

# Environmental Control Challenges of Dioxins, Polychlorinated Biphenyls, and Brominated Flame Retardants

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**Abstract** Over the past few decades, the international community has challenged on persistent organic pollutants (POPs) control issues on both global and local scale. This article deals with problems related to POPs from the standpoint of their total life cycle and examines each category of intentionally and unintentionally produced chemicals. Environmental control challenges and experiences of dioxins, polychlorinated biphenyls, and brominated flame retardants were addressed. Polychlorinated dioxins have their various release sources, but in particular, thermal processes such as waste incineration are the main emission sources. The international community has addressed this issue by adopting technologies for complete combustion and advanced emission gas treatment. With these technologies, Japan has successfully achieved more than 95% reduction of dioxin emission. PCB-containing products manufactured in the past are thought to be the main source of PCB presence now in the environment. Thermal destruction and chemical dechlorination processes have been applied for such waste PCBs. It becomes clear that brominated flame retardants (BFRs) accumulate in the environment as well as in humans. Global-scale efforts have just begun to control BFRs. From now on, we should also address the problem of brominated dioxins and try to improve the related technologies and/or develop new technologies also in the future.

**Keywords** Polychlorinated dibenzodioxins and dibenzofurans (PCDDs/DFs), Polychlorinated biphenyls (PCBs), Brominated flame retardants, Polybrominated dibenzodioxin and dibenzofurans (PBDDs/DFs), Environmental control, Product life cycles

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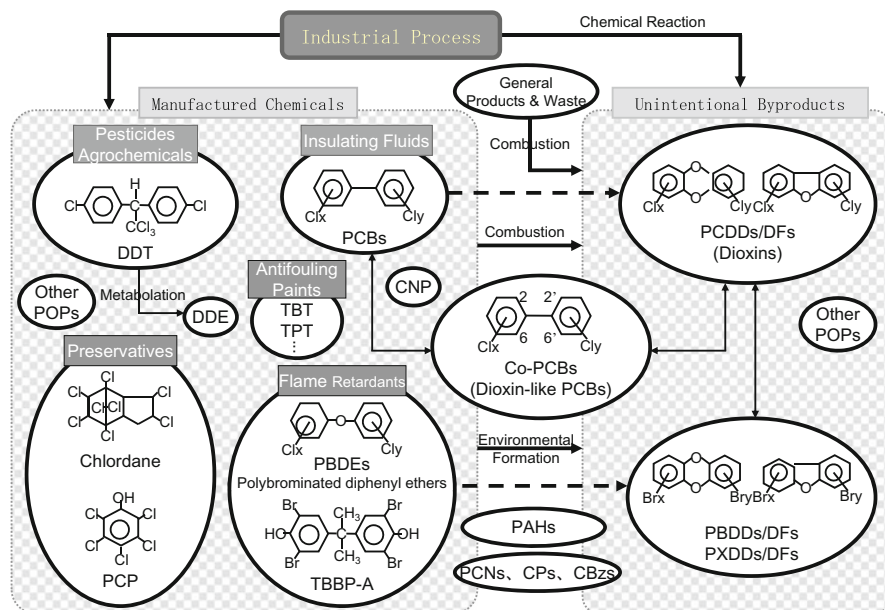
## 1 Introduction

Toxic substances and persistent organic pollutants (POPs) have the potential to cause negative effects on human health and the environment. In the late twentieth century, there were many environmental pollution problems caused by toxic substances and POPs, including the Love Canal incident in the United States, the Seveso disaster in Italy in the 1970s, and the Teshima incident in Japan in the 1980s. Such incidents, which raised concerns about negative impacts on human health and the environment, had a major impact on people's peace of mind and led to detection of POPs on a global scale. At the World Summit on Sustainable Development (WSSD) in 2002, there was a renewed commitment, initially advanced in Agenda 21, to the sound management of hazardous wastes and of chemicals throughout their life cycle, the goal being sustainable development and the protection of human health and the environment [1]. As stated at the WSSD, one of the crucial issues for the world is sound management of chemicals and hazardous wastes.

Over the past few decades, the international community has made efforts and taken action to control POPs, because they are one of the causes of environmental problems on a global scale. This article deals with problems related to POPs from the standpoint of their life cycle and examines each category of intentionally and unintentionally produced chemicals. Each control measure that targets emissions of dioxins and PCBs will be considered, and the results of substance flow analyses for PCBs will also be introduced. In recent years, efforts have been initiated to prevent the use of some brominated flame retardants. The idea of controlling POPs through clean, cycle, and control concepts will also be discussed.

## 2 Persistent Organic Pollutants and Product Life Cycles

POPs have been detected in the environment throughout the world; they have been passively transported and have accumulated in the environment in places as remote as the North and South Poles. To address this global concern, the Stockholm Convention on Persistent Organic Pollutants was adopted in May 2001 [2]. Most



**Fig. 1** Two categories of persistent organic pollutants: manufactured chemicals and unintentional by-products

detected POPs have been derived from human activities; they are less likely to be created in nature. As shown in Fig. 1, POPs produced by various activities can be categorized into two groups:

1. Chemicals intentionally produced for industrial and commercial uses
2. Chemicals unintentionally produced as by-products during chemical reactions and combustion

Representative substances classified in category 1 are polychlorinated biphenyls (PCBs) used as insulating fluids (e.g., transformer oil) and heat-resistant media and hexachlorobenzene (HCB), which is used as an intermediate in the production of solvents. In agriculture, aldrin, dieldrin, endrin, and DDT have been used as pesticides. DDT has even been used to control diseases such as malaria. As a result, there have been cases where these substances have been released into the environment through direct spraying of pesticides on agricultural land, accidental leakage of chemicals, and dumping of waste products. Among the major chemical substances classified in category 2 are dioxins (polychlorinated dioxins and dibenzofurans). Dioxins are formed as by-products and are released into the environment during the chemical manufacturing of pesticides or combustion of waste and refining of metal. Figure 1 includes substances other than the 12 POPs (aldrin, dieldrin, endrin, chlordane, heptachlor, toxaphene, mirex, hexachlorobenzene, PCBs, DDT, dioxins, and furans) specified under the Stockholm Convention.

