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Chapter 1

Persistent Organic Pollutants Monitoring Activities in Japan

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1.1. Introduction

Japanese environmental policy and administration system has been constructed under strong influence from severe pollutions experienced under rapid economical growth and industrialization during the 1950s–1960s, including organomercury poisoning from acetaldehyde production factory (Minamata disease), cadmium poisoning from mining activity (Itai-itai disease) and air pollution at highly industrialized and/or densely populated areas. Pollution by polychlorinated biphenyls (PCBs) has also been a major issue in Japan, not only because of their extensive use in transformer oil, non-carbon paper, etc., but also because of a severe intoxication case, the Yusho incident (the Kanemi cooking oil health incident in 1968), where a number of people suffered from PCB poisoning by ingesting rice oil accidentally contaminated with PCBs used as heating medium. The toxicity mainly came from polychlorinated dibenzofurans (PCDFs) produced by oxidation of PCB during heating process.

Environment Agency was established in 1971 after these severe pollution incidents, and the first environmental monitoring by the Agency was conducted in 1974. The second monitoring was conducted in 1978 followed by the consecutive surveys monitoring conducted every year until present (Ministry of the Environment Japan, 1996, "Chemicals in the environment"). The compounds and the environmental media analyzed in the monitoring until 2003 are summarized in Table 1.1. The analytes had included not only organic compounds but also heavy metals in the first phase but have been shifted to POPs, including PCB, DDT, chlordanes (including heptachlors), hexachlorobenzene (HCB) and drins (aldrin, dieldrin, endrin).

Meanwhile the law concerning the evaluation of chemical substances and regulation of their manufacture, etc. (Law No. 117 of 1973, hereafter

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Table 1.1. Status of POPs monitoring in Japan

	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03
Air																													B2	B2
Aldrin/endrin																														
Dieldrin																													B2	B2
Chlordanes													B1																B2	B2
DDTs																													B2	B2
Heptachlor													B1																B2	B2
Toxaphene/mirex																														B2
HCB																					B1				E	B1			B2	B2
PCBs																								B1		B1	B1		B2	B2
PCDO/DFs													O	O	O	O	O	O	O	O	O	O	O	A	A	A	DA	DA	DA	DA
Water																														
Aldrin/endrin																									E				B2	B2
Dieldrin													B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
Chlordanes									B1				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
DDTs	B1												B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
Heptachlor									B1																				B2	B2
Toxaphene/mirex										B1																				B2
HCB	B1	B1			B1								B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E				B2	B2
PCBs		W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	B1.E,W	B1W	B2W	B2W
PCDO/DFs																									O	O	D	D	D	D
Soil																														
PCDO/DFs																									O	O	D	D	D	D
Bottom sediment																														
Aldrin/endrin																									E				B2	B2
Dieldrin													B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E				B2	B2
Chlordanes									B1				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E	B1	B1	B1	B2	B2

DDTs	B1										B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1.E	B1	B1	B1	B2	B2
Heptachlor							B1																			B2	B2
Toxaphene/mirex								B1																			B2
HCB	B1	B1		B1							B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
PCBs																					B1	B1			B1,E	B1	B2	B2
PCDO/DFs										O	O	O	O	B	B	B	B	B	B	B	B	B	O	O	D	D	D	D
Wildlife																												
Aldrin/endrin				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1		B1		B1					E				B2	B2
Dieldrin				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1		B1,E				B2	B2
Chlordanes							B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
DDTs	B1			B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B1	B1	B2	B2
Heptachlor							B1																				B2	B2
Toxaphene/mirex																												B2
HCB	B1	B1		B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E		B1,E	B1	B2	B2
PCBs				B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1	B1,E	B1	B2	B2
PCDO/DFs										O	O	O	O	B1	B1	B1	B1	B1	B1	B1	B1	B1	O	O	O.E	O	O	O

Notes: B1 = survey on the actual condition of chemical substances in the environment (until 2001); B2 = survey on the actual condition of chemical substances in the environment (after 2002); D = survey under the Law concerning Special Measures against Dioxins; E = survey on the environmental endocrine disrupters; W = survey under the Water Pollution Control Law; A = the air pollutants monitoring; O = other survey.

*Details of the survey on the actual condition of chemical substances in the environment: refer to Ministry of the Environment web site http://www.env.go.jp/chemi/kurchen/index.html (also refer to annual reports before FY1996).

*Details of survey under the Law concerning Special Measures against Dioxins: refer to Minister of the Environment of the web site http://www.env.go.jp/chemi/dioxin/report.html

*Details of the survey on the environmental endocrine disrupters: refer to working group materials on the Ministry of the Environment web site http://www.env.go.jp/chemi/end/index2.html

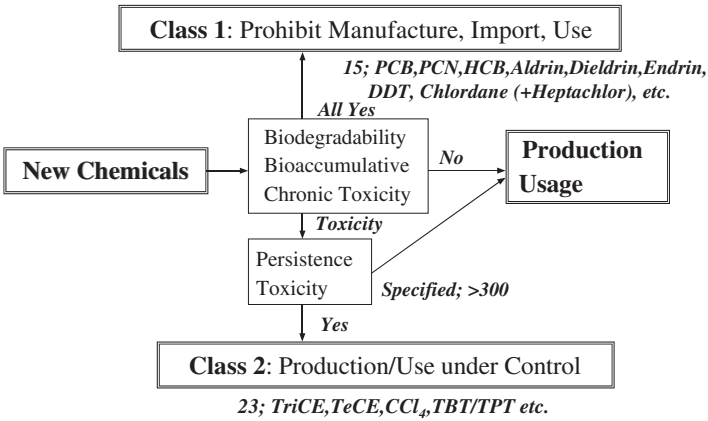

Figure 1.1. Japanese Chemical Management Law.

referred to as the Chemicals Substances Control Law) was promulgated in 1973 (Fig. 1.1). In this law, a priority of regulation was put on stable (not decomposed substantially during sewage sludge treatment), bioaccumulative and toxic chemicals, i.e., POPs-like compounds. Chemicals having these three properties together were classified as the Class 1 Designated Chemicals, and their production, import and usage were banned. PCB was designated as Class 1 in 1974, followed by HCB in 1979, aldrin, dieldrin, endrin and DDT in 1981, and chlordanes (including heptachlors) in 1986. Mirex and toxaphene have never been registered in Japan as agrochemicals, but they were also designated in 2002 as Class 1 Chemicals (Table 1.2).

The Chemical Substances Control Law was amended in 2003, to bring all the chemical substances, which are likely to cause damages to top predators in the ecosystem, within its regulation. Moreover, there were several moves to establish PCBs disposal facilities under the initiative of the private sector in order to dispose of the PCBs already produced. However, such moves failed to ensure understanding and consent from local communities, with the result that much of the PCBs had remained in stockpiling without being disposed of over nearly 30 years. It was also found that during the long-term stockpiling some transformers were lost or became untraceable and there were concerns that such stockpiled PCB might contaminate the environment. Thus, in June 2001, the law concerning special measures against PCB waste (Law No. 65 of 2001, hereafter referred to as the PCB Special Measures Law) was enacted to obligate entities possessing PCB wastes to report the status of their

Table 1.2. List of industrial and agrochemicals banned in Japan

Name	Banned as industrial chemicals	Banned as pesticides
DDT	1981	1971
Aldrin	1981	1975
Dieldrin	1981	1975
Endrin	1981	1975
Chlordane[a]	1986	1968
Heptachlor[b]	1986	1975
Mirex	2002	[c]
Toxaphene	2002	[c]
PCB	1974	
HCB	1979	[c]

[a]Used mainly for termiticides (other than agricultural purposes); between 1979 and 1986.
[b]Heptachlor was also included in technical chlordane as impurity (~10%).
[c]Never registered as agrochemicals in Japan.

stockpiling and to dispose of such wastes within a given time frame in an environmentally sound manner, with a view to facilitate the sure and perfect disposal of PCB waste.

