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REGIONAL OVERVIEW of PTS and POPs issues of ecological concern in the NOWPAP region



POMRAC Technical Report No. 9

*Northwest Pacific Action Plan (NOWPAP)
Pollution Monitoring Regional Activity Center
(POMRAC)*

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concern in the NOWPAP region”**

Vladivostok 2014

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Executive Summary

The overall goal of this regional overview is to provide NOWPAP member countries with a synthesis report on a group of chemicals with potential adverse effects to the environment, i.e. persistent toxic substances (PTS). The report covers their sources, transport, environmental levels, potential health risks to humans and environment, management and research activities as well as the gaps on available information and management systems. Particular emphasis has been paid in the possible ecotoxicological effects of PTS in the marine environment of the region. The report is intended to be a scientific basis for protecting the regional environment and the human health from the adverse effects of PTS, and is expected to be useful for wisely using, developing and managing coastal and marine environment, and obtaining the utmost long-term benefits for the humans of the region.

NOWPAP region consists of semi-enclosed marginal seas, which play indispensable role for the surrounding countries by providing food and mineral resources, marine leisure and transport. Warm current flowing into the central NOWPAP area affects the climate in the region together with the dominant air flow controlled by east-bound jet stream and seasonal heat exchange between continent and ocean, i.e. Asian monsoon. Both flows also transport PTS in the region. Huge human population lives in the region and the surrounding areas, and extensive industrial and agricultural activities have been conducted to support their life. Thus there have been large demands and production/use of PTS as well as their unintentional sources, and therefore proper management of PTS in the region has high priority.

PTS may be categorized as follows: 1) agricultural chemicals and other biocidal, pharmaceutical chemicals, such as DDT, chlordane, etc., which have been developed and used to utilize their potential toxicities to control pests, weeds, etc.; 2) industrial chemicals such as PCBs, PBDEs, PFCs, etc., which have been used as stable, durable chemicals but are found to be unexpectedly toxic to wildlife/human beings, and 3) unintentional by-products, such as dioxins and PAHs, which are unintentionally produced toxic chemicals during production of other chemicals or combustion processes such as waste incineration and steel industry. The long range transport potential of PTS is primarily dependent on their physicochemical properties, i.e. some chemicals like HCB and PFOS are transported through air or seawater in truly global scale while others, such as dioxins, are primarily adsorbed on particles and thus transported shorter distances at a time. Some part of them is transported by migrating wildlife and industrial activities (international trade of PTS-containing products and wastes). Particularly the latter process has been causing a so-called e-waste problem, i.e. severe local pollution by some of PTS in the wastes of electric products or unintentionally produced chemicals through the recovery of valuable materials from the wastes. NOWPAP region and surrounding areas are now becoming major factories of advanced products and chemicals for global market, and many emerging chemicals are produced/used.

In accordance with the massive production/use of PTS as well as part of implementation activity of the Stockholm Convention or other related international regulations, fairly extensive environmental survey data as well as collection of emission inventory information on PTS have been conducted in the NOWPAP region. Summary

of the related information is compiled in the present report. Although information on the temporal trends of PTS is rather limited, data reported in Japan clearly showed general decrease of major POPs, including dioxins, in the last decades. On the other hand, some of emerging PTS, including brominated flame retardants and fluorosurfactants, are shown to be produced in the region until recently or even now, and their environmental levels and trends need to be clarified. There still remain many gaps in long-term environmental monitoring activities, PTS concentration and emission inventory information, and further efforts are needed in the region in harmonized and continuous manner. Also further synthesizing activities are needed for ecotoxicological studies in the region as each country has been conducting studies related to different aspects of the toxicity, i.e. induction of xenobiotic-metabolizing enzymes, analysis of PEC/PNEC relationship, accumulation of PTS in top predators, and analysis of imposex or other specific toxic effects to sensitive organisms.

In many countries, chemical management framework for at least some of PTS has been established in internationally harmonized manner. However there is large difference in the framework of regular environmental monitoring. In Japan, environmental monitoring of PTS has been being conducted for nearly four decades as indispensable part of sound chemical management system, and official or standard sampling/analytical procedures as well as quality assurance and quality control (QA/QC) protocols have been developed. Furthermore, part of the monitoring samples during the whole period have been archived in the environmental specimen bank for enabling future retrospective analysis of newly emerged pollutants to reveal their time trends. The Japanese experience may be useful for other countries for better management of PTS.

In conclusion, establishment of sound chemical management system, particularly on PTS, is important and urgent in the NOWPAP region, where significant amount of chemicals, including PTS are flowing into the semi-enclosed marginal seas through air and water. Environmental monitoring is indispensable as a primary tool to reveal the temporal and spatial trends of PTS, to identify their sources and hot-spots, and to assess effectiveness of regulations. Establishment of regional monitoring network and related activities in harmonized manner, but also considering specific needs and status of each country, is a crucial step. Environmental chemodynamic models of PTS are needed to assess environmental/ecological risks, to predict future status, and to design better management system. Information collection on inventory of PTS emissions to the environment as well as detailed monitoring data are critical for proper design, improvement and use of models. Toxicological/ecotoxicological data on PTS is also needed to assess their risks properly, and collection and sharing relevant information in the NOWPAP region will support better PTS management. Proper assessment of risks of simultaneous and long-term exposure to various chemicals, including PTS, for the wildlife and human beings is a real challenge in the NOWPAP region as well as in the world, and long-term strategy and scientific research to tackle these issues will be needed.

This review has been prepared by Professor Yasuyuki SHIBATA (NIES, Japan) – well known specialist in PTS and POPs fields. Without his generous and extremely high skilled work this overview could never been completed. The contribution and data from the national experts – Dr. Yibing LV (CNEMC, China), Dr. Hyobang MOON (Hanyang University, Korea), Dr. Olga LUKYANOVA (TINRO-Center, Russia) – were also invaluable and vital. The final edition was carried out by Dr. Vladimir SHULKIN (PGI, FEBRAS, Russia) based on the kind and constructive comments of NOWPAP RCU, other NOWPAP RACs, national experts and NOWPAP Focal Points.

Introduction

1.1. Goals and objectives of the Overview

The overall goal of this regional overview is to provide NOWPAP member countries with a synthesis report covering sources, transport, environmental levels, potential risks to human health and environment, management and research activities as well as the gaps in available information and management system on a group of chemicals with potential adverse effects to the environment, i.e. persistent toxic substances (PTS). The report is intended to be a scientific basis for protecting the regional environment and the human health from the adverse effects of PTS, and is expected to be useful for wisely using, developing and managing coastal and marine environment, and obtaining their utmost long-term benefits for the human populations of the region.