It is essential to examine which types of POPs cause problems during product life cycles. First, there are chemicals that are intentionally produced; these chemicals include PCBs and HCB for industrial use and DDT and other substances used for disease control. Substances used in closed systems and chemicals that can be recovered and for which the purpose of use is clear should be collected and destroyed from now on. In contrast, it is hard to identify proper treatment for substances that have been used in open systems. However, it should at least be required that their effects on the environment be examined. Second, there are unintentionally produced chemicals such as dioxins and HCB that are generated during manufacturing processes. The targeted objects are dioxins created as the by-products of chemical reactions involved in the manufacturing of pesticides and from combustion reactions during metal refining. HCB is sometimes present in residual manufacturing solvents or as an impurity in pesticides. Third, there are by-product problems associated with waste management. Dioxins produced in combustion processes have been acknowledged to be especially serious problems. It is also known that PCBs and chlorinated benzenes are produced unintentionally during combustion. Measures need to be taken to control the production of all of these toxic by-products. Fourth, degradation of the waste generated by the above processes should be required. Waste pesticides and intentionally produced, recycled POPs such as waste PCBs and chlordane should, in particular, be destructed by chemical and/or thermal technologies. In addition, what is most important for establishing sound policies for material cycles is that diffusion of POPs be restricted as much as possible when materials containing them are recycled. Especially careful attention should be paid when using feedstuffs, agricultural land, and recycled resources such as indoor materials. Care should be taken to avoid the possibility of exposing children to toxic chemicals and to prevent toxic chemicals from entering groundwater.

### 3 Chlorinated Dioxin Control

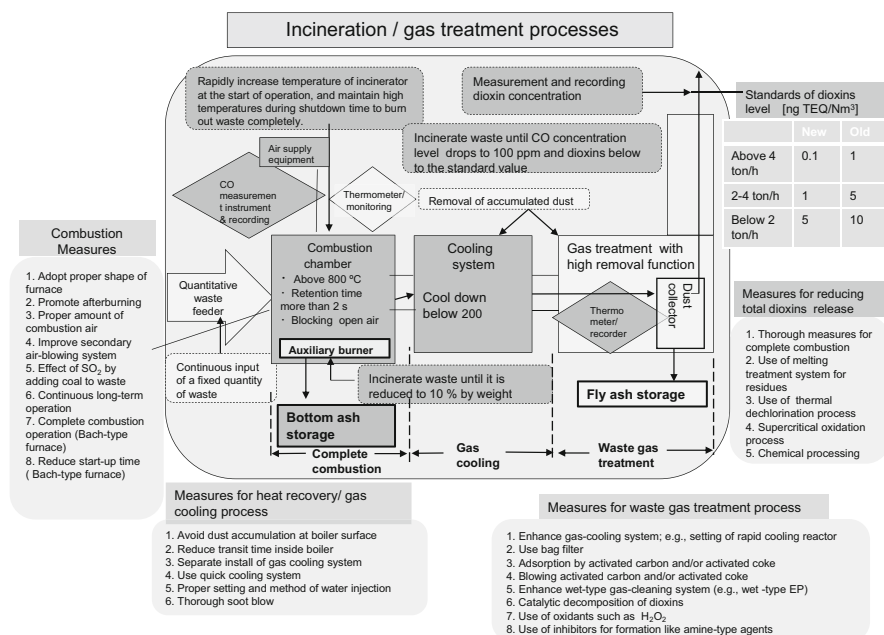
Chlorinated dioxins generally indicate polychlorinated dibenzo-*p*-dioxins (PCDDs), of which there are 75 congeners distinguished by the number of chlorines and their substituent positions. Some of the congeners have chlorines at the 2, 3, 7, or 8 positions and are very toxic. Polychlorinated dibenzofurans (PCDFs), which have characteristics similar to PCDDs, include 135 congeners. This report refers to both PCDDs and PCDFs as dioxins. PCDDs/DFs are produced as by-products in the manufacture of chemicals such as the herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and the antiseptic pentachlorophenol (PCP), and traces of PCDDs/DFs are present in these chemicals. The herbicide 2,4,5-T was used extensively as a defoliant in the Vietnam War, and its use caused great concern because of the suspected relationship between its use and the appearance of deformed children [3]. Even before the latter half of the 1970s, accidents at chemical plants and inadequate treatment of chemical waste have exposed people to PCDDs/DFs.

Examples include the Seveso accident in Italy and the Love Canal and Times Beach incidents in the United States.

The relationship between PCDDs/DFs and municipal solid waste (MSW) incineration, however, was not pointed out until 1977, when Olie and Hutzinger reported that PCDDs/DFs had been detected in the fly ash of MSW incinerators [4]. It is now widely recognized that the sources of PCDDs/DFs are diverse and include industrial processes as well as MSW incinerators. The known sources of PCDDs/DFs include the following: industrial activities, e.g., chemical processes involving chlorine and bleaching of paper pulp; combustion activities, waste incineration; metal smelting; home heating; and fires. Secondary sources include sludge, compost, and contaminated soil. A global inventory of sources of PCDDs/DFs has shown that MSW incinerators are a major source in every country. European countries, which took measures to address the PCDDs/DFs problem earlier than other regions, have focused on the biggest source of PCDDs/DFs, MSW incinerators, as a part of countermeasures to address dioxin pollution problems. In Germany and the Netherlands, treatment of combustion and waste gases had been expected to reduce the load to 1% of the load at the beginning of the 1990s [5]. In fact, Germany reported a decrease from 400 g of toxic equivalent (TEQ) per year to 50 g TEQ/year from 1993 to 1995 and in 1997 achieved 4 g TEQ/year, a 99% reduction [6]. The Netherlands has made similar improvements. They succeeded in reducing their emissions of PCDDs/DFs from MSW incineration by 99.3% from 1990 to 1995 [7]. As a result, in the Netherlands, the total emissions of PCDDs/DFs from MSW incineration were 4–7% of the total emission in 1995 compared to 79% in 1990. During this time, there was a remarkable increase in European countries of the share of industrial processing, including the sintering of iron ore and iron products and the processing of nonferrous metal, but much progress was made in reducing emissions of PCDDs/DFs from MSW incinerators.