Ministry of the Environment of Japan also conducts environmental monitoring of some POPs chemicals, including waste dumping in the seas and oceans, monitoring of water based on regulation of water environment, and monitoring of chemicals suspected to have endocrine disruptive properties (EDCs).

At the same time the issues related to the unintentionally produced dioxins and furans, i.e., polychlorinated dibenzo-*p*-dioxins (PCDDs) and PCDFs, attracted public attention in 1983 when investigations revealed that dioxins were detected in the fly ashes from municipal waste incinerators. Therefore, measures to monitor dioxins in the bottom sediment and aquatic animals and plants in the rivers, lakes, marshes and seawaters as well as the atmosphere were initiated in 1986. Investigations were implemented on the actual status of waste incinerators in 1984 and pulp and paper factories in 1990. On the basis of these findings, guidelines and administrative guidance on controlling emissions of dioxin-related chemicals were derived and established.

Furthermore, from around 1996 onward Japanese public became increasingly concerned about environmental contamination caused by releases from waste incinerator facilities. In 1997 dioxins were designated as hazardous air pollutants and measures were introduced to control their emission into the atmosphere in terms of the preventive actions taken to reduce risks of health hazards under the Air Pollution Control Law (Law No. 97 of 1968). Furthermore, in July 1999, the law concerning special

measures against dioxins (Law No. 105 of 1999, hereafter referred to as the Dioxins Law) was established and the regulatory framework was put in place to implement comprehensive measures such as establishing tolerable daily intake (TDI) and environmental quality standards, regulating the release of emission gases and effluent water from a wide range of facilities, introducing enhanced regulation on waste disposal and conducting investigations on the actual status of contamination and taking measures against contaminated soil and other matters. Now these measures are strictly implemented under the law.

In Japan, under the Dioxins Law, PCDDs, PCDFs and coplanar PCBs are defined as the dioxins. According to the current scientific knowledge, the source categories and the formation processes of PCB and HCB are considered to be similar to those of unintentionally produced dioxins. Therefore, it is assumed that the release of PCBs and HCB has also been reduced through the dioxins reduction measures.

Under the Law concerning Reporting of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management (Law No. 86 of 1999, hereafter referred to as the Chemical Substances Release Reporting and Management Promotion Law), dioxins and PCBs are subject to the requirements of the Pollutants Release and Transfer Register (PRTR) system.

Extensive efforts have been made in the environmental monitoring of dioxins from 1989 in biota and sediments and from 1998 in other media until present (Fig. 1.2) (Ministry of the Environment, 2002, ''Dioxins monitoring in the environment''). It could be seen from these efforts, that emission of dioxins in Japan has been decreasing from 7680–8135 g-TEQ in 1997 to 323–348 g-TEQ in 2005, a 95% reduction from the 1997 level, meeting the reduction target (Ministry of the Environment, 2004, ''Dioxin emission inventory''). In 2005, 3206 atmospheric samples, 2550 water samples, 1730 sediment samples, 924 ground water samples and 1782 soil samples were analyzed for their dioxin levels.

1.2. PCB and POPs pesticides monitoring

1.2.1. Results of biological monitoring by GC-ECD (from 1978 until 2001)

Gas chromatography-electron capture detector (GC-ECD) was originally selected as the analytical instrument for environmental monitoring using organisms until 2001 when MOE decided to reorganize their environmental monitoring by introducing HRGC/HRMS in order to elucidate the present levels of POPs in Japan as the baseline value for the

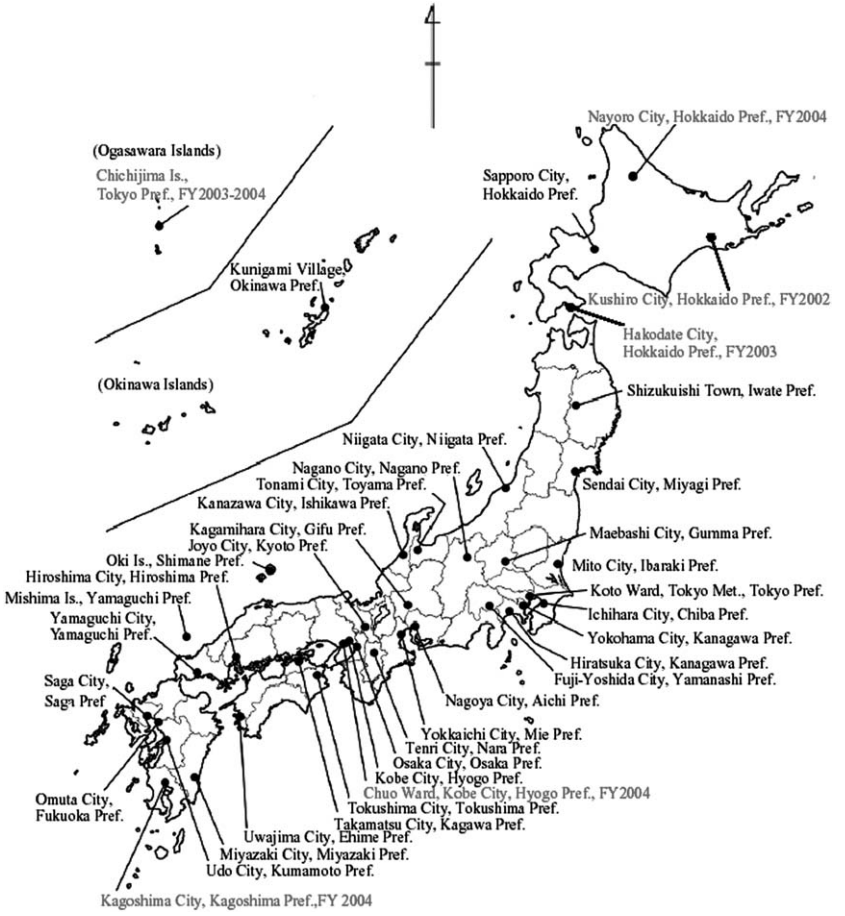

Figure 1.2. Sites for 12 POPs monitoring for atmospheric air and precipitation (FY2002–2004).

effectiveness evaluation of the Stockholm Convention. In fact, the ratios of ND (not detected) in the monitoring data had been increasing while using the GC-ECD method during the last decade of the 20th century, although data without ND have been obtained for some pollutants, such as PCBs and DDTs, in the samples like fishes collected from the coastal waters along densely populated areas, such as Tokyo Bay and Osaka Bay.

Generally speaking pollutant levels in fishes and other wildlife species have been decreasing in recent decades either in their average concentrations or in the detection frequencies (ratios of detectable sites among

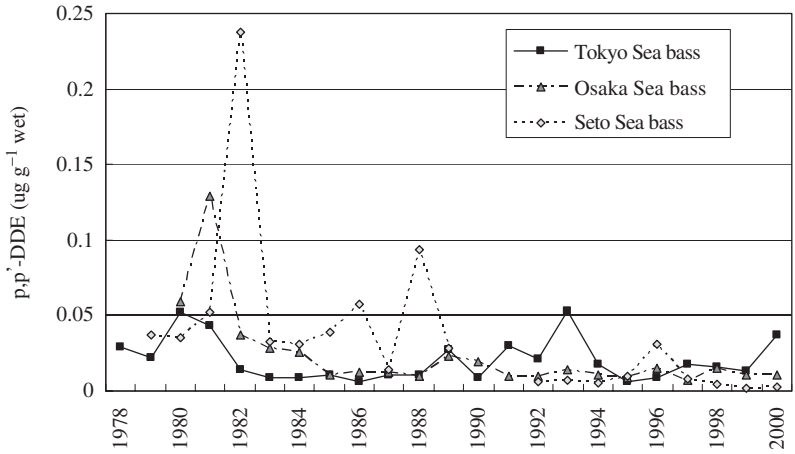

Figure 1.3. *p,p′*-DDE levels (average of five specimens' data in each location) in fishes (Sea bass) in Tokyo Bay, Osaka Bay and Seto Inland sea between 1978 and 2000.

all sampling sites). There seems to be, however, some differences among locations in the time trends of pollutant levels. As an example of such data, Fig. 1.3 shows *p,p′*-DDE levels in fishes from Tokyo Bay, Osaka Bay and Seto Inland sea. *p,p′*-DDE levels have been decreasing continuously during the last three decades in Osaka Bay and Seto Inland sea, while the levels apparently do not show clear decreasing trend in Tokyo Bay although their levels were higher in the early 1980s. All of these areas are semi-enclosed environment and thus are expected to remain polluted for a longer time. DDT concentrations in water of Sumida River and Arakawa River, both flowing into the central Tokyo Bay indicates continuous loading of DDTs, which may contribute to maintain their higher levels in Tokyo Bay. This might be the reason for the differences in the temporal patterns of DDE in these three areas.

