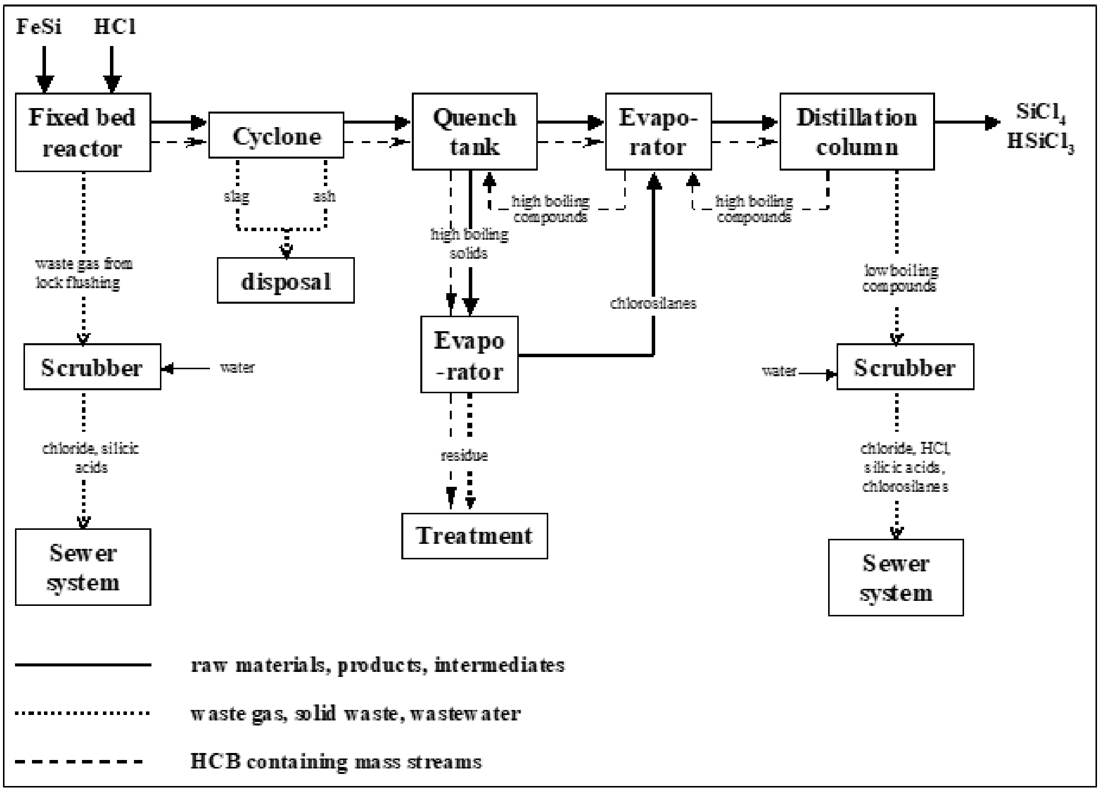
92. Liquid $FeCl_3$ used for coagulating sedimentation in wastewater treatment is recycled from processes such as etching liquid of printed circuit board and waste acid from steel mills (Nakano *et al.* 2007). Also, in this production/recovery of $FeCl_3$ from recycling in the etching process, high levels of dioxin-like PCBs and chlorinated-brominated PXBs were detected (Nakano *et al.* 2007).

2.8.5 Production of chlorosilanes for production of high purity silicone

93. The production of high purity silicone used for semiconductor applications or solar is produced from the reduction of tetrachlorosilane (silicon tetrachloride) or trichlorosilane (Noll 2012). The synthesis of chlorosilanes can be associated with the formation of significant amounts of chlorinated POPs including HCB, PeCB, octachloronaphthalene, and decachlorobiphenyl (DecaCB) (Regierungspräsidium Freiburg, 2004). The flow chart of a production is illustrated in Figure 9. As the synthesis of chlorosilanes is a purely inorganic reaction, first, the formation of HCB and other chlorinated aromatic hydrocarbons as an unintentionally formed by-product could not be understood.

94. The reaction is carried out at temperatures between 800 and 900°C. The raw material is not pure silicon but contains some weight-% of aluminium, iron, titanium and also traces of carbon. The second main raw material is hydrochloric acid gas which results from the synthesis of other compounds, such as from chlorination reactions, and is reused for chlorosilanes synthesis. It can be contaminated with various compounds such as chloromethane, tetrachloromethane, vinyl chloride, methanol and others which may serve as precursors for chlorinated by-products such as HCB. In addition, the temperature may allow radical reactions also and the mentioned metals may function as catalysts. At any rate, HCB and the other detected aforementioned hydrocarbons are unintentionally formed to a relevant extend.

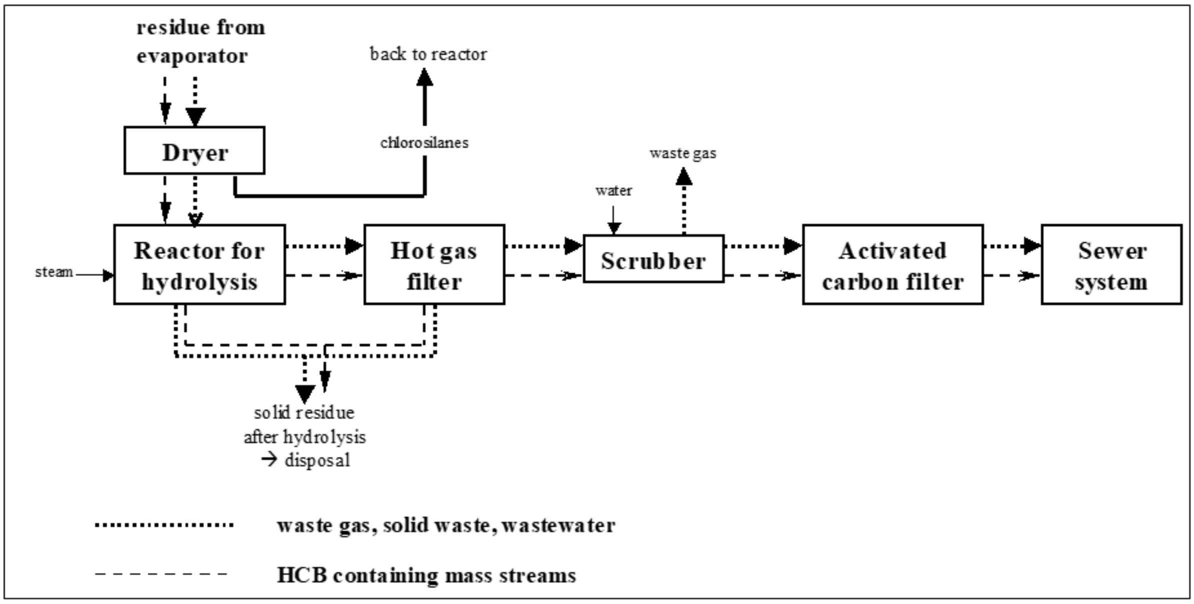
Figure 9. Chloride Flow chart for the production of chlorosilanes (Regierungspräsidium Freiburg, 2004) (the mass streams containing unintentional POPs are indicated



95. Until 1986, the residues from a chlorosilane production site have been hydrolysed with plenty of water and have been directly discharged to the Rhine River without any treatment. The residue consists of high boiling solids such as metal chlorides, silicon containing by-products and the aforementioned chlorinated POPs mainly HCB but also PeCB, OCN and DecaCB. Since 1987, the residues are treated to create a solid residue which can be disposed of or reused. The scheme for the treatment is illustrated in Figure 10.

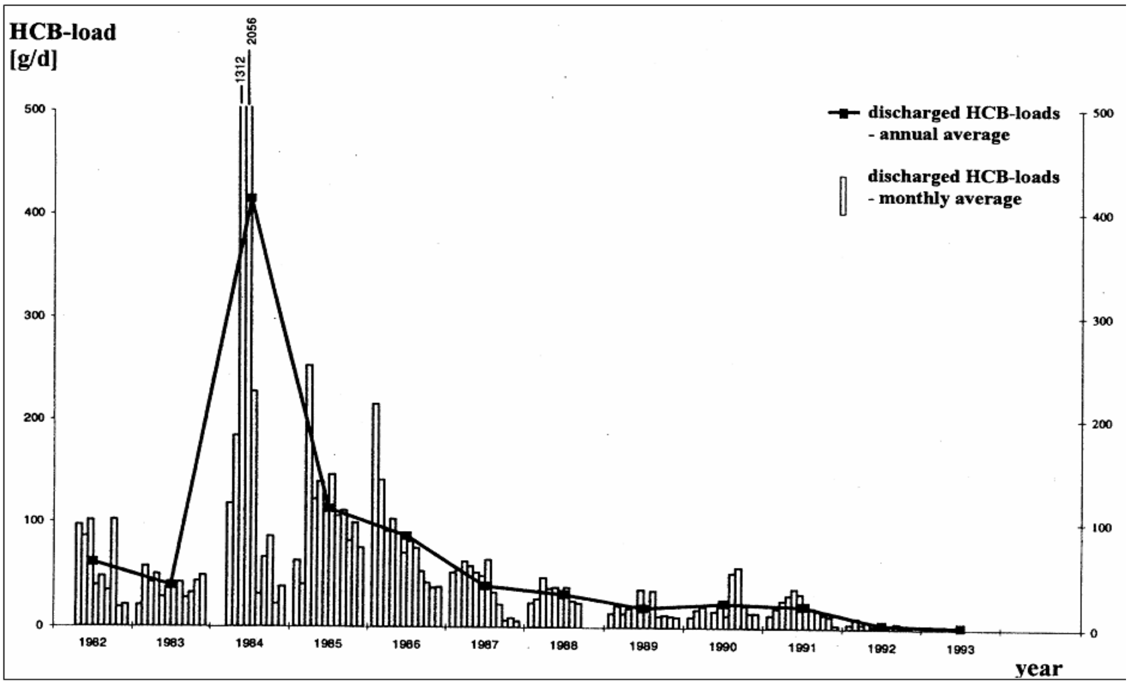
96. This technique avoids the discharge of most the chlorinated compounds. Due to the extremely high bioaccumulation potential of HCB, the load from the rinsing and cleaning operation is also relevant and release should be prevented. Therefore, it is also required to treat the rinsing and cleaning liquids, e.g. by adsorption to activated carbon (Regierungspräsidium Freiburg, 2004).