Looking back on the development of world policy concerning PCDDs/DFs over the past 30 years and on environmental dioxin policy, I would like to clarify the implications and issues we face. First, technological standards have been raised. It should be pointed out that the establishment of technological standards is becoming common throughout the world. This trend has been a countermeasure against emissions of PCDDs/DFs. In 1986, Sweden set an emission gas standard of 0.1 ng TEQ per normal cubic meter ( $\text{Nm}^3$ ). Then the Netherlands, Germany, and Austria adopted the same standard and have advanced the emission control measures. Between 1995 and 1997, the United States and Japan adopted almost the same standards.

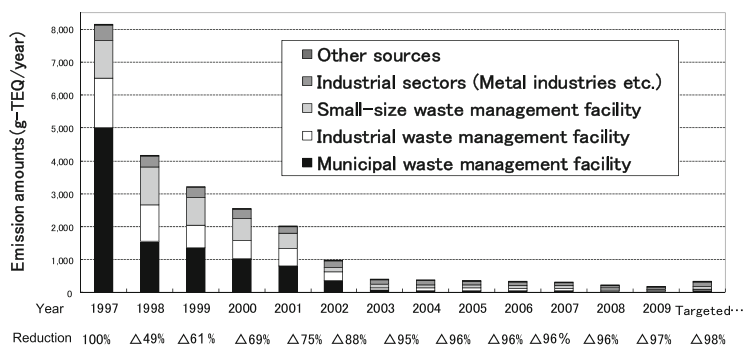
A key point in controlling technological measures is to apply state-of-the-art technologies to waste gas treatment. Some examples are the use of fabric filters for trapping particles, activated carbon for the adsorption of gases, catalytic decomposition technology for the destruction of gases and conversion of nitrogen oxides to  $\text{N}_2$ , and waste gas scrubbers, which are also effective in removing  $\text{SO}_2$ . Complete combustion technology should also be used. Some effective technologies that have been developed to the level of practical feasibility are listed among the high-tech treatment technologies in Fig. 2. They are associated with three principal



**Fig. 2** Dioxin control technologies and standards for incineration/gas treatment

categories: de novo synthesis control technologies, additional technologies for waste gas treatment, and residue destruction and recycling technologies. These advanced technologies have been adopted to promote the application of concepts such as BDAT (Best Demonstrated Available Technology) and MACT (Maximum Achievable Control Technology).

Figure 3 shows the amount of dioxins emitted from various sources in Japan from 1997 to 2009 and the 2010 target rate [8]. The total amount of waste-derived dioxins emitted into the air or water from municipal waste treatment facilities, industrial waste treatment facilities, and small waste incinerators with a treatment capacity of less than 200 kg/h are included in the total. In 1997, when new guidelines were established, the amount of waste-derived dioxins emitted was 7.7 kg of World Health Organization (WHO) TEQ/year and accounted for 94% of the total dioxin emissions from all sources. In 1998, when urgent measures were implemented, the amount was reduced to 3.8 kg of WHO-TEQ/year, a reduction of more than 50%. In 2004, after the promulgation of permanent criteria, the amount was further reduced to 230 g of WHO-TEQ/year, only about 3% of the 1997 emissions. The ratio of incinerator-generated dioxins to the total amount of dioxin emissions from all sources also decreased to 64%. Although it is necessary to pay attention to transport of pollutants through the environment at both the local and global levels, we should first focus on the atmosphere as a conduit, because these pollutants are very mobile after entering the air.



**Fig. 3** Amounts of dioxins discharged in Japan from 1997 to 2009 [8]

Table 1 shows atmospheric dioxin concentrations from 1997 to 2004 [9]. The average concentration was 0.55 pg-WHO-TEQ/Nm<sup>3</sup> in 1997; this decreased to 0.23 pg-WHO-TEQ/Nm<sup>3</sup> in 1998. It then gradually decreased to 0.059 pg-WHO-TEQ/Nm<sup>3</sup> in 2004, or about 10% of the 1997 level. No significant differences were found in atmospheric levels of dioxins in the general environment, in the vicinity of emission sources, and along roadsides. The effect of the urgent measures implemented in 1998 is apparent in the reduction of the dioxin concentrations in the air.

The PCDDs/DFs emitted by the various sources, including those emitted to the atmosphere from MSW incineration, are first adsorbed onto the surface of particles and food and from there find their way into soil, water, and biomedica. Once PCDDs/DFs enter environmental media from phases other than air, they enter the air because of their characteristic volatility. Bioconcentration then occurs, because PCDDs/DFs are concentrated in fat and are resistant to biodegradation. They are present in food, including meat and fish.

Source control to reduce the environmental concentrations of PCDDs/DFs should be considered as part of environmental policy, along with recycling and environmental cycle control. PCDDs/DFs are unintentional by-products, and PCDDs/DFs are of no benefit to humans or the environment, and no emissions and no uptake of PCDDs/DFs would be desirable. The historical trends of PCDDs/DFs reveal that human beings have been exposed to them for more than 100 years. The problem is that human activities have raised background concentrations by a factor of 10 in industrial societies during the past century. Figure 4 shows future strategies for controlling PCDDs/DFs emissions based on fundamental scientific understanding. First, control of the source of emission is important. Control measures are required not only for MSW incineration, regulation of which has become very strict, but also for other sources. With respect to waste management, cooperation must be promoted with extant recycling efforts. The strategy is to focus on waste reduction and recycling. This strategy requires consideration of the following two issues: steps must be taken to effectively control PCDDs/DFs emissions during the incineration process, and the steps taken must not shift PCDDs/DFs problems

**Table 1** Trends of dioxin concentrations in the ambient environment (pgTEQ/m<sup>3</sup>) [9]

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
General environment	Average	0.55	0.23	0.18	0.14	0.14	0.093	0.064	0.058	0.051	0.041	0.035	0.031	0.031	0.028
Surroundings of release sources	Average	0.58	0.20	0.18	0.15	0.13	0.092	0.078	0.063	0.055	0.040	0.041	0.035	0.036	0.032
Roadside	Average	0.47	0.19	0.23	0.17	0.16	0.091	0.076	0.055	0.050	0.044	0.036	0.031	0.028	0.025