Similar trends are also observed in PCB levels in Sea bass in the three coastal water environments as shown in Fig. 1.4. Again a clear decreasing trend was seen in Seto Inland sea, while the levels in Tokyo Bay are rather flat with a couple of fluctuations. The time trend in Osaka Bay is more or less similar to Tokyo Bay but with no clear decrease in recent decades. The difference between *p,p′*-DDE and PCB time trends in Osaka Bay might reflect either the difference in recent loading of the compounds to the Bay or the difference in their pollution histories.

Several other characteristic levels/patterns of pollutants, apparently reflecting local environmental situations were noticeable and these will be described in the next section based on the recent HRGC/HRMS data.

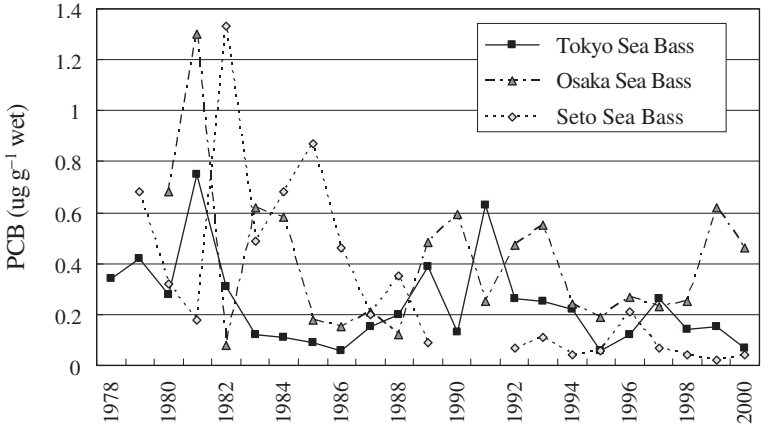

Figure 1.4. PCB levels (average of five specimens' data in each location) in fishes (Sea bass) in Tokyo Bay, Osaka Bay and Seto Inland sea between 1978 and 2000.

1.2.2. Monitoring by HRGC/HRMS (after 2002)

As stated above, MOE decided to introduce HRGC/HRMS-based monitoring method for all POPs (except toxaphene) in all the environmental media in order to clarify the present pollution status of POPs in Japan as a basis for future effective evaluation of the Stockholm Convention, and started new monitoring from FY2002. Basically the same type of samples obtained with the same sampling protocol as the previous environmental monitoring are analyzed by the new methods with ultratrace detection limits and higher fidelity (all available isotope-labeled surrogates are used for recovery correction during sampling or pretreatment before analysis).

The basic idea of sampling site selection is different among the environmental media. For air sampling, the sites are selected to cover all over Japan with similar distance between the sites (roughly 100 km in average). Water and sediments are sampled at the mouth of the major rivers, and the major ports. Biological samples, i.e., fishes, bivalves and birds, are continuously sampled according to the original design, i.e., by categorizing Japanese environment into several typical areas, such as densely populated, highly industrialized, rural area with agricultural activity, remote area, etc. and selecting a few locations in each category to collect typical biological samples in each region representing the environment. In addition to this, human breast milk, and maternal and cord blood samples were collected in two cities to evaluate the status of POPs pollution in human.

As the new monitoring system has been operating only 5 years (2002–2006) until now, it is too early to conduct trend analysis. Here a brief description of the monitoring data by the new POPs monitoring method will be presented.

1.2.2.1. Data reflecting local specificities within Japan

1.2.2.1.1. Air

In general, chlordanes and PCBs were found to be highest in the air among POPs chemicals followed by HCB, heptachlor, dieldrin, DDT, etc. (Fig. 1.5). Their levels are generally lower in winter compared with summer data summarized in Fig. 1.5. It should be noted that the median values representing majority of the sampling sites are several times lower than the average values shown in Fig. 1.5, for there are apparently a few "hotspots" data in each of the chemicals by which average levels were pushed to be higher.

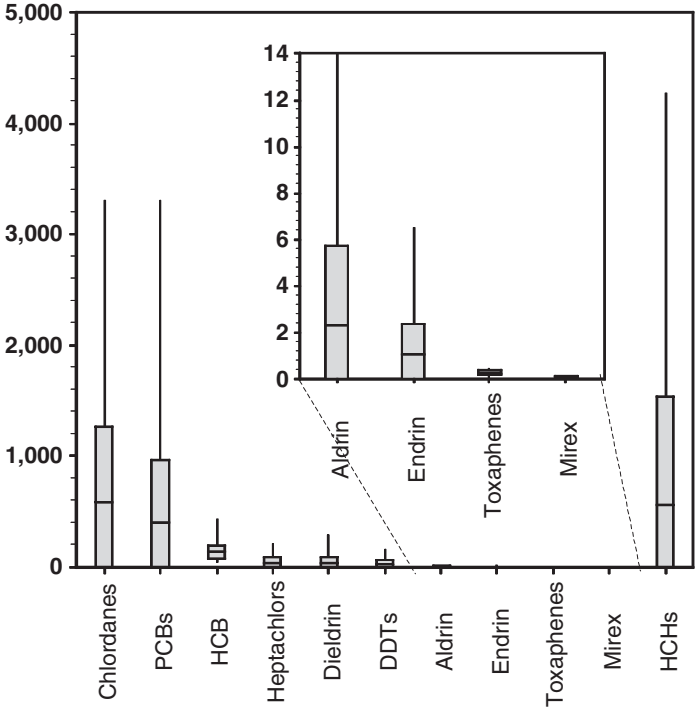

Figure 1.5. Concentrations of POPs in air (pg m^{-3}; summer in FY2004). Box represents average (middle line) $\pm$ SD; bar represents range (max. and min.) of data.

There are several "hotspots" data, i.e., characteristic POPs levels/compositions attributable to some local sources of pollution. For example, PCB level is among the highest in Takamatsu, Kagawa Prefecture with specific congener profile biased to highly chlorinated biphenyls. Their congener profile is rather similar to a PCB product used for anti-rusting paint of steel products, KC600, and above data might be attributable to some steel products or buildings located nearby the sampling site, in which KC600 had been used. Dieldrin level in the air has been among the highest in Fukuoka and Saga Prefecture, both in northern part of Kyushu, again suggesting presence of some local source of dieldrin in the area.

Trace levels of toxaphene and mirex are detected in the air with no clear differences among the sampling sites, although both had never been registered as agrochemicals in Japan. HCHs, now being evaluated as candidates of the additional POPs by POPs review committee under Stockholm Convention, are also in comparable levels to PCB and chlordanes in Japan as shown in Fig. 1.5.