Figure 10. Treatment of the residue from the synthesis of chlorosilanes (Regierungspräsidium Freiburg, 2004)



97. Before the treatment of the residue as well as the rinsing and cleaning water until 1986, the daily HCB load was between 40 - 200 g/d (Figure 11). After the measures, the load was less than 0.1 g/d (Figure 11). As a consequence, discharge of HCB and other chlorinated POPs of less than 0.1 g/d from hydrochlorination of silicon were considered to be BAT for this facility. The formation of unintentional POPs can be minimised by purifying the recycled hydrochloric gas by deep-temperature condensation (-30 °C) which is also considered as BAT.

Figure 11. Discharged HCB loads to River Rhine at D-Rheinfelden from 1982 – 1993; from discharged wastewater, a flow-proportional taken 24 h-composite sample has been daily analyzed for HCB (Regierungspräsidium Freiburg, 2004)



2.8.6 Silicone rubber production using 2,4-DCBP

98. The use of bis(2,4)-dichlorobenzoylperoxide (2,4-DCBP) as cross-linking agent in the production of silicone rubber results in the formation of specific PCBs (PCB-47, PCB-51 and PCB-68). These PCBs partly remain in the silicone rubber and result in indoor exposure (Herkert *et al.* 2018). Also, PCBs can be released from the production facility of silicone into the surrounding (Hombrecher *et al.* 2021; Kaifie *et al.* 2022).

99. While BAT/BEP air pollution measures can reduce and eliminate the releases of PCBs from factories, it cannot eliminate the presence in the product and releases during use.

100. Alternatives for 2,4-DCBP are available (see 3.2.10).

2.9 Other processes and products in contact with elemental chlorine

101. There is evidence that contact of elemental chlorine with organic process equipment (seals, gaskets, fibreglass equipment) that may contain aromatics, polycyclic aromatic hydrocarbons or elemental carbon can give rise to chemicals listed in Annex C, usually PCDF but also a wide range of other unintentional POPs (Takasuga *et al.* 2020) and therefore also modern chlorine production has some PCDD/PCDF formation (US EPA 2004). Recent and former studies show that elemental chlorine or chlorine formed from aqua regia (mixture of concentrated nitric acid and concentrated hydrochloric acid, normally in a molar ratio of 1:3) form PCDD/PCDF even in soils and sediments (Yamamoto *et al.* 2007; Xie *et al.* 2023; Sections 2.9.1 ad 2.9.2 below) and BAT/BEP for these processes and environmental releases are required.

102. The findings also highlight that more systematic monitoring of PCDD/PCDF and other UPOPs should be conducted where elemental chlorine is used or generated (Section 2.10).

2.9.1 Standard digestion for analyses of metals in soils with aqua regia

103. A recent example of relevant formation and release of PCDD/PCDF from a new discovered process is the finding that the standard digestion for analyses of heavy metals in soil with aqua regia (ISO 11466 and similar standard procedures) results in abundant dioxin formation in soil and various organic carbon-containing matrices (Xie *et al.* 2023). Σ17PCDD/PCDFs concentrations were in the range of 66.6−142,834 ng/kg (5.6−17,021 ng WHO2005-TEQ/kg) in 19 soil samples after digestion with aqua regia for 6 h with some of the samples above the Basel Convention low POP content for PCDD/PCDF of 1000 ng TEQ/kg or 15,000 ng TEQ/kg (UNEP 2023a). Compared with cellulose and lignin, humic acid served as an important organic matter component that was converted to PCDD/PCDFs during soil digestion (Xie *et al.* 2023). Strong oxidation and production of reactive chlorine by aqua regia are considered the key factors in the formation of the PCDD/PCDFs. The yearly emission of PCDD/PCDFs due to digestion with strong acids by the inspection and testing industry was estimated to be 83.8 g TEQ in China for 2021 which would be ~0.9% of the total dioxin inventory in China (Xie *et al.* 2023).

104. The measurement of heavy metals in soil with aqua regia is performed globally and is included in the ISO 11466 standard. To control the potential risk of release from laboratories and enterprises (Xie *et al.* 2023) BAT/BEP measures for the ESM of the digested soils should be in place.

2.9.2 Formation of PCDD/PCDF from chlorination of sediments

105. In an experiment for the assessment of the risk of formation of PCDD/PCDF in sediments from disposal of chlorine containing disinfection waste and waste water, PCDD/PCDF were formed over several days by consecutive formation of chlorinated PCDF with the distinct elemental chlorine patter of 2,3,7,8-marker congeners 2,3,7,8-TCDF, 1,2,3,7,8-PentaCDF and 1,2,3,4,7,8-HexaCDF (Yamamoto *et al.* 2007). Therefore, the dibenzofuran (and possibly

dibenzofuran precursor) in sediments is chlorinated analogously as precursors from the graphite electrode but at a longer time scale (Yamamoto *et al.* 2018). Therefore, wastewater containing elemental chlorine can form 2,3,7,8-substituted PCDFs over days and longer periods and should not be released to surface water. Surface water sediments that have received larger loads of elemental chlorine should be assessed for the status of PCDF contamination.

2.10 Improved screening and monitoring of processes for PCDD/PCDF and other unintentional POPs

106. There is a lack of knowledge of formation and release of PCDD/PCDF from a wide range of processes in the chlorine and organochlorine industry even where the formation of PCDD/PCDF or other UPOPs is known (UNEP 2013a; UNEP 2015). This can be seen e.g. by the lack of data for many chemicals listed in the UNEP Toolkit where PCDD/PCDF formation is known but often only one impact factor for release vectors including products is available (see Source Group 7 of UNEP 2013a). For some vectors like water release, only a few systematic studies have been conducted for processes known or suspected to release PCDD/PCDF or other UPOPs (e.g. for Japan Kawamoto and Weber 2021). Furthermore, for several organochlorines compounds it is known that PCDD/PCDF are formed but the database is too sparce to propose emission factors (UNEP 2013a). In addition, for many chemical production processes only data for PCDD/PCDF are available and data for other UPOPs are lacking (UNEP 2013a).

107. Furthermore, in recent years new relevant PCDD/PCDF and other UPOPs sources have been discovered such as the recent finding of high PCDD/PCDF generation and release in the standard measurement of heavy metals in soil with aqua regia (ISO 11466) (Xie *et al.* 2023) or PCBs in pigments (Hu and Hornbuckle, 2010; Anezaki and Nakano, 2014; Anezaki*et al.* 2015; Anh *et al.* 2021) or high unintentional PCB formation and release of specific PCBs (PCB 47, 51 and 68) from silicone rubber production using bis(2,4)-dichlorobenzoylperoxide (2,4-DCBP) as catalyst cross-linking agent (Herkert *et al.* 2018; Hombrecher *et al.* 2021; Kaifie *et al.* 2022).

108. Further, there is a lack of information for PCDD/PCDF content for the more than 40 sources of secondary HCl where only for a few sources data on PCDD/PCDF are available (Wang *et al.* 2014; UNEP 2015) and for other production processes data are lacking. HCl is partly used in the production of feed and food and HCl contaminated with PCDD/PCDF has contaminated gelatine production in a European country (Hoogenboom *et al.* 2007).

109. This highlights that a better systematic assessment of potential new sources and the improvement of emission factors of chlorine and organochlorine productions is needed and can be considered as BEP.

110. The UNEP Toolkit has included an Annex 2 a “Guidance on Identifying Sources of PCDD/PCDF” to improve this situation. The Toolkit refers in the identifying source Annex to some best practice studies conducted in Denmark (Hansen 2000) and in the European Union (Wenborn *et al.* 1999). Furthermore, a national approach for monitoring of the chlorine chain for PCDD/PCDF and dioxin-like compounds has been conducted in the Netherlands (van Hattum *et al.* 2004). The Dutch study used a combination of instrumental analysis and bioassays for analysing PCDD/PCDF and screening dioxin-like toxicity (van Hattum *et al.* 2004). Systematic monitoring of industries using chlorine or involving processes where PCDD/PCDF and other unintentional POPs might be formed can improve understanding of the formation and release of PCDD/PCDF and other UPOPs. It would also enhance understanding of the current emission situation and contribute to risk management control of chlorine and organochlorine production and can be considered BEP. BAT monitoring approaches should also be used. The (pre-)screening of dioxin-toxicity with validated bioassays can be an economic approach for screening

chemicals[1], wastes and effluents, as well as for some chemicals and processes (Huwe *et al.* 2003; van Hattum *et al.* 2004).

111. Relevant data and emission factors generated in such studies could be forwarded to the BRS Secretariat for the clearing house mechanism where it can be considered to improve the emission factors of the UNEP Toolkit and to fill the gaps of the release vectors of the Source Group 7 Production and use of chemicals.

3. Primary measures that reduce or avoid formation of chemicals listed in Annex C

112. Primary measures are regarded as pollution prevention techniques to reduce or eliminate the generation of unintentional POPs. This can be achieved by substitution of chemicals or by alternative production.

3.1 Substitution of chemicals associated with formation of unintentional POPs

3.1.1 General Considerations

113. The Stockholm Convention recognizes the importance of developing and using environmentally sound alternative processes and chemicals (UNEP 2001). Therefore, chemicals known to contain UPOPs might be substituted by alternative chemicals or processes with low or no potential for UPOPs content or formation. Appropriate substitution of POPs or POPs containing products by safer alternatives – chemical and non-chemical – is the best and most effective way to eliminate POPs from articles, products and processes and to reduce and prevent use-related environmental contamination and human health problems (UNEP 2015). For such a substitution care needs to be taken not to select regrettable but sustainable substitutes (Fantke *et al.* 2015). The Stockholm Convention has developed a general guidance (UNEP 2009) and a wide range of tools for alternatives assessment for chemicals have been developed such as the toolbox for alternatives assessment of the OECD (2023) as well as a guidance which aims to identify and outline key considerations for the identification and selection of safer alternatives (OECD 2021).

3.1.2 Use of alternatives to impacted solvents

114. The production and use of solvents like chlorobenzene, dichlorobenzene or 1-chloronaphthalene are associated with UPOPs formation and release (Hannah *et al.* 2022; Klimczak *et al.* 2023). Also, the production of chlorinated aliphatic solvents is associated with formation of unintentional POPs (UNEP 2022a) and occupational exposure has been associated with relevant toxicities (Ruder 2006). Therefore, the substitution of chlorinated solvents by alternative solvents, in particular “green” solvents, can result in the reduction and possibly elimination of unintentional POPs. Guidances for the selection of green and sustainable solvents have been developed (Byrne *et al.* 2016; Prat *et al.* 2016; CHEM21 2020) but not assessed under the Stockholm Convention.