Chemicals having persistency, bioaccumulative properties and toxicities, such as PCBs, DDT and dioxins, sometimes called PTS, POPs (persistent organic pollutants) or PBT (persistent and bioaccumulative toxic substances), have been of major environmental concern for decades, particularly after the publication of epoch-making “Silent Spring” by Rachel Carson in 1962. Since then, extensive research on PTS has been conducted and revealed ubiquitous presence of PTS in the global environment, particularly in top predators. At its 18th meeting in 1995, Governing Council of United Nations Environment Programme (UNEP) adopted the decision 18/32 “Persistent Organic Pollutants (POPs)”, under which development of recommendations and information on international action, including such information as would be needed for a possible decision regarding an appropriate international legal mechanism on POPs, had started (UNEP, 1995). Then at 19th meeting in 1997, the UNEP Governing Council concluded that international action, including a global legally binding instrument, was required to reduce the risks to human health and the environment arising from the release of POPs (UNEP, 1997). Based on this decision, Intergovernmental Negotiating Committees started in 1998 to prepare an international legally binding instrument for implementing international action, and the Stockholm Convention on Persistent Organic Pollutants was adopted at the Conference of Plenipotentiaries held at Stockholm in May 2001 (Stockholm Convention, 2001).

At around the same time, the Global Environment Facility (GEF) funded activity to compile information and identify information/capacity gaps related to PTS pollution in the regional and global scale was conducted (GEF/UNEP, 2003). Many of PTS are subject to atmospheric, aquatic or biological transport over long distances and are globally distributed and detectable even in areas where they have never been used. The lipophilic character of these substances causes them to be incorporated and accumulated in the tissues of living organisms leading to body burdens that pose potential risks of adverse health effects. Toxic chemicals, which are less persistent but for which there are continuous releases resulting in essentially persistent exposure of biota, raise similar concerns. The persistence and bioaccumulation of PTS may also result in increase over time of concentrations at higher trophic levels, including humans. POPs under the

Stockholm Convention are considered as a sub-group of PTS with high long-range transport potential.

Under the GEF program, 28 chemicals or chemical groups were nominated as PTS, including twelve original POPs, other organohalogen chemicals such as organochlorine pesticides, organobromine flame retardants and organofluorine surfactants, polycyclic aromatic hydrocarbons, organometals, and endocrine disruptive chemicals such as phthalate esters and alkyl phenols. In addition to twelve original POPs, pentachlorobenzene and 9 chemicals in PTS list, i.e., α -, β - and γ -hexachlorocyclohexane, chlordecone, hexabromobiphenyl, tetra/penta-brominated diphenyl ethers, hexa/hepta-brominated diphenyl ethers, perfluorooctane sulfonate, and endosulfan have been added to the list of POPs under the Convention while five other chemicals including two in PTS list, i.e. pentachlorophenol and short-chain chlorinated paraffins, are under review as of December, 2012. Except for organometals and PAHs, majority of chemicals listed in PTS programme are now decided to be added to the POPs list, which now covers 23 chemicals as of May 2013 after the COP-6, expanding nearly twice the original number during only 9 years after the entry into force of the Stockholm Convention.

The Northwest Pacific region comprises semi-enclosed marginal seas situated in both the sub-polar and temperate zones. It has spectacular marine life and commercially important fishing and mariculture grounds and rich offshore mineral resources such as oil. Coastal development, industry, transport, oil production and activities such as land reclamation and intensive mariculture take an ever-greater toll on coastal ecosystems. Chemical and industrial wastes, untreated municipal sewage, agricultural pesticides and nutrients in run-off cause widespread damage and stimulate eutrophication and harmful algal blooms. Added to these are pollution from land, accidental oil spills, atmospheric pollution and marine and coastal litter.

It is of particular importance to survey information on the priority chemicals of concern in the NOWPAP region at this moment, in order to respond to the rapid growth of the list of chemicals to be banned/regulated under the national/international activities, including Stockholm Convention, and to establish sound management of chemicals in the region in order to protect the regional marine environment and human health from their adverse effects. The list of chemicals to be surveyed is nominated by the experts from the countries in the NOWPAP region, and the relevant information on their production, ecotoxicological effects, the environmental levels and transport, management systems, research activities and regulatory frameworks as well as gaps to be filled is compiled in this report in order to support member countries of the NOWPAP to take further appropriate action on PTS.

1.2. General background information on NOWPAP

The Northwest Pacific Action Plan and three supporting resolutions including five priority projects were adopted in 1994. NOWPAP member countries established four Regional Activity Centres (RACs) in 2000-2002. From 1994 to 2004, UNEP Regional Seas Coordinating Office acted as Interim Secretariat for NOWPAP. NOWPAP

Regional Coordinating Unit (RCU) established by member countries and co-hosted by Japan and the Republic of Korea, is facilitating the implementation of the Action Plan. The two RCU offices were inaugurated in November 2004 and started operations in January 2005. The NOWPAP Regional Oil Spill Contingency Plan was adopted in 2003. The Memorandum of Understanding on Regional Cooperation regarding Preparedness and Response to Oil Spills in the Marine Environment of the Northwest Pacific Region was signed in 2004/2005. NOWPAP Regional Action Plan on Marine Litter was adopted in 2007.

In order to support the implementation of the priority project activities of the NOWPAP region, a network of Regional Activity Centres (RACs) was established:

- CEARAC, Toyama, Japan (cearac.nowpap.org) - the Special Monitoring and Coastal Environment Assessment RAC;
- DINRAC, Beijing, People's Republic of China (dinrac.nowpap.org) - the Data and Information Network RAC;
- MERRAC, Daejeon, Republic of Korea (merrac.nowpap.org) - the Marine Environmental Emergency Preparedness and Response RAC; and
- POMRAC, Vladivostok, Russian Federation (pomrac.nowpap.org) - the Pollution Monitoring RAC.

These centres are responsible for carrying out activities at the regional level and serve all member states.

1.3. Geographical scope of NOWPAP area related to this Overview

The geographical scope of NOWPAP covers the marine environment and coastal zones from about 121 to 143 E and from approximately 33 to 52 N, without prejudice to the sovereign right of any state, and includes Japan, the People's Republic of China, the Republic of Korea and the Russian Federation. Among 1,637.92 million peoples in the four countries, 356.27 millions are reported to live in the region, including 33.67 million from Japan, 272.60 million from P.R. China, 48.4 million from the Korean Peninsula and 1.60 million from the Russian Far East (POMRAC Technical Report No.3, 2007).

The region is located along the eastern edge of the Eurasian continent and spans from sub-tropical (south) to sub-polar (north) climate. Biogeographically the region belongs to East Palearctic region with major terrestrial vegetation of (from south to north) summer-green broadleaved forests, temperate hardwood-conifer, and boreal forests (or Taiga) as well as marine ecosystems covering from coral reefs to cold and deep-water ecosystem.