1.2.2.1.2. Water, sediments and marine organisms

In Japanese water environment, again PCB and chlordanes are among the highest followed by DDT, dieldrin and others (Fig. 1.6). In sediments, PCBs are by far the highest contaminants followed by DDT, chlordanes, HCB, etc. (Fig. 1.7). It should be noted that the average levels in Figs. 1.6 and 1.7 tend to be pushed higher by few "hotspots" data as in the case of air samples. Chemical concentrations in water and river/port sediments tend to be higher in semi-enclosed bays along densely populated areas, notably PCB and DDT concentrations in water and sediments in Tokyo Bay and Osaka Bay. Specifically *o,p′*-DDE, a minor constituent in technical DDT, in water, and sediments in Sumida River and fishes in Tokyo Bay have been showing unusually significant proportion compared with samples in other locations, suggesting some specific sources of *o,p′*-DDEs (or originally *o,p′*-DDT) in the river and/or Tokyo Bay region. Several local contaminations have been identified for some specific chemicals; i.e., PCB in Sumida River, Osaka Port and Dokai Bay (both water and sediments), DDT in Sumida River, Toba Port, Osaka Port and Naha Port (sediments), chlordanes in Sumida River, Osaka Port, Takamatsu Port and Naha Port (sediments), endrin in Toba Port (sediments), dieldrin in Sumida River, Osaka Port, Takamatsu Port and Naha Port (sediments), HCB in Onahama Port and Dokai Bay (sediments), and mirex in Kure Port (sediments). Mirex levels in the sediments are detectable but rather low except for Kure, but the concentrations tend to be higher near the densely populated areas, suggesting the use of mirex-containing materials

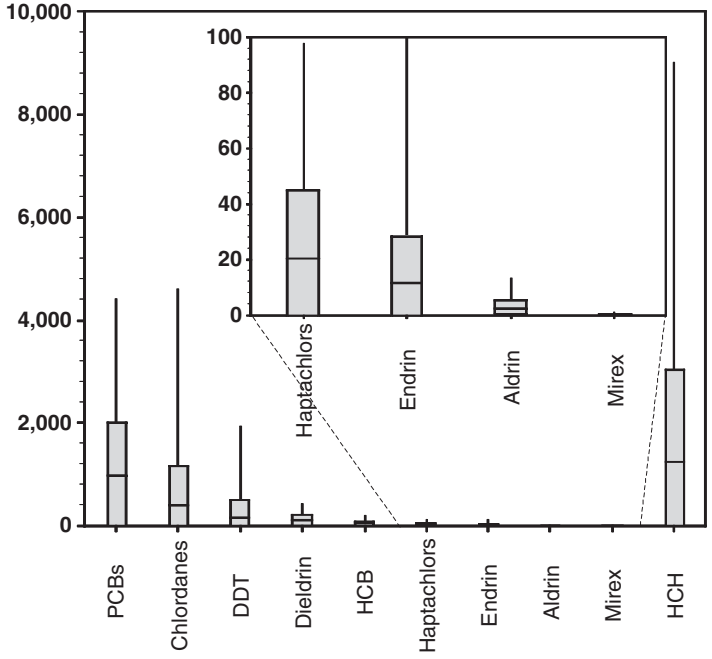

Figure 1.6. POPs levels in water (pg L^{-1}; FY2004). Box represents average (middle line) $\pm$ SD; bar represents range (max. and min.) of data.

in industries/household rather than for agricultural uses. It is reported that mirex has been used as flame retardants and also for termite control, and the above data may suggest the import/use of mirex-containing plastics or wood products. In addition, HCHs are among the highest in water while their levels are relatively moderate in sediments, apparently reflecting their water solubility.

Among fishes, Sea bass in Tokyo Bay showed the highest values for PCB, DDT and chlordanes in relation to their higher levels in waters/sediments. Hard-shelled mussel from Tokushima has been reported to have high levels of dieldrin and also chlordanes with extremely high proportion of *cis*-chlordane, suggesting nearby source(s) of these chemicals. Interestingly, levels of both toxaphene and HCB on wet weight basis is highest in a fish living in the off-shore region of Ibaraki Prefecture compared with other fishes including those living in enclosed bays, such as Tokyo Bay and Osaka Bay, probably reflecting their long-range transportability and status of global pollution as described below.

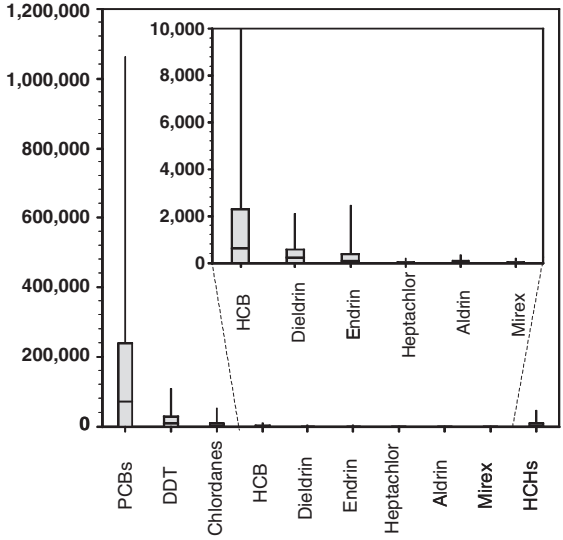

Figure 1.7. POPs levels in sediments (pg g^{-1}-wet; FY2004). Box represents average (middle line) $\pm$ SD; bar represents range (max. and min.) of data.

1.2.2.1.3. Other wildlife

DDT levels in terrestrial bird species caught in Iwate Prefecture showed higher levels of DDT while toxaphene levels are higher in juvenile sea gull compared with other species.

The government has been measuring PCB, HCB, DDT, chlordane, heptachlor epoxide and dieldrin since 1998 to identify their effects on wildlife as part of the Environmental Survey on Endocrine Disruptors. The specimens taken include land animals such as raccoons, bears, monkeys and frog, and marine mammals such as seals and whales, in addition to domestic birds and birds of prey. A relatively high concentration of POPs was seen in birds of prey and *Phalacrocorax carbo*. Eggs of mountain hawk eagles were also found to have a higher concentration of PCB, DDT, heptachlor epoxide, chlordane and dieldrin than other wildlife specimens

1.3. Regional/global transport of POPs

The data of POPs monitoring showed us general overview of the status of local pollution in Japan, although there seems to be some information from which regional/global scale information might be inferred.

1.3.1. HCB

HCB concentration in the air has always been fairly constant irrespective of the location, between 100 and 150 pg m^{-3} in late summer or 50 and 100 pg m^{-3} in early winter. HCB levels even in a background location, remote island Hateruma, are still around 50 pg m^{-3} in average (15–300), supporting the view that HCB is everywhere (Expert Working Group, 2006). Chemical property of HCB shows by far the longest transportability among 12 POPs chemicals. In fact, similar levels of HCB (50–100 pg m^{-3}) have been detected in some of the background sampling locations in East/Southeast Asian countries, such as Korea, Philippines, and Indonesia (Expert Working Group, 2006). Another data supporting the long-range transportability of HCB is its concentrations in fishes. HCB levels in wet weight basis is highest in a fish living in off-shore region of Ibaraki Prefecture followed by Sea bass in Tokyo Bay and another bottom-living fish from off-shore region off Hokkaido. It should be noted that the above mentioned first and third fish species live in off-shore water and thus reflect surface or bottom water concentration of chemicals, respectively. Although HCB levels are higher in coastal environment (e.g., Sea bass in Tokyo Bay) when presented as lipid basis, the data further supports the view that HCB contaminates not only coastal, but also open ocean environment due to its long-range transportability.

1.3.2. Toxaphene

Similar, but more impressive phenomenon was observed for toxaphene. Toxaphene has never been registered or produced in Japan; in fact, it was not detected in sediments/river waters all over Japan. However, toxaphene concentration was highest again in a fish living off-shore region of Ibaraki Prefecture followed by another bottom-dweller in Hokkaido, and Sea bass in Tokyo Bay. This time the second one is highest followed by the first and the third when the concentration is presented on a lipid basis. Although the comparison among fishes should consider various factors, including their trophic levels, the data seems to generally support the view that pollution status of toxaphene in coastal environment of Japan is similar to that of open ocean area of North Western Pacific Ocean. It should also be noted that toxaphene levels in lipid basis shows a clear trend, i.e., higher in northern part (Hokkaido) followed by central Japan compared with western Japan where its levels in any fish are much lower. This might support the view that northern Pacific water above the circumpolar front at around 40–45° north is contaminated by toxaphene more than southern warm water, possibly either reflecting their usage in

northern part of northern hemisphere or reflecting evaporation in southern warm water and condensation/precipitation in cool northern environment (Wania and Mackay, 1993).