3.1.3 Use of alternatives to impacted pesticides and biocides

115. A range of pesticides contained high levels of PCDD/PCDF such as 2,4,5-T and PCP[2] which was one reason to phase out or to restrict these pesticides. The UNEP toolkit lists a range of other pesticides that are known to contain PCDD/PCDF to different degrees depending on the production quality (UNEP 2013a; UNEP 2015). The substitution of pesticides has been

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[1] In addition to dioxin-toxicity, chemicals could also be screened for endocrine effects (Hamers *et al.* 2006).

[2] PCP and its salts and esters have been listed as POPs in the Convention due to their POPs properties

established in the Stockholm Convention for the listed POPs in particular for POPs pesticides listed with exemptions and activities (UNEP 2014). Other UN guidance documents are available on alternatives to pesticides including highly hazardous pesticides (FAO and TECA 2015; Watts and Williamson 2015; UNEP 2022c; UNEP 2023b; Rotterdam Convention 2024).

116. Also, for the biocide triclosan, better alternatives are available and in many uses it is not needed (e.g. cosmetics, toothpaste, soap) and can just be omitted (Halden *et al.* 2017).

3.1.4 Use of alternatives to impacted pigments

117. A wide range of pigments are available including natural pigments which can possibly substitute pigments containing unintentional POPs. A systematic approach to substitute pigments containing unintentional PCBs has been developed and published by ChemFORWARD (Nestler 2019). ChemFORWARD also developed a database "iPCB Pigments Resource" as a free searchable dataset of nearly 400 pigments organized by chemical name, CAS#, colour, and presence of chlorine. The tool can be used to find alternatives by avoiding those containing or manufactured with chlorine and thus reducing the likelihood of containing unintentional PCBs[1] (ChemFORWARD 2024).

118. This could include natural pigments, like those that have been compiled in the reviews by Malik *et al.* (2012) and Muthusamy *et al.* (2020). However, it must be emphasized that quality and safety issues may arise from reduced stability of colorants particularly for safety paints and coatings, wherein adverse effects such as "warping", induced brittleness, "chalking", and reduced lightfastness may not be tolerated.

119. For some applications such as certain plastics, the use of pigment could be eliminated to reduce the presence or formation of UPOPs and also the complexity of plastic product to facilitate recyclability (Fenner and Scheringer 2021; UNEP 2023c).

3.1.5 Use of alternatives to SCCPs

120. For SCCPs partly containing unintentional POPs (Section 2.7), information on alternatives has been compiled due to the listing as a POP and a guidance on alternatives has been developed in the frame of the Stockholm Convention (UNEP 2019b).

3.1.6 Use of alternatives to impacted other industrial chemicals###

121. Further suggestions on substitution to add?

3.2 Alternative production processes that reduce or avoid the formation of unintentional POPs

122. In many cases there are alternative processes by which desired chemicals can be manufactured. For processes where chemicals listed in Annex C are generated, there may be alternative processes that do not involve generation of such chemicals. Consistent with the Convention, the guidance on alternatives in this document, and good business practice, a thorough review of alternative processes and technologies should be conducted before building new or substantially modifying production facilities.

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[1] NOTE: The use or presence of chlorine in a pigment or in the pigment manufacturing process does not definitively determine that inadvertent PCBs are present in a pigment. Manufacturing process changes regularly occur, and current information can be obtained by contacting the pigment manufacturer directly. While it is known that some pigments can contain inadvertent PCBs, such as diarylide yellow, it may not be true for all suppliers of it or other pigments that contain chlorine or could be made with chlorinated solvents (CHEMFORWARD (2024)).

3.2.1 Elimination of carbon electrodes for chloralkali production

123. Older technology in the manufacture of chlorine and caustic soda utilized graphite anodes. Residues found from cells so constructed contained significant amounts of PCDD and especially PCDF and PCNs but also all other unintentional POPs and further persistent, bioaccumulative and toxic chemicals (PBTs) (UNEP 2013a; Takasuga *et al.* 2020). This problem was eliminated in much of the world following the invention of the coated titanium anode by H.B. Beer in 1965 and subsequent substitution for graphite in these processes (European Commission 2014). To the extent that the technology is still employed, the use of graphite electrodes is not a BAT.

124. BAT for chloralkali plants are the membrane technology and diaphragm technology which are, for example, described in the EU BREF (European Commission 2014). The mixture of PCDD/PCDF congeners found on contaminated chlor-alkali sites shows a specific pattern dominated by dibenzofurans, which is different to other sources. Similarly, the pattern of PCN congeners is also specific for contaminated chlor-alkali sites. When measured in parallel, total PCN concentrations on contaminated sites usually exceed those of PCBs and PCDDs/PCDFs by up to one order of magnitude. At PCDD/PCDF-contaminated sites, high levels of mercury in the soil do not necessarily correspond with high levels of PCDDs/PCDFs, and vice versa. This means that the mercury level is not an indicator of the PCDD/PCDF levels (BREF chlor-alkali, European Commission 2014).

3.2.2 Reduction of unintentional POPs in oxychlorination

Use of hydrogen in oxychlorination

125. Oxychlorination process feed purity can be a factor in by-product formation, although the problem usually is only with the low levels of acetylene, which are normally present in HCl from the ethylene dichloride cracking process. Acetylene fed to the oxychlorination reactor can be converted to highly chlorinated C_2 products, and chlorinated C_2 products could give rise to chlorinated aromatics via cyclotrimerization (Figure 3 and Figure 6; Process Economics Program 2000). Selective hydrogenation of this acetylene to ethylene and ethane in a reactor prior to the oxychlorination reaction is widely used as a measure to avoid by-product synthesis, especially of polychlorinated aliphatics (see Figure **7**).

Catalyst maintenance and temperature uniformity control

126. Fluidized bed reactors tend to have better temperature control and more uniform performance, although the previously mentioned attrition of catalyst particles can allow for carry-over into other streams within the facility. For fixed bed oxychlorination catalysts, appropriate packing and maintenance can reduce hot spots and can reduce fouling of the catalyst bed, loss of productivity and the potential for generation of high-molecular-weight products. Catalyst beds are changed on a regular basis to maintain efficiency.

Reduction in aromatic hydrocarbons in feeds to oxychlorination processes

127. Two patents specify pretreatment of air or HCl reagents used in oxychlorination to remove aromatics, presumably precursors to various unintentional POPs (Cowfer *et al.* 1998, 2001). This patented technology is proprietary and as such may not be appropriate for any required implementation of BAT, but indicates another primary approach.

128. Feeds to oxychlorinators should be controlled to minimize or eliminate feed of higher organics and aromatics that could lead to high formation of Annex C compounds. Because raw heavy ends from ethylene dichloride or solvent streams may contain these compounds, heavy ends should be suitably treated prior to use in solvent production.

3.2.3 Elimination of alkali treatment and optimising conditions in the production of chlorophenols and related pesticides

129. In the manufacturing of chlorophenols sometimes alkali treatment has been applied such as in the manufacture of 2,4,5-trichlorophenol by alkali treatment of 1,2,4,5-tetrachlorobenzene or manufacturing of PCP from HCB. The 2,4,5-trichlorinated phenol, in the presence of excess alkali, generates significant amounts of 2,3,7,8-TCDD while PCP generates mainly OCDD. Condensation reaction and formation of PCDD/PCDF also occur in the production of 2,4-D and derivative pesticides and a wide range of TEQ (0.1 µg TEQ/t to 5688 µg TEQ/t) were measured in commercial products (UNEP 2013a). Factors which need to be controlled in the production are the pH and temperature as well as possibly other factors.

3.2.4 Production of tetrachlorophthalic acid (TCPA)

130. There are two manufacturing methods of TCPA (Government of Japan 2006):

a) Gas-phase process (270ºC)

131. TCPA is produced by reacting phthalic anhydride with elemental chlorine in the gas phase.

b) Liquid-phase processes

132. TCPA is manufactured by reacting phthalic anhydride with chlorine gas in the liquid phase. Either solvent fuming sulfuric acid or chlorosulfonic acid is used at 50 to 60ºC, or iodine catalysis is used at 120ºC.

133. The gas-phase process results in higher HCB levels due the higher temperature applied in the gas-phase process (270ºC) and the related decarboxylation of phthalic acid (Government of Japan 2006). Therefore, the liquid-phase processes should be used to minimize HCB formation in combination with reduction of HCB in the final TCPA product by recrystallization (see Section 4.2.3). Also, the amount of chlorine and the control of excess chlorine should be controlled to minimize HCB formation (Government of Japan 2006).

3.2.5 Alternative production of caprolactam

134. Caprolactam (2-Azacycloheptanone; $C_6H_{11}NO$) or ε-caprolactam is an important raw material for the production of nylon 6. Only emissions in caprolactam synthesis using the cyclohexane photonitrosation process have been reported (Kawamoto and Weber 2021). Alternative processes are available and used for the production of caprolactam including the caprolactam synthesis from cyclohexanone or the cyclohexane oxidation method (Kawamoto and Weber 2021).

3.2.6 Acetylene process for vinyl chloride

135. The acetylene process is an alternative route to produce vinyl chloride. In the acetylene process, calcium oxide and coke or coal are heated together at about 2,000 °C to produce calcium carbide (CaC_2). When CaC_2 is reacted with water, acetylene is produced. Vinyl chloride results from a mercury catalyst-mediated addition of HCl to acetylene. The process has high releases of mercury but lower PCDD/PCDF formation.

136. Different levels of PCDD/PCDF were detected in the washing step, likely arising from the use of hypochlorite or sodium hypochlorite (HClO or NaClO), or, in the case of Japan, the use of elemental chlorine (Kawamoto and Weber 2021). In a Korean study an emission factor of 127 µg TEQ/t of acetylene was found (Jin *et al.* 2009). PCDD/PCDF contamination in waste from an acetylene process has been reported for a Brazilian facility (Torres *et al.* 2013).

137. The balanced process for production of ethylene dichloride, and subsequent cracking to vinyl chloride with associated formation of unintentional POPs (UNEP 2013a), has, over the past seventy years, largely superseded production of vinyl chloride via the acetylene route in industrial countries due to economic benefits and the avoidance of release of mercury. The process is still used in China due to abundance of available coal and lime resources necessary for the production of calcium carbide with an estimate of total release of 400 g TEQ/year (Nie *et al.* 2015) but with an ongoing GEF project to reduce the mercury releases (GEF 2017).