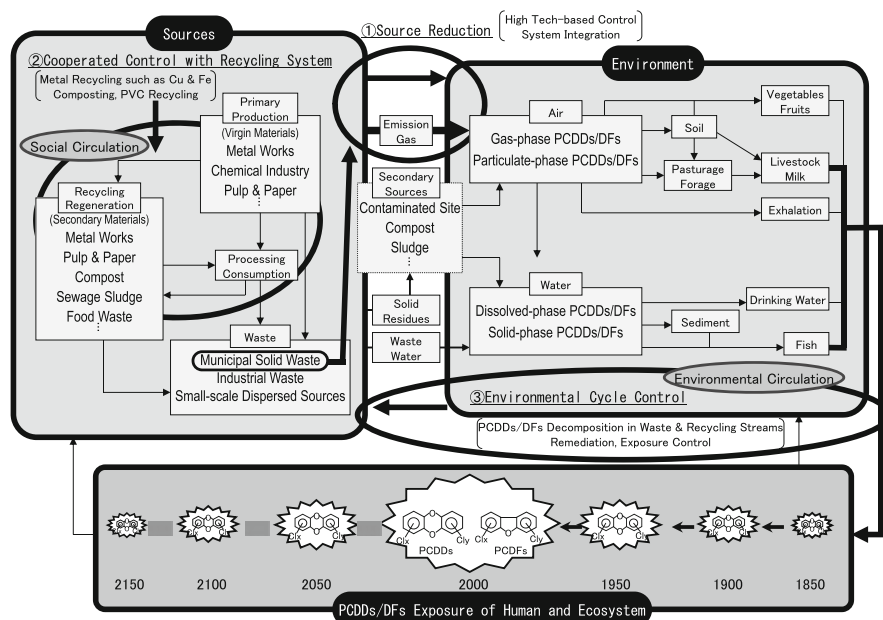


Fig. 4 PCDDs/DFs emission, environmental transport and exposure, and some control points

associated with MSW incineration to problems associated with the recycling process. The recycling of metals, such as copper and iron, leads to a reduction of catalysts that facilitate PCDDs/DFs formation during MSW incineration, and PVC recycling contributes to control of dioxin formation. However, the production of PCDDs/DFs during the process of metal smelting is a problem associated with metal recycling. If recycling is promoted as a measure against the generation of waste, control of recycling should be implemented simultaneously. Therefore, cooperative control with the recycling process is important. Humans and most other living organisms have already been exposed to PCDDs/DFs to a certain extent in the environment. PCDDs/DFs circulate in various environmental media, enter human bodies, and undergo multiple bioconcentrations. This means that long-term reduction of PCDDs/DFs in environmental cycles is important. The following two methods are considered to be the principal strategies for controlling the environmental cycle of PCDDs/DFs. The first method is environmental remediation of hot spots, such as contaminated soil, to prevent local high-level exposure of humans and the ecosystem. The second method is to reduce the amount of environmental cycling by decomposing POPs at appropriate points in their cycle. If waste incineration is the biggest source of PCDDs/DFs, it is critical to change the waste incineration system so that the output of PCDDs/DFs is less than the input. The same strategy applies to many recycling processes. If materials contaminated with PCDDs/DFs can be decomposed through recycling or by incineration, the system deserves to be called environmental cycle control. It would be effective in

reducing not only PCDDs/DFs but also various other hazardous chemical substances, including other dioxin-related compounds and polycyclic aromatic hydrocarbons. Following an environmental strategy based on scientific understanding should be one of the effective countermeasures against PCDDs/DFs among the three long-term strategies, the other two being development of control measures and cooperative controls between recycling and control of environmental cycles. These three strategies must be implemented. As shown at the bottom of Fig. 4, the PCDDs/DFs burden in human beings and other living organisms must be reduced in the next generation through these control measures.

## 4 PCB Destruction and Environmental Control

PCBs are chemical substances that possess excellent insulation properties. They are poor conductors of electricity and are flame resistant. They have been widely used in electrical equipment such as transformers and capacitors. In 1966, PCBs were first detected in fish and seabirds in many parts of the world [10, 11]. Subsequently, it became obvious that PCB transport was expanding across the world. The toxicity of PCBs first became widely known as a result of the Yusho incident in 1968. In that industrial accident in Japan, PCBs used as a heating medium leaked into rice bran oil during the manufacturing process, and people who consumed the contaminated oil suffered significant health problems [12]. As a result, PCB manufacture was discontinued, and the government required that waste PCBs be collected. In 1973, the Law Concerning the Examination and Regulation of Manufacture of Chemical Substances (Chemical Substances Control Law) was established in Japan, and a framework was created to review and regulate the use of chemical substances. The Chemical Substances Control Law bans the use and manufacture of PCBs and requires the safe storage of PCBs. It has been estimated that about 54 kilotonnes (kt) of PCBs were used in Japan from 1954 to 1972, the period during which they were most commonly used.

The toxic nature of PCBs is a threat to human health and the environment at the present time. PCBs also pose a threat of global environmental pollution in future years because they are widely disseminated through the air and mobile living species. Internationally, the Stockholm Convention on Persistent Organic Pollutants was signed in May 2001. This Convention stipulates that governments have to phase out the use of PCBs by 2025 and dispose of PCBs in an environmentally sound manner no later than 2028. In Japan, the Law Concerning Special Measures against PCB Waste was enacted in 2001 to promote secure and appropriate treatment of PCB waste.

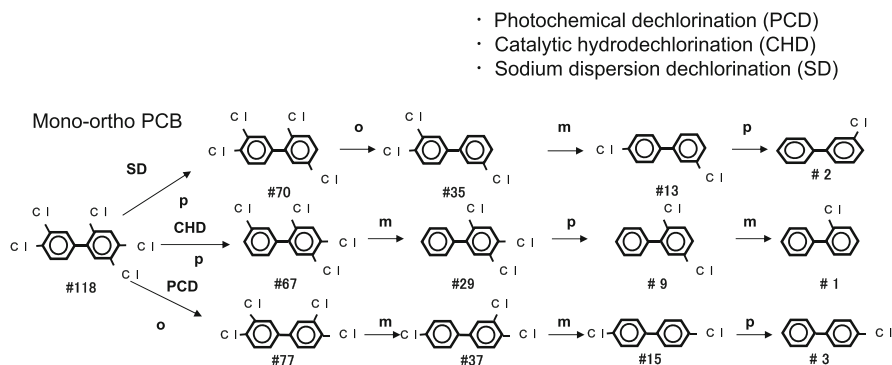
Waste PCBs can be destroyed by noncombustion technology (e.g., chemical treatment) instead of incineration or high-temperature pyrolysis. The criterion for treating PCB-containing oil by chemical decomposition was set at a strict limit of 0.5 mg/kg. PCB treatment has been working very well on the basis of this national program. The Japan Environmental Safety Corporation (JESCO) is a special