1.3.3. DDT

Another interesting phenomenon was observed on DDT in air samples. There are a couple of data showing unusually high proportion of *o,p′*-DDT in the air samples; for example, *o,p′*-DDT occupied ~65% of total DDT (sum of *p,p′*- and *o,p′*-isomers of DDT, DDE and DDD) in Okinawa in the autumn of 2002, and more than 50% in Okinawa, Saga, Shimane and Kumamoto in the summer of 2003. The *o,p′*-DDT is only a minor constituent of technical DDT and thus the above phenomenon may suggest the presence of different sources of *o,p′*-DDT other than technical DDT. In fact, it was recently reported by the Chinese scientists that dicofol, another organochlorine pesticide produced from DDT and sold in China contained fairly large proportions of un-reacted *o,p′*-DDT, up to 11% in weight on average (Qui et al., 2004, 2005). They also found unusually high proportion of *o,p′*-DDT in their air samples, and attributed their findings to the impurity of dicofol sprayed in China. The high *o,p′*-DDT found in Japanese air POPs monitoring might be attributable to long-range atmospheric transport, too.

1.3.4. Heptachlor vs. Chlordanes

Interestingly, ratios of heptachlors vs. chlordanes are higher in environmental samples, i.e., air, water and sediments, in Hokkaido compared with other locations. These data may reflect usage pattern of heptachlor as agrochemicals in Japan.

Heptachlors were spread into the environment either as an agrochemical or as impurities of technical chlordanes. In Japan, technical chlordane was used not only for agrochemicals but also for termite control, especially in south-west part where termite tends to damage houses more actively due to high temperature and humidity. Apparently the technical chlordanes used in Japan had been quite homogeneous, for chlordanes composition (proportions of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and oxychlordane) in air, and also in water, are quite similar to each other among the same media irrespective of the sampling locations. It is also expected that proportions of heptachlors in technical chlordanes were also stable; in fact, similar heptachlors/chlordanes ratios have been observed in many places in Japan in air, water and sediments, and majority of the data plots on chlordanes (*X*)

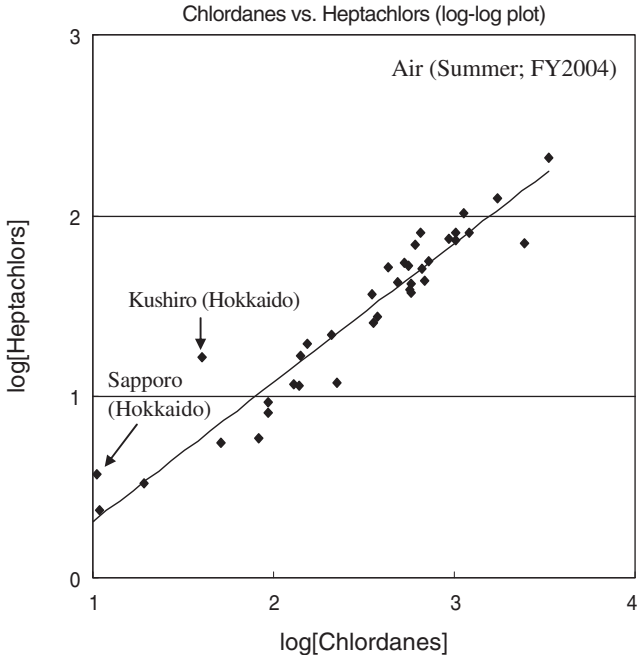

Figure 1.8. Chlordanes vs. heptachlors in air samples (summer; FY2004).

and heptachlors (Y) axes are on the same single line. There are, however, several data considerably biased to heptachlor side as shown in Figs. 1.8–1.10. It should be noted that these data correspond to sampling sites in Hokkaido, showing that the samples from Hokkaido are biased to higher proportion of heptachlors compared with other locations. In fact, heptachlors had been used in Hokkaido mostly for agricultural purposes while chlordanes were not used so much in Hokkaido due to its cold climate and absence of termite problem. This may be the reason why environmental media in Hokkaido showed relatively higher proportion of heptachlors.

1.3.5. Other proposed POPs

The environmental survey and/or monitoring data on the chemicals relevant to the five substances that were proposed for listing in Annex A of Stockholm Convention and considered at the first meeting of the Persistent Organic Pollutants Review Committee (POPRC) held in November 2005, are pentabromodiphenyl ether (PeBDE), chlordecone,

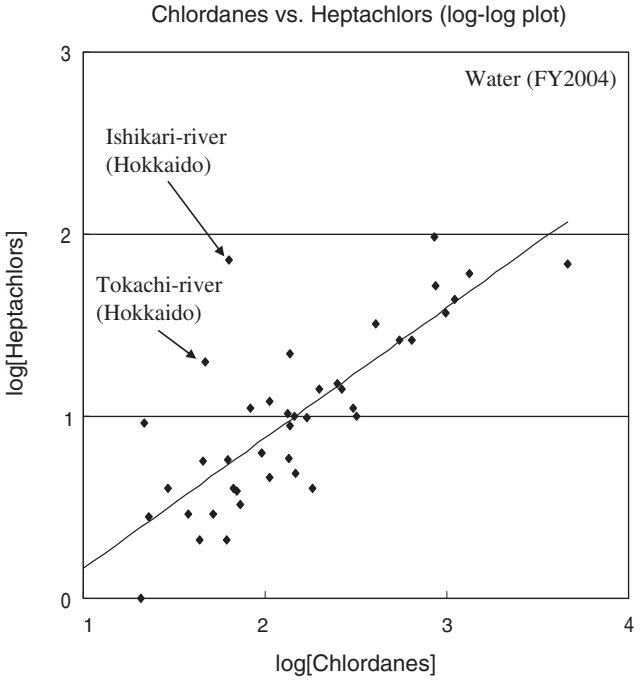

Figure 1.9. Chlordanes vs. heptachlors in water samples (FY2004).

hexabromobiphenyl, lindane and perfluorooctane sulfonate (PFOS). Although the proposal was made for lindane, this chapter includes the data on alpha, beta, gamma as well as delta isomers of HCH.

1.3.5.1. Pentabromodiphenyl ether (PeBDE)

1.3.5.1.1. Atmospheric air and precipitation

A survey was conducted in FY2001 with a detection limit of 0.09 pg m^{-3}, and the substance (PeBDE) was detected at all the 12 surveyed sites with a detection range between 0.10 and 9.3 pg m^{-3}. The survey conducted in FY2004 with a detection limit of 0.06 pg m^{-3} detected the substance at all of the three surveyed sites with a detection range between 0.35 and 5.4 pg m^{-3}. The persistence levels of the substance were comparable to the previous data.