3.2.7 Titanium dioxide, sulphate process

138. For TiO_2, there is an alternative commercial process utilizing sulphuric acid (H_2SO_4) instead of the chlorine. In the sulphate process for TiO_2, ore is dried, ground and classified to ensure efficient sulphation by agitation with concentrated sulphuric acid in a batch or continuous exothermic digestion reaction. Controlled conditions maximize conversion of TiO_2 to water-soluble titanyl sulphate using the minimum acid. The resultant dry, green-brown cake of metal sulphates is dissolved in water or weak acid, and the solution is treated to ensure that only ferrous-state iron is present. The solution temperature is reduced to avoid premature hydrolysis and clarified by settling and chemical flocculation. The clear solution is then further cooled to crystallize coarse ferrous sulphate heptahydrate (known as copperas, $FeSO_4 \cdot 7H_2O$), which is separated from the process and sold as a by-product.

139. The sulphate route for the production of TiO_2 uses concentration sulphuric acid for the digestion of the TiO_2 containing ore. Subsequently, the liquor is reduced using scrap iron and hydrolysed resulting in solid titanium oxyhydroxide. $TiO(OH)_2$ is then filtered, washed and calcinated to obtain the final product (European Commission 2007b). The insoluble “mud” is washed to recover titanyl sulphate liquor. That liquid is filtered to remove final insoluble impurities, then evaporated to a precise composition. Hydrolysis to produce a suspension (“pulp”) consisting predominantly of clusters of colloidal hydrous titanium oxide follows.

140. Precipitation is carefully controlled to achieve the necessary particle size, usually employing a seeding or nucleating technique. The pulp is then separated from the mother liquor and extensively washed to remove residual traces of metallic impurities, using chelating agents if necessary. The washed pulp is treated with chemicals, which adjust the physical texture and act as catalysts in the calcination step. This process can produce either anatase or rutile crystal forms, depending on the additives used prior to calcination (European Commission. 2007b).

141. The sulphate process requires 2.4–3.5 tonnes of concentrated H_2SO_4 per tonne of TiO_2, depending on the used raw material. Sulphuric acid is discharged from the process as sulphate, especially as iron(II) sulphate, or as free sulphuric acid in the spent acid. The total volume of spent acid caused by this process amounts to approximately 6–9 tonnes per tonne of pigment. The recovery of the sulphuric acid from the used acid is divided into two processes:

- Recovery of the free acid by evaporation;
- Thermal decomposition of sulphates and H_2SO_4 production on the basis of sulphur dioxide.

142. The process gives rise to high amounts of contaminated spent acids of different concentrations. The spent acid is concentrated by evaporation to approximately 70%, where iron sulphate has a minimum solubility. After crystallization, the salts are separated from the acid by filtration. The almost salt-free acid can be recycled directly or after further concentration. Alternatively, they can be used for other chemical processes or be decomposed to SO_2.

143. The separated sulphates, strongly loaded with sulphuric acid, are thermally decomposed in flowing bed reactors at temperatures of 800 °C – 1,000 °C (under the addition of sulphur, coal or oil as fuel) to sulphur dioxide and iron oxide. After cleaning, the obtained sulphur dioxide is processed to virgin sulphuric acid. The residual iron oxide can be reused in the cement industry.

144. In the past those spent acids could not be recycled and used in other production processes. Methods for reuse and recycling of spent acids have been developed and are currently standard operation for TiO_2 production in high-income countries (European Commission 2007b).

145. The chloride process does not generate spent acids, and this means far less waste generation. However, high levels of chemicals listed in Annex C are formed and released, specifically highly chlorinated PCDF and PCBs (US EPA 2001; US EPA 2014; UNEP 2013a). Waste generation in the sulphate process, including of sulphuric acid and other mineral waste, is much higher but is not known to involve chemicals listed in Annex C. Trading elimination of small amounts of such chemicals for generation of large quantities of other waste materials may not be the optimal environmental approach. Best available techniques can be plant specific and should be examined on a case-by-case basis.

146. The TiO_2 production presents an interesting case study: the chloride process forms and releases high levels of PCDD/PCDF, PCBs and other unintentional POPs (US EPA 2001; US EPA 2014; UNEP 2015) but produces much less waste compared to the sulphate process. The sulphate process involves more waste, which is a problem as titanium dioxide is a high-volume chemical. There are further alternative processes for TiO_2 production where a life cycle assessment indicated lower cumulative energy demand and total CO_2 emissions for the alkaline roasting of titania slag (ARTS) process (Middlemas *et al.* 2015).

3.2.8 Magnesium production without chlorine

147. In the Pidgeon process, dolomite ($CaCO_3$ $MgCO_3$) is treated in the magnesium plant where it is calcined and briquetted. The resulting magnesium oxide is reduced at high temperatures with silicon, often provided by a ferrosilicon alloy to produce magnesium (Nie *et al.* 2011). The process can also be carried out with carbon at approximately 2300 °C:

$$2MgO(s) + Si(s) + 2CaO(s) \rightarrow 2Mg(g) + Ca\ 2SiO4(s)$$

$$MgO(s) + C(s) \rightarrow Mg(g) + CO(g)$$

148. Also in this thermal process, unintentional POPs are formed and emitted (Nie *et al.* 2011), however, emissions are several orders of magnitude lower when compared to the chlorine process (Section UNEP 2013a).

3.2.9 Production of ferric chloride without elemental chlorine

149. $FeCl_3$ can be manufactured by the exothermic reaction between ferric oxide and hydrochloric acid (Solvay Chemical International 2007) as alternative to the synthesis from iron and chlorine (Section 2.8.4).

150. The reaction is carried out at 80-90°C, under 1 bar abs. and lasts for approximately 5 hour (Solvay Chemical International 2007). No data on the production of unintentional POPs has been published for this process. The PCDD/PCDF and other unintentional POPs level in the product will depend on the contamination levels of the respective HCl used in the production (see Section 2.8.1).

3.2.10 Alternative to 2,4-DCBP in silicone rubber production

151. To avoid the PCB formation in the production of silicone rubber when using 2,4-DCBP (Herkert *et al.* 2018; Hombrecher *et al.* 2021; Kaifie *et al.* 2022) a substitution of 2,4-DCBP is required. At least two techniques are available:

- Alternative chlorine-free peroxide for silicone rubber (Holzmayr and Oggermüller 2020)
- Platinum cure systems (Feix *et al.* 2024)

4. Secondary measures

4.1 Production approaches reducing emission of chemicals listed in Annex C

152. It is beyond the scope of this basic guidance to provide detailed comment on chemical plant and process design. However, responsible operation requires the recognition that chemical processes, while necessary for modern life, carry risks. To mitigate those risks to the greatest extent, processes should be designed to state-of-the-art safety and environmental standards as outlined, for example, in the European Union BREFs (European Commission 2006; European Commission 2007a; European Commission 2007b; European Commission 2014; European Commission 2019; European Commission 2023) and comparable regulations in China, Korea and the United States (OECD 2018). Experienced engineers must be engaged in the design of specific chemical processes.

153. Permitting of installations must take into account the potential for by-products and wastes, and make provisions for their safe handling and destruction. It must be recognized that if the process carries the potential for generation of chemicals listed in Annex C, the four streams being emitted from a facility – air, water, waste and product – also carry that potential. Modern process design takes into account that potential, measures its reality, controls for it and includes operations to reduce or eliminate emission of those materials, commensurate with the requirements of the Convention. Modern safety management includes extensive training for operators and sufficient analytical and control instrumentation so that the facility as a whole operates to responsible standards.

154. The main demands for modern and safe chemical production can be stated as:

- Application of best available techniques, including high-performance technologies, in the design and construction of installations;
- Efficient closed cycles for the control of side products and destruction of wastes and emissions;
- Effective management of side products and handling of wastes;
- Dedicated facilities for destruction of wastes and emissions under the responsibility of the enterprise itself and with external control;
- Commitment to a standard of 0.1 ng I-TEQ/m3 for air emissions in destruction of unintentional POPs and other hazardous by-products, wastes and emissions and control of emission to water;
- Development of a clearly defined regime for internal and external monitoring of key operating parameters.

4.2 Distillation for separation of products and by-products

155. Distillation is a means of separating desired product from unintentional by-products used across the chemical production industry from commodities to pesticides. Distillation is used primarily to produce products of higher purity appropriate to downstream processing. The final concentration of unintentional POP in a product may be a function of the efficiency of distillation and crystallization or other purification. Adapting the design and operation of the distillation apparatus is, in principle, relatively straightforward. Residual by-product contained in commercial products can be minimized by appropriate design and operation of the distillation apparatus. Effecting more complete separation for materials with boiling points that are not so widely separated is for the most part a matter of correct design and construction and operation cost. Differences in concentration of residual chemicals listed in Annex C in commercial product may be due to differences in local regulation of products. Below are some examples for distillation and crystallization of processes containing unintentional POPs.

4.2.1 Distillation of chlorobenzenes

156. In the production of chlorobenzenes by direct chlorination of benzene, PCDD/PCDF and PCBs are formed and present in the resulting product mixtures (Liu *et al.* 2004; Table 4). The distillation results in 4 fractions which are further refined then by crystallization. While the largest PCDD/PCDF and PCB content remains in the bottom of distillation (not shown), the individual fractions also contain PCDD/PCDF and unintentional PCBs (Table 4). After separation of the major products, distillation and crystallization, PCDD/PCDF were not detected in the 1,2-DCBz and 1,2,4-TCBz product while the 1,4-DCBz still contained PCDD/PCDF at low levels. But all polychlorinated benzene PCBz products contained some unintentional PCBs (Table 4) but at levels below unintentional trace contaminants in the US (25 mg/kg) and Japan (50 mg/kg) (Table 4).

Table 4: PCDD/PCDF and PCB in intermediates and polychlorinated benzene products (Liu *et al.* 2004)

Sample	**PCDD/PCDF (ng TEQ/kg)**	**PCB (µg/kg)**
Intermediate: mixture of 1,2- and 1,4-dichlorobenzene after distillation and separation from monochlorobenzene	620	2800
Intermediate: mixture of di- and trichlorobenzenes	1850	443
Residue left from purification of 1,2,4-trichlorobenzene	3370	4614
1,4-Dichlorobenzene (98.1%; distillation and crystallization)	39	1797
1,2-Dichlorobenzene (100%; distillation and crystallization)	ND	50.6
1,2,4-Trichlorobenzene (98.9%; distillation and crystallization)	ND	215

4.2.2 Distillation of chlorinated solvents

157. Chlorinated solvents are separated with distillation from heavy ends and into marketable single solvents. Chlorinated solvents prepared using modern techniques of purification have been tested for HCB and found to be in the low µg/kg (parts per billion) range (< 20 µg/kg HCB for trichloroethylene and < 10 µg/kg HCB for perchloroethylene).