**Table 2** PCB chemical treatment methods [14]

Facility	Pretreatment	PCB decomposition
Kitakyushu (Phase 1)	Precise recovery cleansing method	Dechlorination method
	Vacuum thermal recycling method (VTR method)	Sodium dispersion method (SD method)
(Phase 2)		Plasma melting method
Toyota	Solvent extraction decomposition method (SED method) (includes vacuum heating separation method)	Dechlorination method
		Ontario hydro technologies sodium dispersion method (OSD method)
Tokyo	Chemical cleansing method (includes vacuum heating separation method)	Hydrothermal oxidation decomposition method
		Hydrothermal decomposition method
Osaka	Solvent cleansing method	Dechlorination method
	Vacuum thermal recycling method (VTR method)	Catalyst hydrogenation dechlorination method (Pd/C method)
Hokkaido	Solvent extraction decomposition method (SED method) (includes vacuum heating separation method)	Dechlorination method
		Sodium dispersion method (SP hybrid method)

company wholly owned by the central government. It was established in April 2004 under the Japan Environmental Safety Corporation Law (Law No. 44 of 2003) to conduct treatment of PCB waste as its principal business activity [13]. At the present time, JESCO treats PCB wastes at five PCB facilities. The first was the Kitakyushu facility, which started operations in 2004. It was followed by the Toyota, Tokyo, Osaka, and Hokkaido facilities. In accordance with the company policy to carry out PCB waste treatment with a priority on safe and reliable treatment and full information disclosure, JESCO has designed its facilities in accord with the use of safe and sure treatment methods, use of multiple safety measures based on risk management concepts, and disclosure of information about treatment status. An outline of treatment methods used at JESCO facilities is shown in Table 2. All JESCO facilities use only chemical decomposition methods, because they do not produce combustion gases. The Tokyo facility has adopted the “hydrothermal oxidation decomposition method,” and the other four facilities have adopted the “dechlorination method.”

In order to ensure that PCB destruction is being accomplished satisfactorily, it is important not only to ascertain the disappearance of PCBs but also to know the mechanism associated with the degradation and to check for the absence of other harmful by-products [15]. Thirteen PCB isomers [2-chlorobiphenyl (#1), 3-chlorobiphenyl (#2), 4-chlorobiphenyl (#3), 2,3,4-trichlorobiphenyl (#21), 2,4,4'-trichlorobiphenyl (#28), 2,2',5,5'-tetrachlorobiphenyl (#52), 2,2',4,5,5'-pentachlorobiphenyl (#101), 2,3',4,4',5-pentachlorobiphenyl (#118), 3,3',4,4',5-pentachlorobiphenyl (#126), 2,2',3,4,4',5'-hexachlorobiphenyl (#138), 2,2',4,4',5,5'-hexachlorobiphenyl (#153), 2,2',3,4,4',5,5'-heptachlorobiphenyl



**Fig. 5** Dechlorination pathways of 2,3',4,4',5-pentachlorobiphenyl (#118) [15]

(#180), and decachlorobiphenyl (#209)] were decomposed by three noncombustion methods, catalytic hydrodechlorination (CHD) over a palladium/carbon catalyst, photochemical dechlorination (PCD), and a sodium dispersion (SD) method. The reaction solutions were sampled at intervals during the decompositions and analyzed. On the basis of the identification of the dechlorinated products and the quantitative data obtained during the reactions, the major dechlorination pathways were proposed. Consideration was given to the differences in the pathways and the reactivities of the chlorines between the three methods.

The differences of the degradation mechanisms among the three methods have been compared. The dechlorination pathways of 2,3',4,4',5-pentachlorobiphenyl (#118) are shown in Fig. 5. Although the dechlorinations proceeded via an irreversible stepwise pattern in all three cases, the dechlorination pathways were quite different among the three methods. Whereas the dechlorination pathways were relatively clear via CHD and PCD, the pathways diverged widely in the case of SD. The chlorine at the ortho position was easily dechlorinated via PCD and was removed most slowly via CHD. The chlorine in the para position was removed slightly more easily via SD. The congeners with more chlorines decomposed most quickly and in proportion to the total number of chlorines via SD. This effect was not apparent with the CHD and PCD methods because the presence of ortho chlorine atoms had a large effect on the degradation constants. Furthermore, the results were checked to determine whether dioxin-like PCBs were destroyed and/or produced. When 2,3',4,4',5-PeCB (#118) as the mono-ortho congener was destroyed via CHD and SD, the total TEQ also decreased immediately. In the case of the destruction of #118 via PCD, the TEQ caused by 3,3',4,4'-TeCB (#77) increased in the beginning of the experiment because #77 was the principal product of orthodechlorination of #126. The TEQ, however, gradually decreased with the degradation of #77 and finally became zero. The total TEQ decreased immediately via CHD and SD, and after it gradually decreased via PCD, it finally became zero by all three methods.

Dioxin-like PCBs in the environment can be divided into dioxin-like PCBs derived from products containing PCBs (hereafter, PCB products) and unintentionally generated dioxin-like PCBs. PCB products derived from dioxin-like PCBs enter the environment from equipment that contains PCBs, as well as from improper storage and illegal dumping of PCB wastes. The unintentional generation of dioxin-like PCBs occurs mainly in association with chemical reactions and waste incineration [16, 17]. Comparison of the two types reveals significant differences in congeners and their relative abundance. Dioxin-like PCBs penetrated widely into the environment during the period when PCB products were produced and used, and they also accumulated, primarily in marine areas and lakes.

Well-known sources of dioxin-like PCBs include those released by the use or disposal of industrial PCB products or formed as by-products during MSW incineration. It is also well known that PCBs are thermally decomposable. In Japan, 5.3 kt of waste liquid PCBs, namely, Kanechlors, were thermally destroyed at the Takasago plant of Kaneka Co. Ltd. in 1988. In European countries and the United States, waste PCBs are regularly incinerated at high temperatures. MSW incineration processes have the potential to both produce and destroy PCBs. The results of substance flow analyses have previously been reported from a MSW incineration facility in Kyoto City [16]. The existing MSW incinerator was regarded as a system, and the amounts of dioxin-like PCBs and other PCBs in the MSW inflow and the amounts released via gas emissions and incineration residues were examined. A substance flow analysis for dioxin-like PCBs in a newly constructed facility was also performed, and the results were compared with those from an existing facility. To take into account sources of dioxin-like PCBs in the atmosphere, the bulk deposition of dioxin-like PCBs was measured and compared to amounts released by MSW incineration in the Kyoto City area [17].