A survey of the substance in bottom sediment was conducted for the first time in FY2004 with a detection limit of 0.035 ng g^{-1}-dry, and the substance was detected at one of the four survey sites with a detection value of 0.050 ng g^{-1}-dry. PeBDE has not been surveyed or monitored in

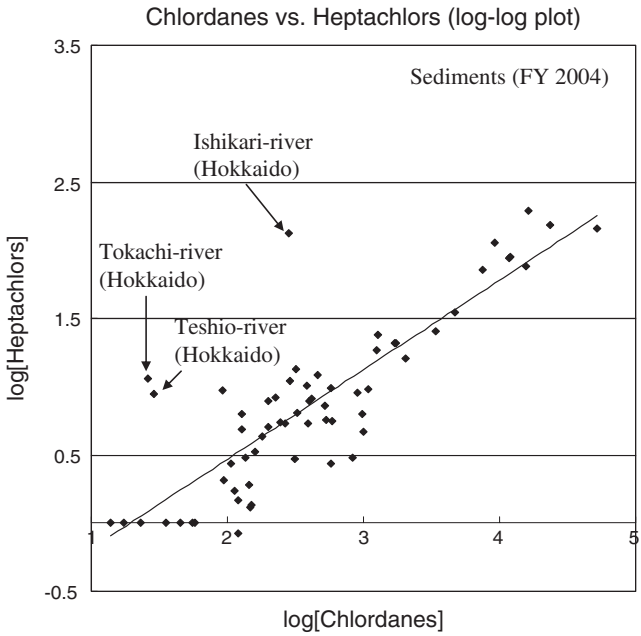

Figure 1.10. Chlordanes vs. heptachlors in sediment samples (FY2004).

other media—wildlife and bottom sediment in the Environmental Survey and Monitoring of Chemicals Program. Many laboratories in Japan have investigated PBDEs in recent years and reported varying levels of contamination by these chemicals in different environmental and biotic matrices including human samples (Ohta et al., 2002; Akutsu et al., 2003; Watanabe et al., 2004; Kajiwara et al., 2004; Ueno et al., 2004; Takasuga et al., 2004; Senthilkumar et al., 2005; Inoue et al., 2006).

1.3.5.2. Hexabromobiphenyl

A survey of this substance in the atmosphere was conducted for the first time in FY2004 with a detection limit of 0.25 pg m^{-3}. The substance was not detected at the single surveyed site.

A survey for hexabromobiphenyl in the surface water was conducted in FY2003. The detection limit was 15 pg L^{-1}. The substance was not detected at any of the four surveyed sites.

A survey of the substance in bottom sediment was conducted in FY2003 with a detection limit of 8700 pg g^{-1}-dry, and the substance was not detected at any of the two surveyed sites.

Hexabromobiphenyl has not been surveyed or monitored in biota in the Environmental Survey and Monitoring of Chemicals Program. There is the first report of PBB detection in cormorants and fish from Japan by Watanabe et al. (2004).

1.3.5.3. PFOS

This was the first survey to investigate PFOS persisting in atmospheric air. The survey was conducted with a detection limit of 0.09 pg m^{-3}, and the substance was detected in 57 of the 60 samples from all the 20 survey sites, with a maximum concentration of 44 pg m^{-3}.

A survey for PFOS in the surface water, which was the first environmental survey/monitoring for the substance in Japan, was conducted in FY2002. The detection limit was 40 ng L^{-1}. The substance was detected at all the surveyed sites (20 sites). Maximum concentration was 24,000 pg L^{-1}.

PFOS has not been surveyed or monitored in the biota and bottom sediment in the Environmental Survey and Monitoring of Chemicals Program.

1.4. Monitoring of dioxins (polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs)

As shown above, dioxins monitoring in various environmental media has been conducted actively in Japan from late 1990s until present together with extensive efforts to make reliable inventories and operate effective regulation to reduce their emission to the environment. The major emission sources were found to be incinerators for both municipal and industrial wastes, thus severe regulation was enforced on the incinerators to reduce total emissions of dioxins. In fact, dioxin levels in the air (Fig. 1.11) have been decreasing significantly during recent years in accordance with the estimated decrease of dioxin emissions inventory (Fig. 1.12).

Dioxin levels in the surface water and ground water have been decreasing steadily but rather slowly compared with levels in air, and their levels in sediments and soil do not seem to have decreased clearly. In general, these tendencies are consistent with the estimated behavior based on their chemical properties.

In addition to the incineration processes, herbicides, CNP (2,4,6-trichlorophenyl-4′-nitrophenyl ether) and PCP (pentachlorophenol) usage was reported as the major source of dioxins, especially during the late 1960s–1970s. While CNP contained particular non-toxic dioxin congeners such as 1,3,6,8-TeCDD and 1,3,7,9-TeCDD (Yamagishi et al.,

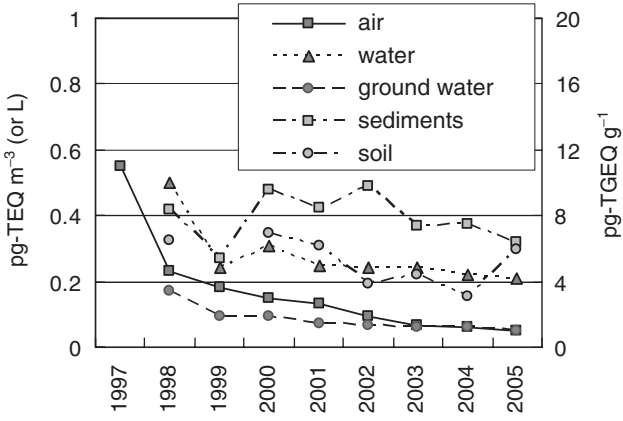

Figure 1.11. Dioxin levels in environmental media. Left axis for air, surface water, ground water; right axis for sediments, soil. Note that the data are sum of PCDDs, PCDFs and dioxin-like PCBs.

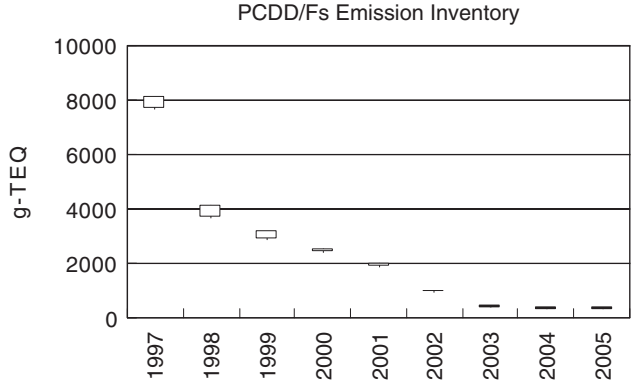

Figure 1.12. Emission inventory of PCDD/Fs in Japan. Each box represents upper and lower estimates of the total emission.

1981), PCP was found to have OCDD/F (Sakurai et al., 1998; Masunaga et al., 2003). Further, studies by Masunaga et al. (2001) indicated the existence of toxic 2,3,7,8-substituted congeners both in CNP and PCP. There are several reports on the time trend of dioxins pollution by analyzing sediment core samples (Yamashita et al., 2000; Kubota et al., 2002; Sakurai et al., 2002; Sakurai, 2003; Okumura et al., 2004). There are also reports concerning the topic by analyzing stored materials, including human samples (Konishi et al., 2001—Fig. 1.13; Choi et al., 2002, 2003).

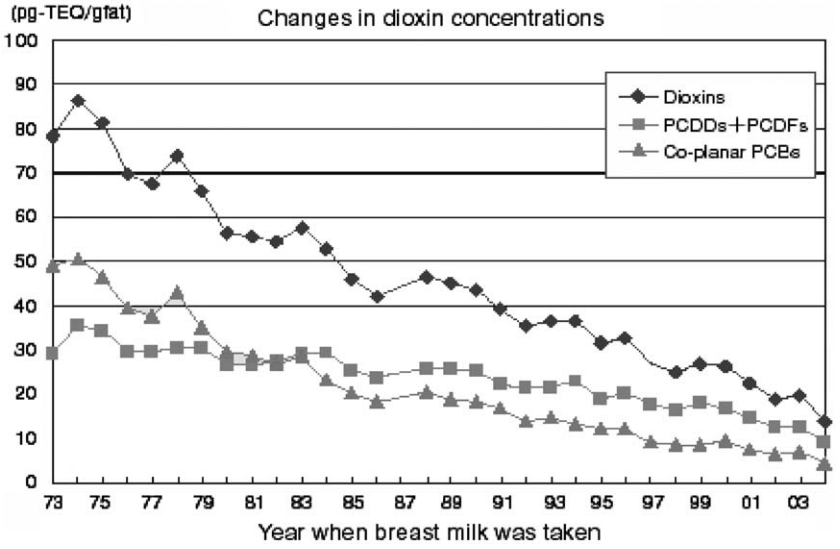

Figure 1.13. Dioxin concentrations in breast milk. Source: FY2004 Health and Labour Science Research Grants "Studies on Dioxins in Breast Milk".