4.2.3 Distillation and internal recycling of by-products

158. As an example, vinyl chloride is manufactured via oxychlorination and purified by distillation. Rigorous distillation is used due to the potential for disruption of subsequent

polymerization process by impurities. Unsaturated materials that might act as co-monomers competing in the polymerization and saturated or aromatic materials susceptible to free radical reactions other than polymerization can negatively impact polymerization reaction kinetics.
159. Distillation and high purity are important for good production. Distillation systems can be designed to effect separation of materials of closely or widely separated boiling points. The boiling points of chemical products of direct chlorination and the boiling points of competing impurities allow for their practical separation. Their boiling points are also sufficiently different from those of the chemicals listed in Annex C, however, that virtually complete separation can be accomplished. European Commission (2017) notes that purified ethylene dichloride does not contain significant amounts of PCDD/PCDF.

160. Destruction of chlorinated by-product materials allows for HCl to be harvested and reused (e.g. Westlake Vinnolit 2024b). This is deemed to have greater impact because small changes in generation of POPs upstream of distillation are not reflected in the quality of desired products after distillation.

4.3 Crystallization and recrystallization of products

161. Crystallization is a highly selective separation and purification technique used in the chemical and pharmaceutical industry (Urwin *et al.* 2020). Ideally after crystallization, the resulting solid particulate product is composed of one single target compound with all other chemical entities remaining in the liquid phase for disposal. In reality, the majority of the impurity is rejected by the growing crystals, but some impurity compromises the final product purity. Three examples are described for chloranil and TCPA below and for chlorobenzenes in Section 4.2.1,

4.3.1 Purification of chloranil

162. Three industrial chloranil samples in China showed PCDD/PCDF levels that differed by several orders of magnitude (Table 2). The different uses of chloranil can lead to distinct differences in the quality and purity of the chloranil produced. The sample for the use as intermediate in pharmaceutical products was extracted and purified using a recrystallization process to form a product with 99% purity. The sample used as a dye and pesticide intermediate had only a purity of 90% and was not further purified and contained 10000 times more PCDD/PCDF compared to the recrystallized product (Liu *et al.* 2012; Table 2).

4.3.2 Recrystallization of tetrachlorophthalic acid (TCPA) to reduce HCB content

163. TCPA can contain 1000 mg/kg or more HCB after synthesis. Manufacturers can reach in the first recrystallization process using a certain organic solvent a reduction of unintentional HCB in TCPA to 200 mg/kg (Government of Japan 2006). In the second recrystallization 80 mg/kg HCB can be achieved and a third recrystallization can reduce levels to 40 mg/kg HCB. The reduction of HCB in the process depends on the solvents used. More than 80% reduction can be reached but some solvents may be too expensive for profitable production (Government of Japan 2006). According to the Japanese survey of manufacturers, a recrystallization step adds approximately 25 to 40% cost to the TCPA price (Government of Japan 2006).

4.4 Best available techniques for waste and waste gas treatment practices

164. The purpose of distillation and crystallization or other purification steps is to separate desired product from by-products, and to concentrate chemicals listed in Annex C and other unwanted hazardous chemicals in the by-product stream.
165. The waste gas emission needs to be controlled and the release of unintentional POPs reduced and where feasible eliminated. Techniques such as catalytic destruction or adsorption are

described in Section V.A of the present guidelines. Detailed descriptions for treatment of waste gases are compiled in the EU BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (European Commission 2016).

166. The POPs which are separated or adsorbed in flue gas treatment or waste water treatment add to the unintentional POPs waste streams of the chemical production that need to be treated in ESM. There are a number of processes that are capable of treating waste streams containing POPs, many of which are described in Section V.A of the present guidelines and in the Basel Convention guideline on POPs waste (UNEP 2023a).

4.5 By-product destruction

167. There are three types of treatment commonly in use for wastes, especially heavy ends: hazardous waste incineration, thermal oxidation and catalytic oxidation. Some detail on each is presented in the chapter on ethylene dichloride and vinyl chloride in European Commission (2014). When heavy ends are burnt chemicals listed in Annex C are generated, as in any waste incineration with high chlorine content.

168. A BAT reference document containing BAT conclusions on waste incineration has been published (European Commission 2019a). For PCDD/PCDF and dioxin-like PCB many countries have set regulatory limits which must not be exceeded. Additionally monitoring requirements are in place for other parameters in some region like e.g. PBDD/PBDF if the waste contains brominated flame retardants or if plants use the injection of bromine. Best available technologies are described in section V.A of this Stockholm Convention BAT/BEP document and already in use in many high income countries (e.g. United States, the European Union and Japan). Alternatives to the incineration of waste, (for example gas phase chemical reduction or mechanochemical dehalogenation) may also be of use for certain types of by-product destruction. Technologies for the destruction and irreversible transformation of POPs wastes are evaluated jointly with the Basel Convention. The Basel Convention technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with POPs provide guidance on approved technologies for the destruction and irreversible transformation of POPs wastes, including unintentionally produced POPs (UNEP 2023a). Only these approved technologies are considered environmentally sound for the destruction of POPs wastes.

169. There are also specific processes such as the Catoxid® process which is a fluidized bed catalytic process for oxidation of organics. It generates a stream of HCl and CO_2, which is sent in totality to the oxychlorination reactor for internal recycling (Randall 1994).

5. Summary of measures

170. Measures for the reduction of chemicals listed in Annex C arising from certain chemical production processes might be summarized as follows:

- Substitute processes and chemicals which generate chemicals listed in Annex C where better processes or chemicals are available considering also other health and environmental impacts (e.g. life cycle assessment);
- Modify processes to reduce generation of chemicals listed in Annex C;
- Incorporate steps that treat impurities in raw materials, and use rigorous operational maintenance;
  - Purify products by distillation where physical properties allow;

  - Purify products by crystallization and possibly recrystallization;
- Internally recycle unintentionally generated high-molecular-weight by-products as an integral part of the process;
- Recover and recycle HCl where appropriate; refine HCl to eliminate unintentional POPs;
- Compile information on BAT/BEP for minimizing and eliminating chemicals listed in Annex C and levels which can be achieved in release vectors and possibly submit information to the clearinghouse mechanism of the Stockholm Convention
- Manage wastes appropriately taking full account of the potential release of chemicals listed in Annex C to air, water and land and avoid any unintentional formation.

6. Performance standards and measures

6.1 Performance standards

6.1.1 Emissions to air and water

171. In the European Union the Industrial Emissions Directive (IED, 2010/75/EUIPPC) is the main instrument regulating pollutant emission from industrial installations including the chemical industry. The permit conditions including emission limit values must be based on the best available techniques (BAT). Best available techniques reference documents (BREFs) are produced under the Directive, the BAT conclusions (BATc) contained are adopted by the Commission as Implementing Decision. The IED requires that these BATc are the reference for setting permit conditions.

172. Furthermore, recently adopted BAT conclusions describe comprehensive requirements for environmentally sound operation of chemical industry installations in the scope of the respective document, including standards for emissions of PCDD/PCDF.

173. The BATc for Waste Gas Treatment in the Chemical Sector have BAT-associated emission levels (BAT-AEL) for channelled emissions to air of PCDD/PCDF from thermal treatment of waste gases containing chlorine and/or chlorinated compounds of <0.01-0.05 ng I-TEQ/Nm^3 (Table 5) as average over the sampling period indicating that these processes can meet the Stockholm Convention BAT level of <0.1 ng TEQ/Nm^3.

174. The BATc for the production of Large Volume Organic Chemicals provide a set of BAT-AELs for the different production processes covered including the parameter PCDD/PCDF indicating that these processes can meet the Stockholm Convention BAT level of <0.1 ng TEQ/Nm^3.

175. The associated techniques described in both documents, the BATc LVOC (European Commission 2017) and the BATc WGC (European Commission 2016), to achieve the values cited above include:

a.) Optimised catalytic or thermal oxidation to promote the oxidation of organic compounds including PCDD/PCDF present in the waste gases, to prevent PCDD/PCDF and the (re)formation of their precursors, as well as to reduce the generation of pollutants such as NO_X and CO.
b.) Rapid waste gas cooling s from temperatures above 400 °C to below 250 °C to prevent the *de novo* synthesis of PCDD/PCDF.
c.) Adsorption using activated carbon

Table 5: BAT-associated emission levels (BAT-AEL) for the production of Large Volume Organic Chemicals (European Commission 2017)

Process	**Medium**	**Parameter**	**BAT-AEL**	**Averaging period and reference conditions**
Toluene Diisocyanate/ Methylene Diphenyl Diisocyanate	Emissions to air	PCDD/ PCDF	0.025–0.08 ng I-TEQ/Nm3	Average over the sampling period no correction for oxygen content
Ethylene Dichloride/ Vinyl Chloride Monomer	Emissions to air	PCDD/ PCDF	0.025–0.08 ng I-TEQ/Nm^3	Average over the sampling period, at 11 vol-% O_2
EDC production via oxychlorination at the outlet of the pretreatment for solids removal at plants using the fluidised-bed design	Emissions to water	PCDD/ PCDF	< 0.8 ng I-TEQ/l	Average of values obtained over 1 year
EDC production by oxychlorination, direct emissions to a receiving water	Emissions to water	PCDD/ PCDF	0.1–0.3 µg I-TEQ/t EDC	Average of values obtained over 1 year

176. For waste incineration BAT/BEP is described in this Stockholm Convention Guideline in “Section V.A Waste Incineration” and in the Basel Convention Technical Guidelines on the environmentally sound incineration of hazardous wastes and other wastes as covered by disposal operations D10 and R1, which consider 0.1 ng TEQ/m^3 as BAT emission limit (UNEP 2022b). Further the European BATc on waste incineration provide BAT-associated emission levels (BAT-AELs) for PCDD/PCDF as well as PCDD/PCDF + dioxin-like PCBs for channeled emission to air. For the emissions to water from flue gas cleaning (i.e. scrubbers etc.) a BAT-AEL was derived for PCDD/PCDF (European Commission 2019a). Air emissions from incinerators in Japan are regulated according to size and whether they are new or retrofitted. New BAT incinerators must achieve the emission limit of 0.1 ng TEQ/Nm^3. Water emissions from these processes are limited to 10 pg TEQ/L effluent.

177. In the United States as well as in other regions, regulations based on maximum achievable control technology (MACT) have been proposed to control HCB and other hazardous air pollutant emissions from incinerators, medical waste incinerators, cement kilns, and lightweight aggregate kilns that burn hazardous wastes. Estonia has set total Emission Limit Values for HCB (and other hazardous substances) per unit of production of PER and tetrachloromethane (CCl_4) by perchlorination, 1.5 g HCB/t combined PER and tetrachloromethane production capacity (Government of Estonia 2003).