To investigate whether dioxin-like PCBs and total PCB homologue groups tended to be formed or decomposed in the MSW incineration facilities, the release/inflow ratio (defined as the value of the amount released in emitted gases, fly ash, and bottom ash divided by the amount of the inflow) was calculated for each congener and homologue, as shown in Fig. 6. For the newly constructed facility, the release/inflow ratios of PCB congeners 126, 169, and 189 were still greater than 1, the implication being that levels of these compounds increased during incineration. For the other congeners, the ratios were less than 1, indicating that these compounds were destroyed within the system. The ratios expressed in terms of TEQ levels were greater than 1. This was mainly due to the greater contribution of congener 126 to the TEQ. However, the total amounts of dioxin-like PCBs and PCB homologues showed a decreasing tendency.

To investigate the behavior of dioxin-like PCBs in the atmosphere, the amount released into the air through MSW incineration was compared with the amount deposited from the air to the ground. The results for dioxin-like PCBs (Fig. 7) were very different from other PCB congeners and homologues. For congeners 81, 126, 169, and 189, the ranges of the amounts deposited fell within the ranges of the amounts released through waste incineration. Conversely, for congeners 105, 114, and 118, the ranges of the amounts deposited were much higher than the ranges of

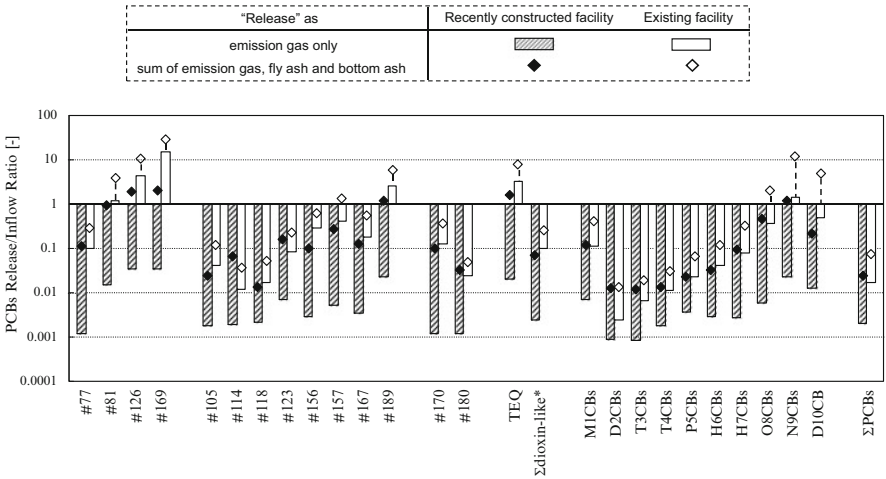


Fig. 6 PCB release/inflow ratio of MSW incineration [17]

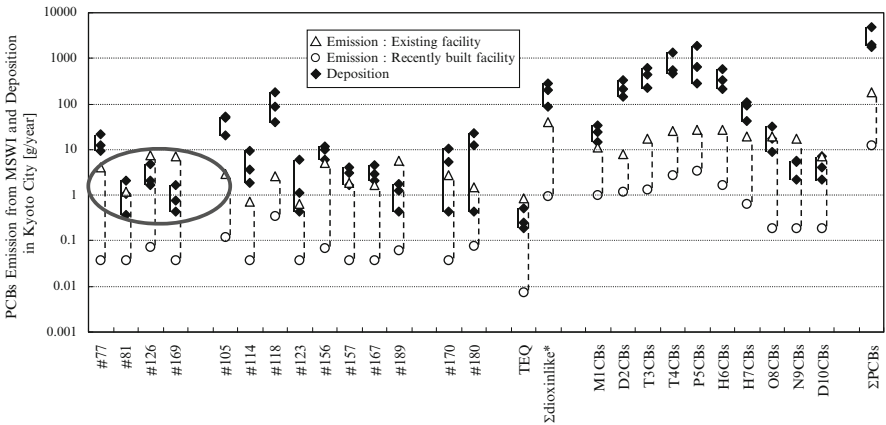


Fig. 7 Comparison of dioxin-like PCBs in incinerator emissions and in depositions in Kyoto City [17]

the amounts released through waste incineration. Summarizing the patterns of each congener and homologue together, the results could be roughly classified into three groups:

- Group 1: Congeners and homologues for which the amounts deposited were much higher than the amounts released through waste incineration, dioxin-like PCBs 105, 114, and 118 and PCBs D<sub>2</sub>CBs to H<sub>7</sub>CBs
- Group 2: Congeners and homologues for which the amounts deposited were of the same order of magnitude as the amounts released through waste incineration,

dioxin-like PCBs 81, 126, 169, and 189, PCBs O<sub>8</sub>CBs to D<sub>10</sub>CB, PCDDs/DFs 2,3,7,8-substituted congeners, and all homologues except TeCDDs and PeCDDs  
Group 3: Those falling between the two previous groups

With reference to group 1, congeners 105 and 118 are found in high concentrations in the industrial PCB product Kanechlor. Dioxin-like PCBs 170 and 180 are very abundant in the highly chlorinated PCB product KC-600. With regard to the congener profiles of dioxin-like PCBs in the atmosphere, percentages of congeners 77, 105, 118, and 180 are high, and their trends are similar to those of industrial PCB products. As for PCB homologues, the amounts of T3CBs to H7CBs are very high in industrial PCB products. With reference to group 2, the percentages of nonortho dioxin-like PCB congeners are high in incinerator emission gases. As mentioned before, the release/inflow ratios of these congeners were greater than 1, the suggestion being that these congeners tend to form during the waste incineration process. The release/inflow ratios of O<sub>8</sub>CBs to D<sub>10</sub>CB were higher than the ratios of D<sub>2</sub>CBs to H<sub>7</sub>CBs. Conversely, congeners 126, 169, and 189 and O<sub>8</sub>CBs to D<sub>10</sub>CB are very rarely found in industrial PCB products. From the above findings, the general trend is assumed to be as follows: (1) For congeners found in high concentrations in industrial PCB products, the amounts deposited are much higher than the amounts released through incinerator emission gases (group 1). (2) For congeners commonly found in waste incineration emission gases, the amounts deposited are similar to the amounts released with the emission gases (group 2).