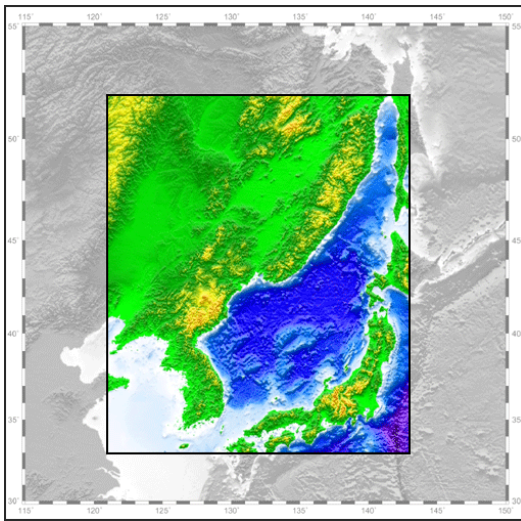


Figure 1-1 NOWPAP region

In the global atmospheric circulation, the region is under Ferrel circulation and affected by the westerlies, particularly by polar jet stream in winter. The climate of the region is governed primarily by the heat exchange between the Eurasian continent and the Pacific Ocean. During summer, a strong high pressure area (or anticyclone) is developed in Pacific and send out hot and humid air, which provide major precipitation to the southern part of NOWPAP region. In winter, on the other hand, cold and dry air is sent from the high pressure area at Siberia to the ocean. The air obtains humidity from the warm current flowing through the central NOWPAP and provides large precipitation as snow falls to the north-western part of Japan. The anticyclone at Siberia also pushes polar jet stream down to around 40 degrees north in winter, and this, together with subtropical jet stream at the polar limit of tropical Hadley cell, governs the east-bound movement of air mass in the region. The south-western part of the region is affected by Asian monsoon with rainy seasons in early summer and early autumn, and also by the occasional Typhoons during summer and early autumn season.

The region is separated in an outer area and an inner area by the archipelagic arches including Japan. The inner includes several seas known as the Asian Inland Seas (or marginal seas). These seas include a number of local current patterns as well as local influences like the large rivers and the monsoon cycle. The region is influenced by the warm Kuroshio and the cold Oyashio current systems, both of which constitute part of great ocean current system in the North Pacific. Oyashio current is particularly rich in nutrients. The front of these current systems meets off pacific coast of North-east Japan and induces one of the most productive marine areas in the world from the eastern edge of the NOWPAP region towards the central North Pacific. The main stream of Kuroshio Current flows in the Philippine Sea along the southern coastline of Japan. Its branch, Tsushima current, is flowing east/north east bound along the southern side of the central part of NOWPAP sea area while the cold Liman current flows in the northern side along the Eurasian continent to the south west direction. Tsushima current passes between Japan (Kyushu island) and Korean peninsula with a volume transport of 2.65 Sv (Sv (Sverdrup) = 10^6 m³/sec) in average, and flows partly through Tsugaru Strait to the North Pacific and partly between Hokkaido and Sakhalin (or La Perouse / Soya Strait)

to the sea of Okhotsk. Liman current, on the other hand, is thought to be mainly composed of cooled Tsushima current water and river water of Amur coming through Tatarskiy Strait.

There are tides of various patterns along the coasts. Higher amplitude areas are located in western part of the region where tidal amplitude reaches 6 - 7 m in western Kyushu, Japan, and more than 10 - 12 m in some areas of Korea. Muddy tidal flats are developed along the coastlines in higher amplitude areas. On the other hand, those around the central NOWPAP region generally show much smaller tidal amplitudes in both daily and seasonal variations. Strong wind and rough wave, especially in northern part of the central NOWPAP in winter season, affects land shape of the coastal zone strongly, particularly in sand and / or pebble beaches, and the areas are known to have large seasonal erosion / deposition process. This physical process as well as organic contents of the coastal sediments affects the behavior of PTS chemicals strongly; i.e., sediments with high organic content and limited physical movement tend to absorb PTS and may play as a secondary emission source of PTS for long term.

The inner seas and the outer seas are separated from the open ocean by quite shallow passes and straits (a few hundred meters in depth). Off the archipelagic arch, the sea bed is very steep and reaches great depths (e.g. 9,600 m off Japan). The continental shelf is wide in the western part of NOWPAP, which overlaps with high amplitude tidal areas, whilst on the oceanic side there is almost no continental shelf. The archipelagic arch is one of the most intensive volcanic and seismic activity regions in the world.

In a particularly cold winter, surface sea water in the northern part near Vladivostok becomes dense enough to start sinking into the bottom of the ocean to make a unique water body (bottom water or proper water) (Kumamoto et al., 2008; Aramaki et al., 2013). This process provides oxygen to the bottom water. Pollutants are also transported vertically either by the process or as sediments (fecal pellets etc.). There are several reports suggesting / indicating the slowing down of the production rate of the bottom water in the central NOWPAP region in recent decades; for example, dissolved oxygen levels in bottom water was reported to be decreasing in recent decades by potentially reflecting the global climate change (global warming) (Gamo, 1999). This process may affect the ecosystem of the central NOWPAP region as well as PTS cycling.

The coastal environment is influenced by rivers. Some of the largest rivers in the world are present in the surrounding areas; for example, Yangtze River and Amur River with drainage areas of 1,808,500 and 1,840,000 km², respectively. In China alone there are more than 150 rivers covering a drainage area over 10,000,000 km². In Japan there are many rivers with rather short and small drainage areas; among the largest river is the Shinano River, 367 km in length with drainage areas of 11,900 km², the Tone River with 322 km and 16,840 km², and the Ishikari River with 268 km and 14,330 km².

Major river systems supplying terrestrial water to the water body in / around the region include; Shinano (15 km³/a), Agano (13 km³/a), Mogami (12 km³/a), Omono

(8.7 km³/a), Ishikari (4.7 km³/a), Teshio (4.4 km³/a), Kitakami (12 km³/a), and Tone (8.0 km³/a) rivers in Japan (data from Ministry of Land, Infrastructure etc. Japan, 2000), Songhua (76.2 km³/a), Liaohe (14.8 km³/a), Haihe (22.8 km³/a), Yellow (65.8 km³/a), Huaihe (62.2 km³/a) and Yangtze (Changjiang) (953.1 or 924 km³/a) (POMRAC Technical Report No.2, 2006, Tian et al., 1993) Rivers located in/around the region in China, and Nakdong (131 km³/a), Han (189 km³/a), Geum (66 km³/a), and Seomjin (39 km³/a) Rivers in Korea (POMRAC Technical Report No.2, 2006). The main rivers in Russian are the Tumannaya (Tumen) (9 km³/a), Razdolnaya (Suifun) (2.3 km³/a), Samarga (2.6 km³/a), Koppi (2.2 km³/a) and Tumnin (7.9 km³/a) Rivers with a total annual input about 27 km³. Total annual input of all rivers in the Russian part of the NOWPAP was about 43 km³ (POMRAC Technical Report No.2, 2006). Amur River (310 km³/a) in Russia may affect the region partly through the Tatarskiy strait.