178. China set an emission standard for HCBD for waste water of for the petroleum chemistry industry of 0.006 mg/L. (GB 31571-2015, Ministry of Ecology and Environment of People’s Republic of China 2015).

6.1.2 Performance standards and regulatory limits of chemicals and products

179. A range of performance standards and regulatory limits for unintentional POPs in chemicals, mixtures and articles exist in various countries and regions. Also, the UNEP unintentional POPs Toolkit has listed BAT levels for some chemicals where information and data were available (UNEP 2013a).

180. In the US, the concentration of unintentional PCBs in products must have an annual average of <25 mg/kg, with a 50 mg/kg maximum, except that the concentration must be <5 mg/kg in the components of detergent bars (US Code of Federal Regulations 2024). The US FDA recognizes PCBs as an unavoidable, environmental contaminant and a tolerance of 10 mg/kg in paper packaging in direct contact with food have been set and temporary food tolerances for PCBs ranging from 0.2 to 1.5 mg/kg (US Food and Drug Administration 2023).

181. Japan has a regulatory limit for PCBs of 50 mg/kg and restricts the import and use of e.g. pigments above this limit (METI 2013). The unintentional trace contaminant limit of the European Union for PCBs in substances, mixtures or articles is <10 mg/kg (European Commission 2022a).

182. Japan has also a regulatory limit for PCDD/PCDF and dl-PCBs in pesticides which requires contamination levels below 100 ng TEQ/kg for each 2,3,7,8-substituted PCDD/PCDF congener and dioxin-like PCB (Japanese Government 2002).

183. The US EPA regulates the maximum allowable concentrations of HCB as a contaminant in certain pesticides. The established microcontaminant level for HCB in certain pesticides is in the order of 40–50 mg/kg. As noted in Bailey (2001), because of process improvements, actual HCB concentrations in pesticide products may be significantly lower. The European Union has set an unintentional trace contaminant limit of 10 mg/kg for HCB in substances, mixtures or articles (European Commission 2022b),

184. In Canada, as in many countries, HCB is a prohibited substance. Canadian law prohibits the manufacture, use, sale, offer for sale or import of HCB and products containing the substance, unless it is incidentally present in a product or another exemption applies.

185. In Germany, there are regulatory limits for fertilizers and other products such as biosolids which are brought into soil: 8 ng TEQ/kg (ΣPCDD/PCDF+PCB) for products brought on pasture land and other agricultural land without ploughing and 30 ng TEQ/kg (ΣPCDD/PCDF+PCB) for other agricultural land (German Federal Ministry of Justice and Consumer Protection 2017). Such low limits are needed for the protection of soils and related food production including grazing livestock and poultry (Weber *et al.* 2018; Weber *et al.* 2019; Petrlik *et al.* 2022).

186. A range of large food and feed contamination resulted from inorganic chemicals like HCl, $CuSO_4$ and ZnO (Hoogenboom *et al.* 2015). For chemicals used as food and feed additive particular care in respect to the unintentional POPs content is required and the European Union established regulatory limits for PCDD/PCDF in feed additives (1 pg TEQ/g) and for the sum of PCDD/PCDF and dl-PCB (1.5 pg TEQ/g) (European Commission 2019b). Such levels determine the levels of chemicals which are used as feed additives. Therefore, it is stressed for the chemicals that are used in sensitive application such as feed or food require low UPOP levels that do not result in exceedance of PCDD/PCDF or PCB limits.

6.1.3 Unintentional POPs in waste

187. The Basel Convention sets provisional low POP content values for waste. For PCDD/PCDF, the provisional definition is 1, 5 or 15 µg TEQ/kg); for HCB, PeCB and PCBs, it is 50 mg/kg; for HCBD it is 100 mg/kg; and for PCNs it is 10 mg/kg (UNEP 2023a).

6.2 Performance measures

188. These may include analytical chemistry on emission streams and, in some areas, reporting of persistent organic pollutants to a pollutant release and transfer registry, such as the Toxics Release Inventory in the United States (US EPA 2006) and efforts of the industry to provide data (Dyke *et al.* 2004).

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Annex I. Synthesis of commodity chemicals with risk of unintentional POPs

Table 6. Synthesis of commodity chemicals (Wiley Interscience 2000) with risk of unintentional POP formation

Chemical	Process	Process use	Co-products
Chlorine, caustic soda	$NaCl + H_2O \rightarrow Cl_2 + NaOH + H_2$ See European Commission 2014	More common	
Organics			
Allyl chloride	Direct chlorination of propylene > 300 °C	More common	HCl
	Pyrolysis of 1,2-dichloropropane	Less common	Chlorinated olefins, HCl
Chloranil dye	See UNEP 2013a		
Chloroprene (2-chloro1,3-butadiene)	$C_2H_2 + CuCl/NH_4Cl \rightarrow$ vinyl acetylene + HCl → chloroprene	Less common	
	Vapour phase: butadiene + $Cl_2 \rightarrow$ 1,4- and 3,4-dichloro; isomerized (Cu catalyst) to 3,4-dichloro; HCl via NaOH; distilled to separate low-boiling mono-Cls; 3,4-di; 1,4-di; heavies	More common	NaCl; overchlorinated products
Chlorinated benzenes	Vapour phase: benzene + chlorine + HCl	Less common	Mixed product
	Liquid phase: $Cl_2/FeCl_3$ to yield mix; controlled by amount of chlorinating agent (monos); some other specialized processes for certain isomers; high-Cl materials can precipitate. Purified by distillation and crystallization; separations difficult	More common	HCl
Epichlorohydrin	Allyl chloride + HOCl (chlorine water) → glycerol chlorohydrins + $NaOH/(CaOH)_2 \rightarrow$ epichlorohydrin Steam stripped then distilled Also: propylene + O_2 (Pd catalyst) → allyl acetate → allyl alcohol + $Cl_2 \rightarrow$ allyl chloride	More common	Hydrolysed product; polymers
Isocyanurate disinfectants	Isocyanuric acid + NaOH + Cl_2		
Phosgene	CO + Cl_2 used virtually immediately to produce polycarbonate and polyurethane		
Chlorinated phenols	Lesser chlorinated phenols; phenol + Cl_2; various Lewis acid catalysts; $FeCl_3$, $ZnCl_2$	More common	

Pentachlorophenol (PCP)	Phenol + Cl_2; $AlCl_3$ as main industrial catalyst; 100 °C – 180 °C	More common	HCl
	hexachlorobenzene (HCB) + NaOH	Less common	NaCl
Sodium pentachlorophenate	PCP + NaOH	More common	NaCl
	HCB + NaOH	Less common	NaCl

Chemical	Process	Process use	Co-products
Vinylidene chloride ($ViCl_2$)	1,1,2-trichloroethane + NaOH or $Ca(OH)_2$; can also be a co-product of high-temperature chlorination of C_2 materials	More common	NaCl or $CaCl_2$
Vinyl chloride (VCM)	Acetylene + HCl → vinyl chloride; Hg catalyst	Less common	
	Ethylene + Cl_2 → EDC (direct; Fe catalyst); HCl + O_2 + ethylene → EDC (oxychlor; Cu catalyst) See European Commission 2017	More common	
C_1 products			
Methyl chloride	CH_4 + Cl_2 via heat or light	More common	
	$CH_3OH + HCl \rightarrow CH_3Cl$	More common	
Other chlorinated methanes	$CH_3Cl + Cl_2$ heat or light → CH_2Cl_2, $CHCl_3$, CCl_4	More common	
	$CS_2 + Cl_2 \rightarrow S_2Cl_2 + CCl_4$ $CS_2 + S_2Cl_2 \rightarrow S + CCl_4$	Less common	
C_2 products			
Chlorinated ethanes			
1,1-di	VC + $HCl/FeCl_3$	More common	
1,2-di (EDC)	Ethylene + Cl_2 → EDC (Fe cat) (direct chlorination) Ethylene + HCl + O_2 (Cu cat) → EDC (oxychlorination)	More common	
1,1,1-tri	1,1-di + Cl_2 (photochemical)	More common	HCl
	1,1,2-tri → 1,1,1-tri	More common	
	Ethane + Cl_2	Less common	
1,1,2-tri	VC + Cl_2	More common	
	EDC + Cl_2	More common	HCl

1,1,1,2-tetra, 1,1,2,2tetra	EDC + Cl_2 (can include oxychlor)	More common	HCl
	C_2H_2 + Cl_2		
	C_2H_4 + Cl_2	More common	HCl
1,1,1,2,2-penta	TCE + Cl_2 → penta		
Chlorinated ethylenes			
Trichloroethylene (TCE) and perchloroethylene (PCE)	EDC + Cl_2 → TCE + PCE	More common	HCl HCl
	EDC + Cl_2 → PCE + CCl_4	More common	
	2 CCl_4 → PCE	More common	
	EDC + Cl_2 + O_2 → PCE/TCE	More common	
	Tetrachloroethanes + heat → TCE	More common	HCl
	Pentachloroethane + heat → PCE	Less common	HCl
Chemical	**Process**	**Process use**	**Co-products**
Inorganics			
HCl	By-product; salt + sulphuric acid; hydrogen + chlorine; recovery from combustion of chlorinated organics	More common	
TiO_2	C, Cl_2, TiO_2 ore → $TiCl_4$ + O_2 → TiO_2	Predominantly used	Cl_2, recycle
	TiO_2 ore + H_2SO_4 → $Ti(SO_4)_2$ → TiO_2		sulphates
$FeCl_3$	Iron or iron oxide + HCl → $FeCl_3$		
Hypochlorites	Na: 2NaOH + Cl_2 → NaOCl		NaCl
	Ca: $Ca(OH)_2$ + 2Cl_2 → $Ca(OCl)_2$ also via NaOCl used as aid in chloride removal; recovered, then dried		$CaCl_2$
$ZnCl_2$	Zn + HCl → $ZnCl_2$		
ClO_2	Generated from $HClO_2$ or $NaClO_3$		

Annex II. Chemicals suspected to be accompanied by PCDD/PCDF or other unintentional POPs with a lack of data

There are a range of processes and chemical productions for which the formation of PCDD/PCDF and other UPOPs are suspected but data are lacking. The US EPA and some studies has stressed this for a range of pesticides (Table 7). The same is true for pigments and dyes where the monitoring of the Japanese government revealed that a range of pigments/dyes were above 50 mg/kg (see Table 3). Therefore more monitoring of chemicals and mixtures are necessary to clarify the relevance of UPOPs formation and release of individual products and processes are needed to clarify on the relevance of unintentional POPs formation in these production and to where needed to optimize processes in respect to minimization of unintentional POPs in production and products.