When PCB regulation began, the concentrations of dioxin-like PCBs in the environment decreased. Because of this reduction, the proportion of incineration-derived, dioxin-like PCBs has increased. The use of advanced dioxin control measures has drastically reduced the amount of incineration-derived, dioxin-like PCB formation, but the level of dioxin-like PCBs remains high in fish and seafood. Therefore, control of dioxin-like PCBs is considered to be crucial for preventing human exposure to PCBs.

## 5 BFRs and PBDDs/DFs Control

Flame retardants are used to protect the public from accidental fires by reducing the flammability of combustible materials such as plastics, synthetic polymers, and textiles [18]. The most important group of flame retardants is the brominated flame retardants (BFRs), which represents various chemicals. Some BFRs, such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBP-A), and hexabromocyclododecane (HBCD), have been studied with respect to environmental pollution and human exposure for the past three decades. Recently, environmental problems related to BFRs have become a matter of greater concern than ever before. One of the reasons is the marked increase in PBDE levels observed in human milk in Sweden [19] and North America [20]. In particular, the PBDE levels in human milk around the year 2000

in North America were reported to be two orders of magnitude higher than those in Sweden or Japan. Another reason for concern is the recent analysis of toxicological data that has demonstrated that some BFRs have the potential to cause health effects because they have thyroidogenic, estrogenic, and dioxin-like activities [21]. The emerging problem is therefore whether environmental levels of PBDEs and other BFRs will continue to increase and possibly cause toxic effects in humans.

For the past several decades, another social concern related to BFRs has been their breakdown products, which include polybrominated and mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans (PBDDs/DFs and mixed PXDDs/DFs). The German Government amended its existing Hazardous Substance Ordinance in 1994 to include eight 2,3,7,8-substituted PBDDs/DFs. The WHO has published a document concerning brominated dibenzo-*p*-dioxins and dibenzofurans [22]. This document includes and reviews studies on the physical and chemical properties, methods of formation and sources, environmental behavior, environmental levels and human exposure, kinetics and metabolism, and toxicity of PBDDs/DFs and mixed PXDDs/DFs. The WHO concluded that PBDDs/DFs are contaminants that are more or less similar to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) in terms of their persistence and toxicity and that humans and the environment should be protected from these compounds.

Control of BFRs and PBDDs/DFs is the target of the fields of recycling and waste management of e-waste and end-of-life vehicles (ELVs). Automobile ownership worldwide exceeded one billion in 2010. The generation of ELVs was estimated at 40 million, which accounts for 4% of total automobile ownership [23]. ELVs are recycled as secondary materials and disposed of as waste. The recycling rate of ELVs in general ranges from 75% to 80%. In normal recycling and disposal procedures, ELV bodies are crushed, and the automobile shredder residue (ASR) remaining after the recovery of metals is disposed of mainly in landfills. However, landfills for industrial waste are becoming increasingly scarce. ASR has the following characteristics: (1) it has a high calorific value and high ash content; (2) it contains many fine particles with diameters of 5 mm or smaller as well as considerable crushed waste with diameters of 50 mm or larger, the result being a low bulk specific gravity; and (3) it contains large amounts of heavy metals, BFRs, and chlorine. Because of these characteristics, ASR is considered to be a type of waste that is very difficult to treat. ASR treatment requires an evaluation of the technology needed to decompose and control emissions of toxic substances. Osada et al. conducted an ASR melting test using a shaft-type direct melting furnace to identify the behavior of the BFRs and PBDD/DFs and the distribution of heavy metals in the slag and fly ash [24].

The test facility consisted of a melting furnace, a combustion chamber, a gas cooler, a bag filter, an induced draft fan, and a catalytic reactor. The capacity of the test facility was 10 t/day (when 100% ASR was processed). ASR introduced into the melting furnace was gradually dried and preheated in the upper section. Subsequently, combustible waste was thermally decomposed, and pyrolysis gas was discharged from the top of the melting furnace. The pyrolysis gas was transferred to the combustion chamber and was then completely burned. Meanwhile,



incombustible waste and remaining residues descended to the bottom of the melting furnace and melted completely, the heat being generated by burning coke. Finally, molten materials were discharged from the taphole, quenched with water, and magnetically separated into slag and metal. The gas emission control system consisted of a gas cooler, bag filter, and catalytic reactor. The temperature of the melt was about 1,700°C, which allowed smooth delivery of the melt during the test period. The temperature at the outlet of the combustion chamber was 960°C, and the exhaust gas from the stack amounted to 11,000 Nm<sup>3</sup>/t dry weight. Furthermore, the fact that the CO concentration of the exhaust gas was only 4 ppm proved that complete combustion of the pyrolysis gas generated from the melting furnace was possible.

Table 3 shows the behavior of dioxin-related compounds and BFRs. Although the ASR contained 30 mg/t of PBDD/DFs, this amount was reduced to 1.3 µg/t at the outlet of the combustion chamber, the indication being that the gasification and combustion process had decomposed more than 99.99% of the PBDD/DFs. The cooling process showed almost no resynthesis, unlike the behavior of PCDD/DFs. With a total emission at 14 µg/t, 99.9% of the input PBDD/DFs had been decomposed, with 79% of the total emissions accounted for by fly ash. No PBDD/DFs were detected in the slag or metals; similarly, mono-BrPCDD/DFs were not detected in the exhaust gas or slag. Because mono-BrPCDD/DFs were detected in the fly ash, resynthesis during the cooling process may have taken place. PBDEs at the outlet of the combustion chamber amounted to 22 µg/t, the indication being that more than 99.99999% of the PBDEs input to the melting furnace had been decomposed by the gasification and combustion process. The total emission was 170 µg/t, which means that 99.9999% of the brominated diphenyl ethers input to the melting furnace were decomposed, with 71% of the emission discharged as fly ash. The TBBP-A at the outlet of the combustion chamber was 156 µg/t, the indication being that more than 99.99% of the input TBBP-A had been decomposed by the gasification and combustion process. The total emission of TBBP-A was 350 µg/t, which means that more than 99.99% of the input TBBP-A had been decomposed, with about 89% of the emission discharged as exhaust gas. Based on these results, the melting method was proven to be effective in the decomposition of POPs such as PBDEs, TBBP-A, PBDD/DFs, and PCBs.