Far Eastern regions of Russia adjoining NOWPAP region are Primorsky Krai, south part of Khabarovskiy Krai, and the Sakhalin Island. Overall length of the Russian part of NOWPAP regional sea is about 6,230 km of shoreline. The total catchment area is about 142,000 km². About 80% of Primorsky Krai and the adjoining part of Khabarovskiy Krai are occupied by the mountain ridges belonging to the Sikhote Alin mountain system. Average elevation is 600 meters, with the highest peaks reaching 1,855 meters. Southwestern Sakhalin Island has low mountains and hills. Almost 80% of the territory is covered by forest and an additional 8.1% is occupied by wildlife reserves.

Cold dry winters and moderate warm humid summers are typical for the Primorsky Krai – Russian mainland part. There is clear shift of air temperature decrease in winter and increase in summer in moving away from the coast to the west even for the distance 30-50 km. The average temperature in coastal zone is – 10-12°C in winter, and +16°C in summer. Annual precipitation decreases from about 800 mm at the sea coast to 650 mm near the Khanka Lake 200 km away the sea. 80-95% of annual precipitation comes in the April to October period, and major part of river runoff takes place in summer.

The highest industrial and transport activity in the Russian area of NOWPAP region is located on the southern coast of Primorsky Krai, around Peter the Great Bay. This Bay is located in the northern-western part of the central NOWPAP region. Major city-ports Vladivostok and Nakhodka are located on the Bay's shore. The Bay is very important area for fishing, mariculture, shipping and recreation. Density of population along Bay's coastline is the highest in the Far Eastern Federal district.

The overview of PTS and POPs focus on the pollution situations about Heilongjiang, Liaoning, Jilin, Shandong and Jiangsu provinces, but literatures about other regions of China also included to provide more information. Among the five provinces, the climates in Jiangshu and Shangdong are warm temperate zone and semi-humid continent monsoon climate and have four sharp seasons. Jiangsu is often affected by typhoons. The annual precipitation in Jiangsu province is about 1000 mm and 550 - 950 mm in Shandong province. The other three provinces belong to temperate continental monsoon climate with more drought and cloudy days in spring and hot and

rainy days in summer. The winter days in these three provinces last longer than in other provinces. Of the three provinces, annual precipitation of Liaoning province is 600-1100mm. The major parts of Jiangsu province, Shandong province and Liaoning province are hilly and plain regions, while mountainous regions cover a big proportion in the other two provinces. Besides, water area of Jiangsu province is quite large with 17% of the area of the whole province. The vegetation coverage rate of Liaoning province, Heilongjiang province and Jilin province is 28.7% , 41.9% and 42.4% respectively; but on the contrary, for other two provinces vegetation coverage is much lower, 21.5% in Shandong province and 10.56% in Jiangsu province. Among the five target provinces, Heilongjiang and Liaoning provinces have 84 natural conservation areas covering 2.3 million hectares and occupying 5.05% area of province territory and 81 natural conservation areas covering 2.848 million hectares occupying 9.7% area of the province territory respectively. In Shandong Province, there are 66 natural conservation areas covering about 6% area of whole province, while Jiangsu and Jilin provinces only have 26 and 27 natural conservation areas covering 0.738 million hectares and 1.846 million hectares respectively (POMRAC Technical Report No.3, 2007)

The Korean Peninsula is located in the northeastern part of Asia, which lies between 33.1°N and 43.1°N parallels, 124.1°E and 132.1°E meridians bordered on the north by China and Russia. South Korea is about 1100 km long and 300 km wide with total land area of 222,000 km². The geomorphology of South Korea is characterized by mountains and hills. Such hilly terrain, while occurring mostly in the eastern part of the Korean peninsula accounts for about 70% of its territory. More than 3200 islands are scattered along or near the southern and southwestern coastlines. Due to the many islands that make up parts of Korea, the coastal length of the islands (~8600 km) is almost equal to that of main peninsula (~8700 km). Most of the rivers flow into the western and southern sides after draining the western and southern slopes of the peninsula. POPs study as well as other regular monitoring programs have covered the eastern islands and the southern Jeju Island.

The climate of South Korea is temperate monsoon, in general, but geographically and seasonally varied. The western coast open to continental Asia is vulnerable to the influence of the winter monsoon. In contrast, the eastern coast is sheltered from the winter monsoon by the Taebaeksan range, the backbone mountain of the Korean Peninsula. Winter is dry and cold and is influenced primarily by the Siberian air mass. Summer is hot and humid with temperatures ranging from 23 to 35°C. The climate is the result of the maritime Pacific high-pressure ridge. Temperatures in all seasons are somewhat less than those that occur at corresponding latitudes in other continents, such as North America or Western Europe. Annual precipitation is about 1500 mm in the central region. More than half of the total rainfall is concentrated in summer, while precipitation of winter is less than 10% of the total.

South Korea, the southern half of the Korean Peninsula, is composed of Seoul, seven major cities, and nine provinces with a total population of ca. 48 million (2005 Census). Seoul, the capital city of South Korea, is densely populated (11 million), accounting for about a quarter to the total population in South Korea. Other seven major

cities with population of greater than 1 million are Busan, Daegu, Incheon, Gwangju, Daejeon, Ulsan, and Suwon. Since the early 1960s, South Korea has achieved a rapid economic growth, which has been termed the ‘Miracle on the Han River’. Recently, the size of the economy of South Korea has grown up to be the 10th largest in the world, and the 3rd largest in Asia, next only to China and Japan.

Substantial urbanization has followed economic growth. South Korea is one of the countries where available area per capita is the least in the world (population density of South Korea is 473 km⁻²). Further, the concentration of population density and industries within its urban regions (viz. Seoul and seven major cities) has reached serious proportions, accounting for approximately 50% of the total population in only 5.5% of the land area and approximately 55% of the manufacturing industries in only 11.8% of the land area. In recent years, the government has sought to minimize the urbanization in the capital region, but the trend of urbanization continues to increase. Urbanization rate, the ratio of population in urban area to total population, has increased dramatically, from 28.3% in 1960 to 82% in 2012. This implies that pollution is likely to be localized in urban and industrial areas. Furthermore, urbanization means a significant increase in the surfaces without vegetation such as asphalt and building cover. Surface conditions could substantially influence the residence time and fate of POPs and related compounds in a system. Agricultural activities, of which the dominant activity is rice cultivation, occur primarily in the western and southern areas of the South Korean peninsula. Thus, the water quality of the inland rivers is associated with organo-chloride pesticides use history and agricultural products contamination in South Korea.