Table 7. Pesticides known or suspected to be accompanied by PCDD/PCDF formation during production but with a lack of information on levels and BAT/BEP to minimize unintentional formation (US EPA 2005; Bretthauer *et al.* 1991; UNEP 2015)

Common Name	**Pesticide**	CASN	Reference
	Dichlorodifluoromethane	75-71-8	US EPA 2005
Bromophos	O-(4- Bromo- 2,5- dichlorophenyl) O, O- dimethyl phosphorothioate	2104-96-3	US EPA 2005
	Dimethylamine 2,3,5- triiodobenzoate	17601-49-9	US EPA 2005
Neburon		555-37-3	US EPA 2005
Crufomate		299-86-5	US EPA 2005
	MCPB, 4- butyric acid [4-(2- Methyl- 4- chlorophenoxy) butyric acid]	94-8 1-5	US EPA 2005
	MCPB, Na salt [Sodium 4-(2- methyl- 4- chlorophenoxy) butyrate]	6062- 26- 6	US EPA 2005
	4- Chlorophenoxyacetic acid	1 22- 88- 3	US EPA 2005
Chloroxuron		1 982- 47- 4	US EPA 2005
Dichlobenil		1 1 94- 65- 6	US EPA 2005
Propanil	3', 4'- Dichloropropionanilide	709- 98- 8	US EPA 2005
Dichlofenthion	O-(2,4- Dichlorophenyl) O, O- diethyl phosphorothioate)	97- 1 7- 6	US EPA 2005
DDT	Dichloro diphenyl trichloroethane	50- 29- 3	US EPA 2005
Dichlone	2,3- dichloro- US EPA 2005 ,4- naphthoquinone	1 1 7- 80- 6	US EPA 2005
Ammonium chloramben	3- amino- 2,5- dichlorobenzoic acid	1 076- 46- 6	US EPA 2005
Sodium chloramben	3- amino- 2,5- dichlorobenzoic acid	1 954- 8 1 - 0	US EPA 2005
Disul	Sodium 2-(2,4-dichlorophenoxy) ethyl sulfate	1 36- 78- 7	US EPA 2005
DCNA	2,6- Dichloro- 4- nitroaniline	99- 30- 9	US EPA 2005
	Potassium 2-(2- methyl-4-chlorophenoxy) propionate	1 929- 86- 8	US EPA 2005
MCPP, DEA Salt	Diethanolamine 2-(2- methyl- 4- chlorophenoxy) propionate	1 432- 1 4- 0	US EPA 2005
MCPP, IOE	Isooctyl 2-(2- methyl- 4- chlorophenoxy) propionate	28473- 03- 2	US EPA 2005

Dicapthon	O-(2- chloro- 4- nitrophenyl) O, O- dimethyl phosphorothioate	2463- 84- 5	US EPA 2005
Monuron trichloroacetate	3-(4- chlorophenyl)- US EPA 2005 ,US EPA 2005 - dimethylurea trichloroacetate	1 40- 4 1 - 0	US EPA 2005
Diuron	3-(3,4- dichlorophenyl)- 1,1 - dimethylurea	330- 54- 1	US EPA 2005
Linuron	3-(3,4- dichlorophenyl)- 1- methoxy- US EPA 2005 - methylurea	330- 55- 2	US EPA 2005
Metobromuron	3-(p- bromophenyl)- 1- methoxy- US EPA 2005 - methylurea	3060- 89- 7	US EPA 2005
Methyl parathion	O, O- Dimethyl O- p- nitrophenyl phosphorothioate	298- 00- 0	US EPA 2005
Dichlorophene	Sodium 2,2'- methylenebis(4- chlorophenate)	97- 23- 4	US EPA 2005
Dichlorophene, sodium salt	Sodium 2,2'- methylenebis(4- chlorophenate)	1 0254- 48- 5	US EPA 2005
	1,2,4,5- Tetrachloro- 3- nitrobenzene	1 1 7- 1 8- 0	US EPA 2005
Ethyl parathion	O, O- diethyl O- p- nitrophenyl phosphorothioate	56- 38- 2	US EPA 2005
Carbophenothion	S-(((p- chlorophenyl) thio) methyl) O, O- diethyl phosphorodithioate	786- 1 9- 6	US EPA 2005
Ronnel	O, O- dimethyl O-(2,4,5- trichlorophenyl) phosphorothioate	229- 84- 3	US EPA 2005
Mitin FF	Sodium 5- chloro- 2-(4- chloro- 2-(3-(3,4- dichlorophenyl) ureido) phenoxy) benzenesulfonate	3567- 25- 7	US EPA 2005
	Orthodichlorobenzene	95- 50- 1	US EPA 2005
	Paradichlorobenzene	1 06- 46- 7	US EPA 2005
Chlorophenols	2- Benzyl- 4- chlorophenol	1 20- 32- 1	US EPA 2005
	Potassium 2- benzyl- 4- chlorophenate	3547 1 - 49- 9	US EPA 2005
	Sodium 2- benzyl- 4- chlorophenate	3 1 84- 65- 4	US EPA 2005
	Chlorophenol	95- 57- 8	US EPA 2005
	2- Chloro- 4- phenylphenol	92- 04- 6	US EPA 2005
	Potassium 2- chloro- 4- phenylphenate	1 8 1 28- 1 6- 0	US EPA 2005
	4- Chloro- 2- phenylphenol	not available	US EPA 2005
	4- Chloro- 2- phenylphenol, potassium salt	53404- 2 1	US EPA 2005
	6- Chloro- 2- phenylphenol	85- 97- 2	US EPA 2005
	6- Chloro- 2- phenylphenol, potassium salt	1 8 1 28- 1 7- 1	US EPA 2005
	4- Chloro- 2- phenylphenol, sodium salt	1 0605- 1 0- 4	US EPA 2005
	6- Chloro- 2- phenylphenol, sodium salt	1 0605- 1 1 - 5	US EPA 2005
	4 and 6- Chloro- 2- phenylphenol, diethanolamine salt	53537- 63- 6	US EPA 2005
	2- Chloro- 4- phenylphenol, sodium salt	3 1 366- 97- 9	US EPA 2005
	4- Chloro- 2- cyclopentylphenol	1 3347- 42- 7	US EPA 2005
Fentichlor	2,2'- Thiobis(4- chloro- 6- methylphenol)	44 1 8- 66- 0	US EPA 2005
Fentichlor	2,2'- Thiobis(4- chlorophenol)]	97- 24-	US EPA 2005
	4- Chloro- 2- cyclopentylphenol, potassium salt of	3547 1 - 38- 6	US EPA 2005
	4- Chloro- 2- cyclopentylphenol, sodium salt	53404- 20- 9	US EPA 2005
Chlorophacinone		369 1 - 35- 8	US EPA 2005

ADBAC	Alkyl* dimethyl benzyl ammonium chloride *(50% C14, 40% C12, 10% C16)	68424- 85- 1	US EPA 2005
ADBAC	Alkyl* dimethyl 3,4- dichlorobenzyl ammonium chloride *(61 % C12, 23% C14, 11% C16, 5% C18)	not available	US EPA 2005
Niclosamide	2- Aminoethanol salt of 2', 5- dichloro- 4'- nitrosalicylanilide	1 420- 04- 8	US EPA 2005
	5- Chlorosalicylanilide	4638- 48- 6	US EPA 2005
	2- Methyl- 4- isothiazolin- 3- one	not available	US EPA 2005
Tetradifon	4- chlorophenyl 2,4,5- trichlorophenyl sulfone	1 1 6- 29- 0	US EPA 2005
	6- Chlorothymol	89- 68- 9	US EPA 2005
Anilazine	2,4- Dichloro- 6-(o- chloroanilino)- s- triazine	1 0 1 - 05- 3	US EPA 2005
Chlorothalonil	Tetrachloroisophthalonitrile	1 897- 45- 6	US EPA 2005
Fenac, Chlorfenac	Sodium 2,3,6- Trichlorophenylacetate	2439- 00- 1	US EPA 2005
Chlorfenvinphos		470- 90- 6	US EPA 2005
	O-(2- Chloro- 1-(2,5- dichlorophenyl) vinyl) O, O- diethyl phosphorothioate	1 757- 1 8- 2	US EPA 2005
PCMX	4- Chloro- 3,5- xylenol	88- 04- 0	US EPA 2005
Piperalin	3-(2- Methylpiperidino) propyl 3,4- dichlorobenzoate	3478- 94- 2	US EPA 2005
Fenamiphos		not available	US EPA 2005
	p- Chlorophenyl diiodomethyl sulfone	200 1 8- 1 2- 6	US EPA 2005
Metribuzin		2 1 087- 64- 9	US EPA 2005
Bifenox	methyl 5-(2,4- dichlorophenoxy)- 2- nitrobenzoate	42576- 02- 3	US EPA 2005
Methazole	2-(3,4- dichlorophenyl)- 4- methyl- 1,2,4- oxadiazolidine- 3,5- dione	20354- 26- 1	US EPA 2005
Diflubenzuron	N-(((4- chlorophenyl) amino) carbonyl)- 2,6- difluorobenzamide	35367- 38- 5	US EPA 2005
Oxadiazon	2-Tert- butyl- 4-(2,4- dichloro- 5- isopropoxyphenyl)- delta 2 -US EPA 2005 ,3,4- oxadiazoline- 5- one]	1 9666- 30- 9	US EPA 2005
Fenvalerate		5 1 630- 58- 1	US EPA 2005
Fluvalinate	N- 2- Chloro- 4- trifluoromethyl) phenyl- DL- valine (+-)- cyano(3- phenoxy- phenyl) methyl ester	69409- 94- 5	US EPA 2005
Iprodione	3-(3,5- Dichlorophenyl)- N-(1 - methylethyl)- 2,4- dioxo- 1-imidazolidinecarboxamide (9CA)	36734- 1 9- 7	US EPA 2005
Triadimefon	1-(4- Chlorophenoxy)- 3,3- dimethyl- 1 -(1H- 1,2,4- triazol- 1- yl)- 2- butanone	43 1 2 1 - 43- 3	US EPA 2005
Diclofop - methyl	Methyl 2-(4-(2,4- dichlorophenoxy) phenoxy) propanoate	5 1 338- 27- 3	US EPA 2005
Profenofos	O-(4- Bromo- 2- chlorophenyl)- O- ethyl S- propyl phosphorothioate	4 1 1 98- 08- 7	US EPA 2005
Oxyfluorfen	2- chloro- US EPA 2005 -(3- ethoxy- 4- nitrophenoxy)- 4-(trifluoromethyl) benzene	42874- 03- 3	US EPA 2005
Imazalil	US EPA 2005 -(2-(2,4- Dichlorophenyl)- 2-(2- propenyloxy) ethyl)- US EPA 2005 H- imidazole	35554- 44- 0	US EPA 2005
Bromothalin	N- Methyl- 2,4- dinitro- n-(2,4,6- tribromophenyl)- 6- (trifuloromethyl) benzenamine	63333- 35- 7	US EPA 2005