1.5. Stockpiles and wastes of POPs

1.5.1. Development of detoxification methods for agricultural chemicals containing POPs

In Japan, organic chlorine agricultural chemicals including certain POPs (aldrin, dieldrin, endrin, DDT and BHC) are usually stored underground. The result of the investigation on the conditions of stored chemicals published by the Ministry of Agriculture, Forestry and Fisheries in December 2001 shows that the total amount of stored agricultural chemicals and the number of the stored places identified on this investigation was 3680 tons and 174 places, respectively. A field investigation was carried out by MOE in two districts with a view to assessing the actual conditions of the storage by farmers of agricultural chemicals containing POPs, etc., which revealed that approximately 1–2% of farmers had held 2066 kg of agricultural chemicals containing POPs, etc. 97,228 kg of the agricultural chemicals containing dioxins were collected by farmers' cooperation, etc. from 1998 to 2002.

The detoxification methods for agricultural chemicals containing POPs, etc. have been verified and these chemicals are properly disposed of by these methods.

1.5.2. State of PCB waste in storage and disposal under the PCB special measures law

MOE has released the state of PCB waste in storage that has been reported under the PCB Special Measures Law. The data on the storage and disposal status of PCB waste as of March 31, 2003, was submitted from businesses to prefectural and municipal governments.

Compared with the previous report as of March 31, 2002, the amount of PCBs stored has been increasing while the use of PCBs has been decreasing. This trend is due to the progress in gathering information on PCB waste because of the enforcement of reporting under the Law. Besides this, shift from using PCBs to storing them during this period also influenced such a trend.

The government will implement a project to develop wide-area waste disposal facilities nationwide in the pivotal cities of Kitakyushu, Toyota, Tokyo, Osaka and Muroran, as listed below, through the Japan Environmental Safety Corporation (JESCO), and in co-ordination with local public authorities.

Most PCB wastes come from high-voltage transformers and a limited number of other products, and these would require immediate attention.

The project will therefore focus initially on these products. As to smaller waste electrical devices such as stabilizers and other contaminated materials, including carbonless copying paper, which contain only a small amount of PCB, deliberation will be accelerated on the establishment of a treatment system for these materials. At the same time, it is necessary to evaluate new and existing waste disposal technologies, with top priority placed on ensuring safety. The recent advancement of disposal technology for PCB wastes from stabilizers now enables safer treatment of stabilizers. In project sites where large volumes of disused stabilizers are left untreated, an appropriate treatment system will be launched as soon as possible. For other devices and project sites, effort will be strengthened to develop a comprehensive waste disposal system in line with new technologies expected in the future.

In the construction of wide-area waste disposal facilities, JESCO is targeting small- and medium-sized enterprises and other business institutions which can commission JESCO to treat their PCB wastes and in doing so reduce their financial burden. The corporation plans to ensure the minimum treatment capacity for these facilities by having these wastes brought to the facilities in a systematic manner during the treatment period.

Enterprises which hold large volumes of waste PCBs, PCB-containing waste oils and disused pole-mounted transformers that contain PCB-containing insulation oils are building or planning to build treatment facilities on their own. It is essential for the government to assist and encourage their effort. For pole-mounted transformers and insulation oils extracted from these pole-mounted transformers, concerted actions will be taken in line with the efforts of electric power companies which store those PCB wastes.

Tables 1.3–1.5 show the estimated disuse volume, storage volume and disposal volume of wastes generated from disuse of PCB-containing high-voltage transformers and high-voltage condensers, and other large electrical devices during the period up to 2016, when treatment of PCB wastes is to be terminated under the law.

1.5.3. Study for proper disposal of POPs wastes

Stored agricultural chemicals containing the chemicals mentioned above and ashes from incineration plants, etc. containing dioxins must be disposed of appropriately as wastes containing POPs. Wastes containing dioxins are properly disposed under the Dioxins Law and the Waste Management and Public Cleansing Law (Law No. 137 of 1970, hereafter

Table 1.3. High-voltage transformer and other devices

Fiscal year	Disused volume (units)	Disposal volume (units)	Storage volume (units)
Current March–2002	–	–	High-voltage transformer 11,079; high-voltage condenser: 219,106; other devices: 40,744
2002–2008	High-voltage transformer: 1800; high-voltage condenser: 31,200; other devices: 5900	High-voltage transformer: 4400; high-voltage condenser: 83,400; other devices: 15,500	(March 2009); high-voltage transformer: 8500; high-voltage condenser: 166,900; other devices: 31,100
2009–2016	High-voltage transformer: 1600; high-voltage condenser: 26,800; other devices: 5000	High-voltage transformer: 10,100; high-voltage condenser: 193,700; other devices: 36,100	High-voltage transformer: 0; high-voltage condenser: 0; other devices: 0

Note 1: "Disused volume" refers to the amount of wastes generated from electronic devices as they are used during the corresponding period.
Note 2: "Other devices" refers to any of low-voltage transformers, low-voltage condensers, reactors, discharge coils, surge absorbers, meter transformers, switches, breakers and rectifiers that are as large as a high-voltage transformer or high-voltage condenser.
Note 3: Figures are rounded to 100 units except for the current storage volume.

Table 1.4. Waste polychlorinated biphenyl (waste PCBs) and other wastes

Fiscal year	Disused volume (t)	Disposal volume (t)	Storage volume (t)
Current–March 2002	–	–	Waste PCBs: 70; PCB-containing waste oils: 2610
2002–2008	Waste PCBs: 0; PCB-containing waste oils: 0	Waste PCBs: 0; PCB-containing waste oils: 800	(March 2009); waste PCBs: 100; PCB-containing waste oils: 1800
2009–2016	Waste PCBs: 0; PCB-containing waste oils: 0	Waste PCBs: 100; PCB-containing waste oils: 1800	(July 2016); waste PCBs: 0; PCB-containing waste oils: 0

Table 1.5. Pole-mounted transformer

Fiscal year	Disused volume (units)	Disposal volume (units)	Storage volume (units)
Current–March 2002	–	–	Case: 1,863,225; oil equivalent: 178,320 t
2002–2008	Case: 1,072,000; oil equivalent: 61,000 t	Case: 1,228,000; oil equivalent: 143,000 t	(March 2009); Case: 1,702,000; oil equivalent: 95,000 t
2009–2016	Case: 880,000; oil equivalent: 38,000 t	Case: 2,582,000; oil equivalent: 133,000 t	(July 2016); Case:0; oil equivalent: 0

Note: Figures are rounded to 1000 units or 1000 t except for the current storage volume.

referred to as the Waste Management Law). Wastes containing PCB are disposed under the PCB Special Measures Law.

The following are being addressed for other POPs based on the outcomes of the above mentioned development of detoxification methods with a view to understand the actual wastes emissions and formulating their disposal standards.

- Estimation of the existing quantity of unintentionally produced POPs.
- Compilations of technical issues to be considered in respect of methods of collection, transportation and storage of POPs wastes.
- Necessary studies for the development of POPs wastes disposal standard.
- Studying the monitoring method on the maintenance and management of POPs wastes disposal process.