Formation of polybrominated dibenzofurans (PBDFs) was clearly found by Kajiwarara et al. [25] in the flame-retarded plastics. They investigated the high-impact polystyrene and DecaBDE samples and found that the PBDF concentration increased by about 40 times after 1 week of exposure under natural sunlight conditions, with a concomitant decrease in BDE 209. Formation mechanism of brominated dioxins and dibenzofurans should be taken care, and more studies are necessary.

Table 3 Behavior of BFRs and PBDD/DFs in ASR treatment [24]

	Charged	Outlet of each section		Emissions				Total emissions (Unit: ug/ton of waste)
		Exhaust gas at outlet of combustion chamber	Exhaust gas at outlet of gas cooler	Exhaust gas at outlet of catalytic reactor	Fly ash at bag filter	Slag discharged from melting furnace	Metals discharged from melting furnace	
ASR								
PCDDs/DFs	970	3.1	—	1.7	4,300	71	140	4,500
Co-PCBs	30,000	1.9	—	1.8	200	7.1	3.7	210
PBDDs/DFs	30,000	1.3	ND	2.2	11	ND	ND	14
MoBrPCDDs/DFs	ND	ND	—	ND	1,900	ND	4.0	1,900
Brominated diphenyl ethers	310,000,000	22	270	ND	120	26	25	170
Tetrabromobisphenol A	15,000,000	156	150	310	13	18	6.1	350
PCBs	270,000	17	—	29	960	24	18	1,000

ND not detected, — not measured

## 6 Hierarchy of Persistent Chemical Management

The global consensus on the basic concept of hierarchical measures for solid waste management is (1) reduction, (2) reuse, (3) recycling, and (4) proper treatment and disposal. This concept also makes it possible to develop an in-depth discussion on management measures, especially for hazardous wastes and persistent chemicals that have high potential to cause environmental damage. The concept of “clean, cycle, and control” represents what measures should be taken to control persistent chemical substances [26]. This concept means that the use of hazardous chemicals should be avoided (clean), the principle of recycling (cycle) should be introduced when appropriate alternatives are not found and the material must be used for its effect, and waste from previous use should be decomposed as much as possible and stabilized, the focus being on control of the waste (control).

The use of clean measures is a concept similar to green chemistry, the philosophy of which was first developed in 1990s [27]. It promoted both technological and policy development that encourages design of products and processes that minimize use and generation of hazardous substances. The principles of green chemistry include the following concepts:

- Chemical products should be the ones that possess minimum toxicities to human health and the environment.
- Substances with the lowest toxicity among those with similar functionality should be used as much as possible.

This idea of “green chemistry” is one of the effective measures to realize the clean concept. It can be said that implementation of this concept has brought about a dramatic change to the basic modus operandi of the chemical industry, and similar ideas will hopefully spread to other industries. The clean principle should be applied wherever possible; however, if this is not possible, or in cases where other, other management practices are required, then the second principle of cycle should be adopted.

The basic elements of technologies for control are the following: separation, recovery, reuse and decomposition, and stabilization/solidification. When treating hazardous waste and/or persistent chemicals, the following steps should be taken in the given order: (1) separation/recovery, (2) detoxification, and (3) stabilization. First, it is necessary to design products from the standpoint of their separation, recovery, and reuse. Then, the detoxifying processes, which can remove hazardous substances contained in waste products or waste materials, should be given priority. In other words, use thermochemical treatment such as incineration and melting that bring about essential changes of hazardous characteristics. Thermochemical treatment under proper conditions is particularly effective for various organic compounds, including organochlorine compounds contained in organic materials. This treatment is the ultimate goal of effective technologies for detoxification. For metal-containing wastes, solidification/stabilization technologies should be the

**Table 4** Clean, cycle, and control concept and some examples for POPs

	Clean	Cycle	Control
General concept	Avoid the use of hazardous chemicals and use alternatives	When there are no appropriate alternative substances and the use of specified material is essential because of its crucial effect, recycling should be the principle	Control of emission to the environment and the decomposition and stabilization of stock substances and wastes which have been used in the past
PCB	Use of PCB should have been almost completely stopped from the viewpoint of adverse effects on human health and the environment	Recycling used in closed system, but too difficult to control without emission over the whole life cycle	Control of emissions in the stages of repair, demolition, and disposal must be fully enforced. Complete destruction of waste PCB should be carried out
Chlorinated dioxins	Chlorinated dioxins are produced as by-products by chemical or thermal reactions. Therefore, avoidance of unintentional formation of chlorinated dioxins is a first priority	No way for cyclical use. Environmental cycles should be avoided and reduced	Control of the environmental emissions should be done by the Best Demonstrated Available Technology (BDAT) measures. Additional monitoring on food to have minimum human exposure is also one kind of control measure
BFRs	PeBDEs and OBDEs received a risk assessment as toxic, and their production was stopped internationally. DBDE is still produced and used in various products	Part of BFRs is reused and recycled. The regulation on PBDEs exempts recycling activities	Continue to develop clean and control measures for BFRs

principal effective disposal process, because metals are not subject to decomposition.

Table 4 shows some examples of the 3C concept (clean, cycle, and control principle), with POPs as an example. The first priority for intentionally produced POPs is implementation of the clean concept. This concept was applied to PCBs as soon as their toxicity and environmental transport were confirmed, their manufacturing was stopped, and their use was limited to closed systems only. At the same time, the Stockholm Convention on POPs designated PeBDEs and OBDEs, which are used in BFRs, as substances targeted for reduced use. In other words, the basic principle here is that toxic substances and substances with the potential for global environmental transport should not be used, and hazardous chemicals that were used in the past without an awareness of their toxicity should no longer be used. The second priority is that unintentionally produced POPs like dioxins should be regulated via the clean concept. Their formation and emission

and transport into the environment should be avoided, and the control concept should be applied to the control of their exposure to humans or to the environment. The third priority is that the cycle concept be adopted in some cases; targeted objects are useful, but metals like mercury and lead are toxic. Among the POPs, it is reasonable that the recycling process for only PBDEs is exempt from regulation.

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