Heavy industrialization together with urbanization brought by rapid economic growth has resulted in serious environmental problems in some areas. Now, more than 570 Industrial Complexes (ICs) (30 national ICs, more than 210 regional ICs, and more than 330 agricultural ICs) are in operation nationwide. Majority of large scale ICs are located near large coastal cities such as Incheon, Busan, Ulsan, Masan, and Pohang. Since many of the ICs are situated near the big cities, large amounts of industrial wastes together with municipal wastes from inland areas are discharged into the coastal regions. Organic contaminants could also be transported into nearby coastal areas by rivers and/or streams. Thus, greater environmental pollution with the POPs and related contaminants would be expected to occur along the coastal areas of highly industrialized regions.

The development-oriented coastal utilization has resulted in deterioration of marine ecosystem, loss of tidal mudflats, large-scale and long-lasting red-tides in South Korea, which have emerged as major coastal environmental issues since 1990s. Because the coastal areas of semi-enclosed bays in South Korea have been targets of the land-based developmental activities such as industrial complexes construction, city development, and coastal reclamation, pollutants discharged without proper treatment and consideration of environmental carrying capacity of the bays have caused anoxia in water column, red-tides and degradation of coastal water quality. Representative contaminated bays with these environmental problems are Yeongil Bay, Jinhae Bay, Masan Bay, Ulsan Bay, Onsan Bay, and Busan Bay, which are located at the

southeastern coastal regions. These bays have been suffered from the intensive industrial and shipping activities for over 30 years.

The development such as reclamation of coastal environment for industrial and agricultural purposes has destroyed many useful and productive functions in Korean coastal waters. Representative site is Lake Shihwa, which is located at west coast of South Korea. Overall, atmospheric deposition and direct and indirect (e.g. soil runoff) discharges from industrial activities are primary distribution pathways of persistent toxic substances (PTS) into marine and coastal ecosystems. In South Korea, a variety of air pollution reduction measures, including the use of clean fuels, expanded supply of low sulfur fuels, and introduction of low-emission vehicles, have improved air quality in those cities gradually. In spite of the wider use of clean fuels and more strict emission standards, concentrations of particulate matter in the atmosphere have been rising due to increase in vehicle gas emission and Asian dust event. Most of wastewater treatment plants (WWTPs) are directly emitting effluents to major rivers and/or coastal zones in Korea. In recent years, the PTS and persistent organic pollutants (POPs) have been of great concern in coastal regions of Korea. Under the Stockholm Convention, the Korean government has performed the POPs monitoring for multimedia such as air, water, soil, sediment and biota from terrestrial and coastal regions. This report aims to investigate the contamination status and trends of PTS and POPs in South Korea and to assess their ecological effect in marine and coastal waters based on nationwide monitoring program of South Korea.

Japan arch separates central NOWPAP region from Okhotsk, Philippines and Pacific oceans. Majority of Japan with 377,914 km² land area and 126.5 millions population is within NOWPAP region, though nearly three quarters of population live facing to the Pacific or Philippines Sea rather than the central NOWPAP area. Japan is composed of more than 6,800 islands, with five major islands (Hokkaido, Honshu, Shikoku, Kyushu and Okinawa) on which almost all people live. 61% of the land area is categorized as mountains (with altitude more than 300 m), and majority of population lives in alluvial plains developed along the downstream of rivers nearby the coast. Many of the rivers are rather short with steep gradient. Annual precipitation is 1,718 mm in average, c.a. twice of the world average, with considerable local and seasonal variations. Precipitation is generally higher in rainy season (Baiu) in early Summer (June to July) in many places except Hokkaido where Baiu is not present. On the other hand, another higher precipitation is seen in Typhoon season (Autumn) in the southern – middle part of Japan, while precipitation as snow falls are rather evident in winter season in north-western to northern Japan along the central NOWPAP region. The climate of Japan includes sub-tropical, temperate and sub-polar, and average monthly temperatures span from 16.6 ~ 28.5 °C in Naha, Okinawa to -3.6 ~ 22.3 °C in Sapporo, Hokkaido. It was reported that the average temperature in Japan has been increasing 1.15 °C in the last 100 years.

Among the top 20 large cities with total population of 35.6 millions, only 4, i.e., Sapporo (No.5, 1.9 millions), Fukuoka (No.8; 1.5 millions), Kitakyushu (No.14, 0.97 millions) and Niigata (No.16, 0.81 millions), are faced to central NOWPAP while the rests are to Pacific or Philippines oceans. As a consequence, impact of industrial

activities tends to be generally stronger along Pacific/Philippines Sea than along central NOWPAP region. Agriculture and stock farming, both of which need large field, are rather active in the region along the central NOWPAP. For example, top three of the rice production prefectures, i.e., Niigata, Hokkaido and Akita, face to the area. Total coastline of Japan is reported to be 33,889 km with many different landscapes with rich species variations from tropical to sub arctic. Coastal environment plays a fundamental role as a nursery to keep diversity of marine ecosystems, and has been supporting human activities such as fisheries, aquacultures and marine leisure. At present no oil/coal production nor other mining activities are conducted in the area. Transportation of raw materials, fuels and products by ships, on the other hand, is another important aspect to support human society and economic activity, and large industrial plant complexes, ports and power stations as well as large petroleum reserves have been constructed along the coastlines. All the 15 large scale petroleum processing plants have been constructed along the coastlines of bays faced to Philippines Sea or Seto Inland Sea. There are many small-sized complexes or individual factories located in each prefecture, mainly along the coastline, including those in the central NOWPAP. Among 17 nuclear power plant stations, 9 are faced to central NOWPAP. On the other hand, large part of oil/coal power plants are located nearby densely populated areas, such as Tokyo, Osaka and Nagoya, along the Pacific/Philippines Sea sides. Ministry of Land, Infrastructure, Transport and Tourism Japan recently reorganized Japanese ports system and identified 23 specially designated major ports to play as a hub in the international trades. Among the 23 ports, 5, i.e., Niigata, Fushiki-Toyama, Fukuoka, Kitakyushu and Shimonoseki, are faced to or nearby the central NOWPAP region and are supporting large scale transport of raw materials as well as variety of industrial / agricultural products between the countries.