1.6. Conclusion

Brief outlines of POPs monitoring activities in Japan are summarized in this chapter. In Japan, government has been carrying-out extensive environmental monitoring as the basis to plan and conduct environmental management of chemicals. After more than two decades of operation, the monitoring was reorganized recently to use HRGC/HRMS in order to know precisely and accurately the present levels of POPs contamination in Japan. Also the new monitoring method is now being implemented to East Asian countries to conduct regional monitoring of POPs in the background air sampling locations as per the requirement of Stockholm Convention (Expert Working Group, 2006). The government has also

been conducting development of new analytical methods for compounds not yet monitored, including those evaluated as additional chemicals for Stockholm Convention, such as PBDEs and PFOS, and perform exposure assessment of these new chemicals to human. Furthermore, parts of the samples collected for regular environmental monitoring under the framework of "Chemicals in the Environment" were stored in frozen state for future (Environmental Specimen Banking). These activities, together with extensive researches and monitoring in national/local governmental institutes, universities and private sectors, will help the world to keep and improve quality of life by managing these chemicals properly.

REFERENCES

Akutsu, K., Kitagawa, M., Nakazawa, H., Makino, T., Iwazaki, K., Oda, H., Hori, S., 2003. Time-trend (1973–2000) of polybrominated diphenyl ethers in Japanese mother's milk. Chemosphere 53, 645–654.

Choi, J.W., Fujimaki, S., Kitamura, K., Hashimoto, S., Ito, H., Suzuki, N., Sakai, S., Morita, M., 2003. Polybrominated dibenzo-*p*-dioxins, dibenzofurans, and diphenyl ethers in Japanese human adipose tissue. Environ. Sci. Technol. 37, 817–821.

Choi, J.W., Miyabara, Y., Hashimoto, S., Morita, M., 2002. Comparison of PCDD/F and coplanar PCB concentrations in Japanese human adipose tissue collected in 1970–1971, 1994–1996, and 2000. Chemosphere 47, 591–597.

Expert Working Group, 2006. POPs Monitoring Project in East Asian countries, "Background air monitoring of persistent organic pollutants in East Asian countries 2004–2006," Ministry of the Environment, Japan.

Inoue, K., Harada, K., Takenaka, K., Uehara, S., Kono, M., Shimizu, T., Takasuga, T., Senthilkumar, K., Yamashita, F., Koizumi, A., 2006. Levels and concentration ratios of polychlorinated biphenyls and polybrominated diphenyl ethers in serum and breast milk in Japanese mothers. Environ. Health Perspect. 1141, 1179–1185.

Kajiwara, N., Ueno, D., Takahashi, A., Baba, N., Tanabe, S., 2004. Polybrominated diphenyl ethers and organochlorines in archived northern fur seal samples from the Pacific coast of Japan, 1972–1998. Environ. Sci. Technol. 38(14), 3804–3809.

Konishi, Y., Kuwabara, K., Hori, S., 2001. Continuous surveillance of organochlorine compounds in human breast milk from 1972 to 1998 in Osaka, Japan. Arch. Environ. Contam. Toxicol. 40, 571–578.

Kubota, A., Someya, M., Watanabe, M., Tanabe, S., 2002. Contamination status of PCBs (including coplanar congeners), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in sediments from Uwa sea, Japan. Nippon Sui. Gakk. 68, 695–700.

Masunaga, S., Takasuga, T., Nakanishi, J., 2001. Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. Chemosphere 44, 873–885.

Masunaga, S., Yao, Y., Ogura, I., Sakurai, T., Nakanishi, J., 2003. Source and behavior analyses of dioxins based on congener-specific information and their application to Tokyo Bay basin. Chemosphere 53, 315–324.

Ministry of the Environment, Japan, 1996. "Chemicals in the environment," (every year in Japanese; English version available on FY2005~2001, 1998, 1996). English

version: http://www.env.go.jp/chemi/kurohon/en/index.html Japanese version: http://www.env.go.jp/chemi/kurohon/index.html

Ministry of the Environment, Japan, 1998. "Environmental monitoring survey of exogenous endocrine disrupting chemicals" English version: http://www.env.go.jp/en/chemi/ed/eeds/MonitoringSurvey.html (results of 1998 survey).

Ministry of the Environment, Japan, 2000. "Dioxin monitoring in the environment" English version: http://www.env.go.jp/en/chemi/dioxins/survey2000.html (monitoring data on 2000), Japanese version: http://www.env.go.jp/chemi/dioxin/report.html

Ministry of the Environment, Japan, 2002. "Marine environment monitoring" English version: http://www.env.go.jp/en/press/2004/0906a.html (report of FY2002), Japanese version: http://www.env.go.jp/earth/kaiyo/monitoring.html

Ministry of the Environment, Japan, 2004. "Dioxin emission inventory" English version: http://www.env.go.jp/en/press/2005/1125a.html (inventory in 2004), Japanese version: http://www.env.go.jp/chemi/dioxin/report.html

Ohta, S., Ishizuka, D., Nishimura, H., Nakao, T., Aozasa, O., Shimidzu, Y., et al., 2002. Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. Chemosphere 46, 689–696.

Okumura, Y., Yamashita, Y., Kohno, Y., Nagasaka, H., 2004. Trends of PCDD/Fs and co-PCBs in a sediment core collected in Sendai Bay, Japan. Water Res. 38, 3511–3522.

Qui, X.H., Zhu, T., Jing, L., Pan, H.S., Li, Q.L., Miao, G.F., Gong, J.C., 2004. Organochlorine pesticides in the air around the Taihu Lake, China. Environ. Sci. Technol. 38, 1368–1374.

Qui, X.H., Zhu, T., Yao, B., Hu, J.X., Hu, S.W., 2005. Contribution of dicofol to the current DDT pollution in China. Environ. Sci. Technol. 39, 4385–4390.

Sakurai, T., 2003. Dioxins in aquatic sediment and soil in the Kanto region of Japan: Major sources and their contributions. Environ. Sci. Technol. 37, 3133–3140.

Sakurai, T., Suzuki, N., Masunaga, S., Nakanishi, J., 1998. Origin attribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment and soil from a Japanese freshwater lake area through congener-specific data analysis. Chemosphere 37, 2211–2224.

Sakurai, T., Suzuki, N., Morita, M., 2002. Examination of dioxin fluxes recorded in dated aquatic-sediment cores in the Kanto region of Japan using multivariate data analysis. Chemosphere 46, 1359–1365.

Senthilkumar, K., Takasuga, T., Ishizuka, M., Tanikawa, T., Fujita, S., 2005. Contamination profiles of UNEP POP'S and PBDEs in brown rat collected from urban and rural regions of Japan. Organohalogen Compd. 67, 615–618.

Takasuga, T., Senthilkumar, K., Takemori, H., Ohi, E., Tsuji, H., Nagayama, J., 2004. Impact of fermented brown rice with *Aspergillus oryzae* (FEBRA) intake and concentrations of polybrominated diphenylethers (PBDEs) in blood of humans from Japan. Chemosphere 57, 795–811.

Ueno, D., Kajiwara, N., Tanaka, H., Subramanian, A., Fillmann, G., Lam, P.K.S., Zheng, G.J., Muchitar, M., Razak, H., Prudente, M., Chung, K.H., Tanabe, S., 2004. Global pollution monitoring of polybrominated diphenyl ethers using skipjack tuna as a bioindicator. Environ. Sci. Technol. 38(8), 2312–2316.

Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of volatile organochlorine compounds in polar regions. Ambio 22, 10–18.

Watanabe, K., Senthilkumar, K., Masunaga, S., Takasuga, T., Iseki, N., Morita, M., 2004. Brominated organic contaminants in the liver and egg of the common cormorants (Phalacrocoraxcarbo) from Japan. Environ. Sci. Technol. 38, 4071–4077.

Yamagishi, T., Miyazaki, T., Akiyama, K., Morita, M., 1981. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in commercial diphenyl ether herbicides, and in freshwater fish collected from the application area. Chemosphere 10, 1137–1144.

Yamashita, N., Kannan, K., Imagawa, T., Villeneuve, D.L., Hashimoto, S., Miyazaki, A., Giesy, J.P., 2000. Vertical profile of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons, and alkylphenols in a sediment core from Tokyo Bay, Japan. Environ. Sci. Technol. 34, 3560–3567.