Vinclozolin	3-(3,5- Dichlorophenyl)- 5- ethenyl- 5- methyl- 2,4- oxazolidinedione (9CA)	5047 1 - 44- 8	US EPA 2005
Fenridazon	Potassium US EPA 2005 -(p- chlorophenyl)- US EPA 2005 ,4- dihydro- 6- methyl- 4- oxo- pyridazine- 3- carboxylate	83588- 43- 6	US EPA 2005
Tridiphane	2-(3,5- Dichlorophenyl)- 2-(2,2,2- trichloroethyl) oxirane	58 1 38- 08- 2	US EPA 2005
Paclobutrazol		76738- 62- 0	US EPA 2005
Linalool		78- 70- 6	US EPA 2005
Finarimol	[a-(2- chlorophenyl)- a-(4- chlorophenyl)- 5- pyrimidinemethanol]	60 1 68- 88- 9	US EPA 2005
Dicamba dimethylamine	[3,6- dichloro- o- anisic acid]	2300- 66- 5	US EPA 2005
Diethanolamine dicamba	[3,6- dichloro- 2- anisic acid]	25059- 78- 3	US EPA 2005
2,4-D related pesticides (please note: PCDD/PCDF data are available for 2,4-D and some derivatives; information on BAT/BEP to minimize formation is lacking)	2,4-Dichlorophenoxyacetic acid	94- 75- 7	US EPA 2005
	Lithium 2,4-dichlorophenoxyacetate	3766- 27- 6	US EPA 2005
	Potassium 2,4- dichlorophenoxyacetate	1 42 1 4- 89- 2	US EPA 2005
	Sodium 2,4- dichlorophenoxyacetate	2702- 72- 9	US EPA 2005
	Ammonium 2,4- dichlorophenoxyacetate	2307- 55- 3	US EPA 2005
	Alkanol* amine 2,4- dichlorophenoxyacetate *(salts of the ethanol and ispropanol series)	not available	US EPA 2005
	Alkyl* amine 2,4-dichlorophenoxyacetate *(US EPA 2005 00% CUS EPA 2005 2)	22 1 2- 54- 6	US EPA 2005
	Alkyl* amine 2,4 dichlorophenoxyacetate *(US EPA 2005 00% CUS EPA 2005 4)	28685- 1 8- 9	US EPA 2005
	Alkyl* amine 2,4- dichlorophenoxyacetate *(as in fatty acids of tall oil)	not available	US EPA 2005
	Diethanolamine 2,4- dichlorophenoxyacetate	5742- 1 9- 8	US EPA 2005
	Diethylamine 2,4- dichlorophenoxyacetate	20940- 37- 8	US EPA 2005
	Dimethylamine 2,4- dichlorophenoxyacetate	2008- 39- 1	US EPA 2005
	N, N- Dimethyloleylamine 2,4- dichlorophenoxyacetate	53535- 36- 7	US EPA 2005
	Ethanolamine 2,4- dichlorophenoxyacetate	3599- 58- 4	US EPA 2005
	Heptylamine 2,4- dichlorophenoxyacetate	37 1 02- 63- 9	US EPA 2005
	Isopropanolamine 2,4- dichlorophenoxyacetate	6365- 72- 6	US EPA 2005
	Isopropylamine 2,4- dichlorophenoxyacetate	5742- 1 7- 6	US EPA 2005
	Morpholine 2,4- dichlorophenoxyacetate	6365- 73- 7	US EPA 2005
	N- Oleyl- US EPA 2005 ,3- propylenediamine 2,4- dichlorophenoxyacetate	22 1 2- 59- 1	US EPA 2005
	Octylamine 2,4- dichlorophenoxyacetate	22 1 2- 53- 5	US EPA 2005
	Triethanolamine 2,4- dichlorophenoxyacetate	2569- 0 1 - 9	US EPA 2005
	Triethylamine 2,4- dichlorophenoxyacetate	2646- 78- 8	US EPA 2005
	Triisopropanolamine 2,4- dichlorophenoxyacetate	3234 1 - 80- 3	US EPA 2005
	N, N- Dimethyl oleyl- linoleyl amine 2,4- dichlorophenoxyacetate	55256- 32- 1	US EPA 2005

	Butoxyethoxypropyl 2,4- dichlorophenoxyacetate	1 928- 57- 0	US EPA 2005
	Butoxyethyl 2,4- dichlorophenoxyacetate	1 929- 73- 3	US EPA 2005
	Butoxypropyl 2,4- dichlorophenoxyacetate	1 928- 45- 6	US EPA 2005
	Butyl 2,4- dichlorophenoxyacetate	94- 80- 4	US EPA 2005
	Isobutyl 2,4- dichlorophenoxyacetate	1 7 1 3- 1 5- 1	US EPA 2005
	Isooctyl(2- ethylhexyl) 2,4- dichlorophenoxyacetate	1 928- 43- 4	US EPA 2005
	Isooctyl(2- ethyl- 4- methylpentyl) 2,4- dichlorophenoxyacetate	25 1 68- 26- 7	US EPA 2005
	Isooctyl(2- octyl) 2,4- dichlorophenoxyacetate	1 9 1 7- 97- 1	US EPA 2005
	Isopropyl 2,4- dichlorophenoxyacetate	94- 1 1 - 1	US EPA 2005
	Propylene glycol butyl ether 2,4- dichlorophenoxyacetate	1 320- 1 8- 9	US EPA 2005
	4-(2,4- Dichlorophenoxy) butyric acid	94- 82- 6	US EPA 2005
	Sodium 4-(2,4- dichlorophenoxy) butyrate	1 0433- 59- 7	US EPA 2005
	Dimethylamine 4-(2,4- dichlorophenoxy) butyrate	2758- 42- 1	US EPA 2005
	Butoxyethanol 4-(2,4- dichlorophenoxy) butyrate	32357- 46- 3	US EPA 2005
	Butyl 4-(2,4- dichlorophenoxy) butyrate	6753- 24- 8	US EPA 2005
	Isooctyl 4-(2,4- dichlorophenoxy) butyrate	1 320- 1 5- 6	US EPA 2005
	2-(2,4- Dichlorophenoxy) propionic acid (Dichlorprop, 2,4-DP)	1 20- 36- 5	US EPA 2005
	Dimethylamine 2-(2,4- dichlorophenoxy) propionate	53404- 32- 3	US EPA 2005
	Butoxyethyl 2-(2,4- dichlorophenoxy) propionate	53404- 3 1 - 2	US EPA 2005
	Isooctyl 2-(2,4- dichlorophenoxy) propionate	2863 1 - 35- 8	US EPA 2005
	[2-(2- Methyl- 4- chlorophenoxy) propionic acid]	7085- 1 9- 0	US EPA 2005
MCPP, DMA	Dimethylamine 2-(2- methyl- 4- chlorophenoxy) propionate	3235 1 - 70- 5	US EPA 2005
Bromoxynil	3,5- Dibromo- 4- hydroxybenzonitrile	1 689- 84- 5	US EPA 2005
Hexachlorophene	2,2'- Methylenebis(3,4,6- trichlorophenol)	70- 30- 4	US EPA 2005
Hexachlorophene, sodium salt	Monosodium 2,2'- methylenebis(3,4,6- trichlorophenate)	5736- 1 5- 2	US EPA 2005
Hexachlorophene, potassium salt	Potassium 2,2'- methylenebis(3,4,6- trichlorophenate)	67923- 62- 0	US EPA 2005
Triclosan	5- Chloro- 2-(2,4- dichlorophenoxy) phenol	3380- 34- 5	US EPA 2005
	Tetrachlorophenols	25 1 67- 83- 3	US EPA 2005
	Tetrachlorophenols, sodium salt	25567- 55- 9	US EPA 2005
	Tetrachlorophenols, alkyl* amine salt*(as in fatty acids of coconut oil)	not available	US EPA 2005
	Tetrachlorophenols, potassium salt	53535- 27- 6	US EPA 2005
Bithionolate sodium	Disodium 2,2'- thiobis(4,6- dichlorophenate)	6385- 58- 6	US EPA 2005
Phenachlor	2,4,6- Trichlorophenol	88- 06- 2	US EPA 2005
	Potassium 2,4,6- trichlorophenate	259 1 - 2 1 - 1	US EPA 2005
	2,4,6- Trichlorophenol, sodium salt	3784- 03- 0	US EPA 2005
Phenothiazine		92- 84- 2	US EPA 2005
Dacthal- DCPA	Dimethyl tetrachloroterephthalate	1 86 1 - 32- 1	US EPA 2005

Endosulfan	Hexachlorohexahydromethano- 2,4,3- benzodioxathiepin- 3- oxide	115- 29- 7	US EPA 2005
Silvex	2-(2,4,5-Trichlorophenoxy) propionic acid	93- 72- 1	US EPA 2005
Tetrachlorvinphos	2- Chloro- 1-(2,4,5- trichlorophenyl) vinyl dimethyl phosphate	961- 11- 5	US EPA 2005
Edolan	Sodium 1,4', 5'- trichloro- 2'-(2,4,5- trichlorophenoxy) methanesulfonanilide	69462- 14- 2	US EPA 2005
et al.,4-DB	4-(2,4-Dichlorophenoxy)butanoic acid and its salts		Bretthauer *et al.* 1991
	Dimethyl-(2,3,5,6-tetrachloro-1 ,4-benzodicarbonate)		Bretthauer *et al.* 1991
MCPA	4-Chloro- 2-methylphenoxy acetic acid		Bretthauer *et al.* 1991
Chloroneb	2 ,4-Dichloro-Bretthauer *et al.* 1991,5- dimethoxybenzene		Bretthauer *et al.* 1991
Erbone	2(2,4,5-Trichlorophenoxy)-ethyl-2,2-dichloropropionate		Bretthauer *et al.* 1991
Daconil	1,3-dicyano-2,4,5,6-tetrachlorobenzene		Bretthauer *et al.* 1991