2. General characteristics of PTS

The term PTS (Persistent Toxic Substances) represents the chemical substances with persistent and toxic properties. The synonyms with similar meanings include POPs (Persistent Organic Pollutants) and PBT (Persistent, Bioaccumulative and Toxic substances).

The term POPs has been used under the Stockholm Convention, and also under the Aarhus Protocol on Persistent Organic Pollutants in United Nations Economic Commission for Europe (UN ECE). POPs possess toxic properties, resist degradation, tend to be bioaccumulated, and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they are accumulated in terrestrial and aquatic ecosystems. Even very low exposure to POPs may induce cancer, damage central and peripheral nervous system, cause immunity system diseases and procreation disruption, and disturb the normal growth of infants. As a result, an international legal binding, the Stockholm Convention, was established to protect human and the environment from POPs. The list of POPs under the Stockholm Convention originally included 12 chemical substances (or groups), i.e., dioxins, furans, PCBs, HCB, DDTs, chlordane, heptachlor, aldrin, dieldrin, endrin, toxaphene and mirex. The list is extended further by the addition of 11 more chemicals (or groups) including Te/PeBDEs (tetra-/pentabromodiphenylethers), Hx/HpBDEs (hexa-/heptabromodiphenylethers), HBBs (hexabromobiphenyls), chlordecone, PeCB (pentachlorobenzene), PFOS (perfluorooctane sulfonate) and its salts and PFOSF (perfluorooctane sulfonyl fluoride), lindane (γ -HCH), α -HCH, β -HCH, endosulfan and HBCD (hexabromocyclododecane) as of COP-6 in 2013.

The term PBT was used by US EPA for the control of priority chemicals from late 1990's. The list of PBT Class I (top priority substances) included 12 substances or groups, i.e., PCBs, dioxins/furans, HCB, dieldrin/aldrin, DDTs, chlordane, toxaphene, mirex, benzo(a)pyrene (BaP), octachlorostyrene, mercury and alkyllead.

PTS, on the other hand, was used under the GEF/UNEP Chemicals programme of "Regionally based assessment of persistent toxic substances" (2000-2003) to represent a group of chemicals to be controlled with high priority, including 12 original POPs + 10 among 11 new POPs (except PFOS; Te/PeBDE and Hx/HpBDE were jointly defined as PBDE (polybrominated diphenyl ethers), and α -/ β -/ γ -HCH were combined into HCHs) + PAHs (polycyclic aromatic hydrocarbons), chlorinated paraffins, atrazine, PCP (pentachlorophenol), organotins, organomercuries, organoleads, phthalates, octylphenols and nonylphenols.

As summarized above, the definition of original PTS includes almost all POPs (both original and newly added POPs) and PBT (except inorganic mercury and octachlorostyrene). Here we will follow this original view of PTS, and will include all the previous PTS, PBT and POPs (original and newly added ones). Furthermore, those being reviewed under the POPs Review Committee (POPRC) as candidates of further additional POPs, i.e., short-chain chlorinated paraffins (SCCPs), PCP, PCN (polychloronaphthalene), HCBd (hexachlorobutadiene) and the newly proposed

candidate chemical, dicofol are also included. Other newly proposed chemical in 2013, commercial decabrominated diphenyl ether, will be treated as PBDE together with commercial tetra- and octabrominated diphenyl ethers in this report. In addition, some other chemical substances with persistence and known toxicities, like perfluoroalkyl carboxylates, such as PFOA and PFNA, and other current use pesticides with potential to be transported for long range (see later section), will be included within the scope of the present report. The target chemical substances are summarized in Figures 2-1 ~ 2-4.

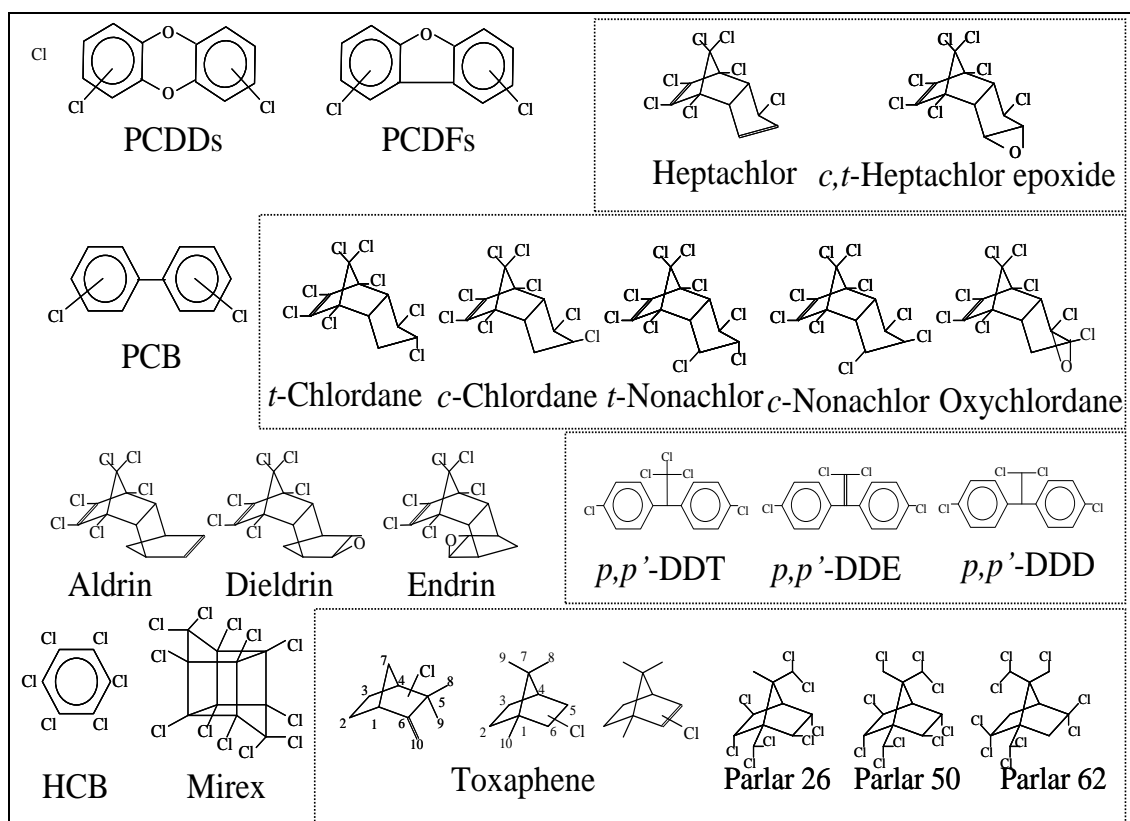


Figure 2-1 Original 12 POPs structures

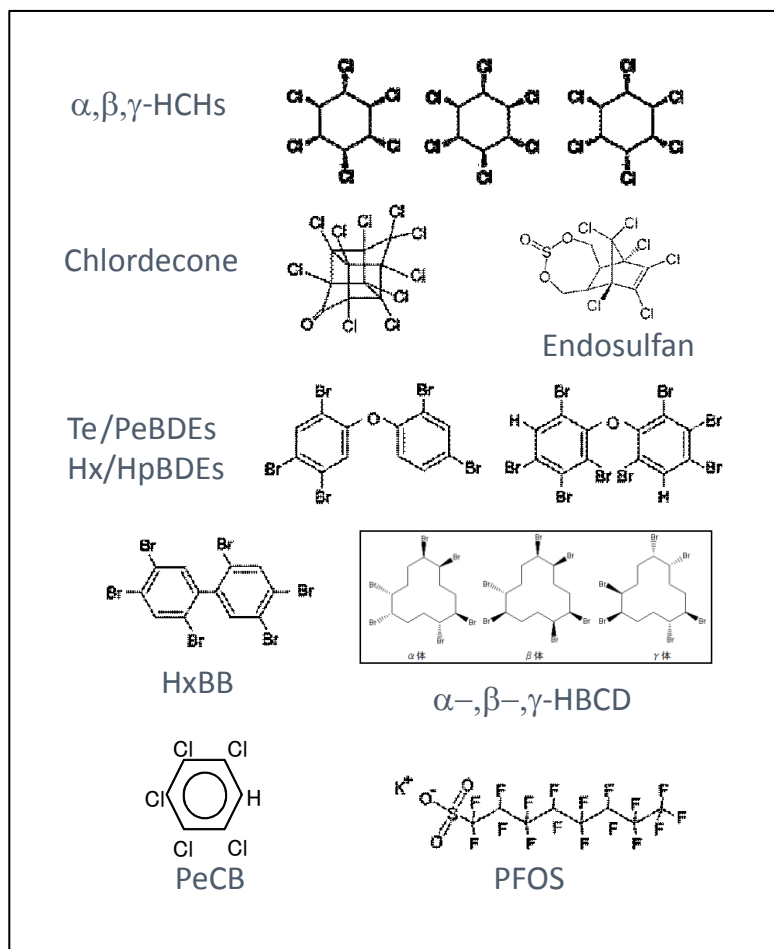


Figure 2-2 Newly added 11 POPs structures

Figure 2-3 Candidate POPs and other agricultural chemicals of related structures

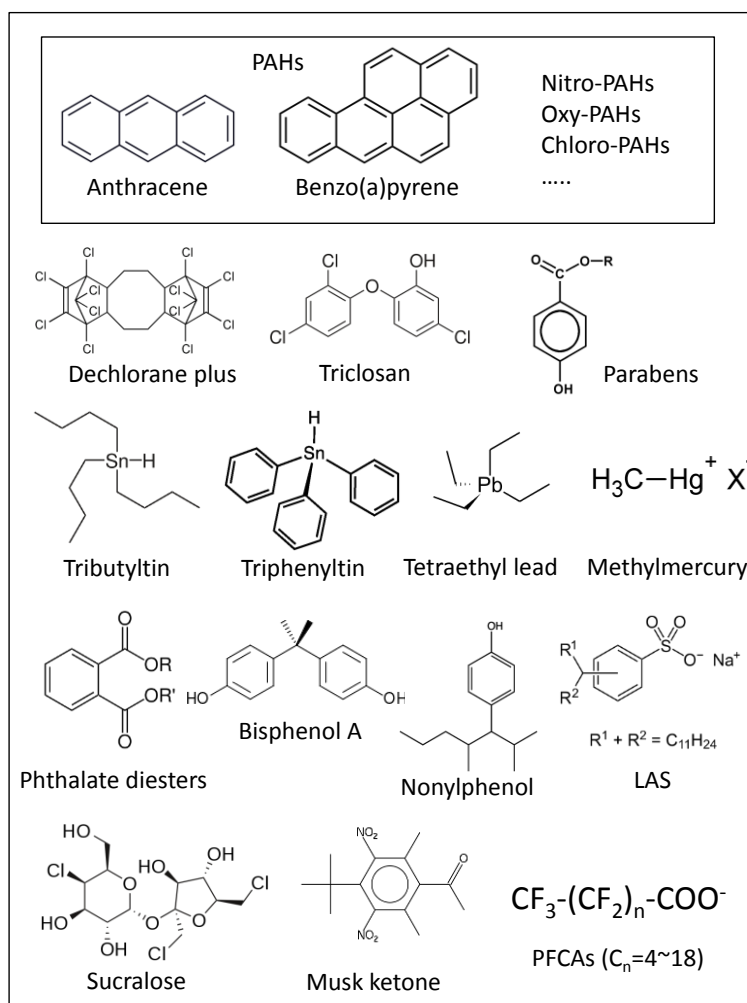


Figure 2-4 Other PTS chemicals / substances of concern

The information on the purposes and production mechanisms as well as the long-range transport potentials of PTS will be indispensable for their efficient elimination / management. From the former standpoint, PTS may be categorized into bioactive chemicals (agricultural chemicals, pharmaceuticals etc., being developed to utilize their biological activities for controlling pests, weeds, bacteria, etc.), industrial products (insulating oils, plastic additives etc., being developed primarily to use their chemical properties (stability etc.)), and unintentionally produced chemicals. From the latter standpoint, on the other hand, PTS will be separated in global, regional or national/local pollutants based primarily on their chemical properties related to the long-range transport through either air or water. In the latter standpoint, on the other hand, transboundary transport of chemicals through human activity, particularly those in commercial products and wastes (such as flame retardants in TV cases), is another important issues to be considered. Here the target of chemicals will be briefly explained based on the former criteria, i.e., (1) agricultural chemicals and pharmaceuticals and personal care products (PPCPs), (2) industrial chemicals, and (3) unintentional products, followed by the brief explanation of their long range transport properties, which will be discussed further in relation to model development and regional transport in section 3.3.

2.1. Persistent Toxic Substances – Agricultural chemicals

2.1.1 Agricultural chemicals related to Stockholm Convention

The agricultural chemicals considered in this report include those that are defined by the Stockholm Convention, as well as others that have drawn attention due to their properties as well as their high volume of production / use and their regular detection in the environment. Because of low persistence of organophosphorous pesticides (OPs), most of studies on pesticides in environment and human have been focused on the organochlorine pesticides (OCPs), which have strong bonds between chlorine and carbon components. These chemicals are easily accumulated in fat tissues and highly insoluble in water. The widest application for OCPs is as an insecticide. OCPs can be released into the environment via direct application, contaminated waste disposal, incinerator emissions or runoff. The major exposure source of OCPs to human and wildlife could be diet.

The pesticides originally defined by the Stockholm Convention were aldrin, chlordane, DDT, dieldrin, toxaphene, mirex, endrin, heptachlor and HCB, and those added later include chlordecone, pentachlorobenzene (PeCB), lindane (γ -HCH), α -HCH, β -HCH, and endosulfan. Majority of these chemicals were produced and used intentionally as agrochemicals, but are also used for vector control, pest control of human or pets, etc. HCB and PeCB, on the other hand, were synthesized also for industrial purpose (for manufacturing organochlorine (OC) chemicals, including solvents and other agricultural chemicals like PCNB (pentachloronitrobenzene)). In addition, HCB and PeCB have unintentional production sources. Some OC agricultural chemicals, including mirex, were also used for flame retardants, while the fluorosurfactant, PFOS, includes usage to control leaf-cutting ants. It should be pointed out that some of pesticides, such as chlordane and mirex, also used for termite or parasite control in or around houses / buildings and thus may have different exposure route to human beings from ordinary agricultural chemicals. Other OC chemicals, including pentachlorophenol (PCP) and chloronitrophenene (CNP), have been produced and used mainly as herbicides. A brief description of each pesticide is given here.

Aldrin is an insecticide primarily used against soil and crop pests, such as corn rootworm, wireworm, rice water weevil and grasshoppers. Aldrin is most commonly used on corn, potato and cotton crops and also used to protect wooden structures from termites. Aldrin is readily converted to dieldrin in plants and animals and, therefore, residues of this chemical are usually found in small amounts. Aldrin has low toxicity to plants, but has adverse effects on aquatic invertebrates, particularly insects. Acute exposure to aldrin has caused death in waterfowl, shorebirds, fish and humans. The International Programme on Chemical Safety (IPCS) estimates the fatal dose for humans to be five grams. The most common human exposure pathway is via food, particularly dairy products and meat.

Dieldrin is an insecticide used against termites, textile and agricultural pests, and insect vectors of disease. The main crops treated with dieldrin include corn, cotton and potato. The use of dieldrin as a vector control has been banned in some countries

because of concerns related to the environment and human health. Dieldrin has low toxicity to plants but high toxicity to insects, fish and aquatic animals (frog embryos, for example, have been noted to develop spinal deformities when exposed to dieldrin). Toxic effects on birds and mammals vary. Dieldrin is suspected of negatively affecting the immune response in humans. Humans are exposed to dieldrin through their food (mainly dairy products and animal meats). It is important to note that because aldrin easily converts to dieldrin in plants and animals, levels of dieldrin reflect total concentrations of both chemicals.

Endrin is an insecticide used against pests of cotton, rice and corn. It has also been used as a rodenticide to combat mice and voles. Many animals can metabolize Endrin. Therefore, it does not accumulate as severely as some of the other persistent organic pollutants. However, endrin is highly toxic to fish and other aquatic organisms. Endrin is suspected of suppressing the human immune system. As with many of the other POPs, humans are exposed to endrin through their diet, although intake levels are usually noted to be very low.

HCB and **PeCB** are a member of chlorobenzenes and have been used not only as pesticides but also as intermediates for the production of other organochlorine chemicals and also produced unintentionally as a by-product of producing other organochlorine chemicals (carbon tetrachloride, perchlorethylene, trichloroethylene, etc.) or industrial as well as combustion processes including chlor-alkali plants that utilize graphite in their electrolytic cells, aluminium manufacture, pyrotechnic production, municipal and industrial incinerators. HCB and PeCB are among the most volatile PTS and are transported for a long distance through the air to reach and deposit in a cold region, such as arctic region or high mountains, and produce pollution in such a remote area distant from their sources.

HCB was first manufactured in 1945 for using as a seed treatment, especially for control of bunt wheat. By the mid 1980s most nations had ceased its manufacture. HCB has been detected in emissions of a variety of industrial processes, and often appears as a contaminant in chlorinated pesticides (including pentachlorophenol, pentachloronitrobenzene dicloram, chlorothaloril, picloram, simazine, and atrazine). Other documented uses include as a raw material for synthetic rubber, a PVC plasticizer, a rubber-peptizing agent in the production of nitroso- and styrene- rubbers, and a chemical intermediate in dyes, and wood preservation. A substantial portion of HCB measured in the present atmosphere is thought to come from volatilisation of "old" HCB on the soil from past agricultural use and contamination (Bailey 2001). Only a small fraction of the HCB generated as a by-product may be released depending on the process technology and waste-disposal practices employed. For example, according to the US Toxic Chemical Release Inventory (TRI), releases of HCB from the ten largest processing facilities in North America were 0.46 t, most of this to air, compared with almost 54.2 t transferred offsite as waste for treatment in regulated facilities.

Chlordane is a mixture of various isomers with different number of chlorines, and was a broad-spectrum agricultural insecticide used on crops, such as vegetables, grains, maize, potatoes, sugarcane, fruits, nuts, cotton and jute. It was also used to

combat termites. Chlordane can kill aquatic invertebrates, fish and birds. Bio concentration, rather than bioaccumulation, seems to be the process of greatest concern. Chlordane is suspected of damaging the human immune system and is listed as a possible human carcinogen. The most common human exposure pathway is through the air, particularly from indoor environments.

Heptachlor is also a mixture of isomers and was used as an insecticide to combat soil and crop pests (particularly of cotton), termites, grasshoppers, fire ants, and mosquitoes (to control malaria). Heptachlor is metabolized to heptachlor epoxide, which has a similar toxicity level to heptachlor. Heptachlor is toxic to wildlife even at low concentrations. In birds, exposure to the chemical has induced behavioral changes, reduced reproductive success, and mortality. Heptachlor is listed as a possible human carcinogen. The main exposure pathway for humans is through food, particularly meat. Major isomers of heptachlor are also included in technical chlordane, and total heptachlor / total chlordane ratios of heptachlor-sprayed areas are sometimes significantly higher than those sprayed with only chlordane.

DDT was broadly used during World War II to control insects (mainly mosquitoes) that spread diseases such as malaria, dengue fever and typhus. After the War, DDT was also used on agricultural crops such as cotton. DDT is still used in many countries in tropical region to control insect vectors that carry disease. Concerns about the serious environmental effects of DDT, particularly on birds, resulted in many countries banning or severely restricting its use in the 1970s. DDT's breakdown products include DDD/TDE and DDE, each of which possesses its own toxic characteristics. DDT is highly toxic to fish, causing severe behavioral changes and death. Acute toxicity of DDT in birds has been observed to affect reproductive success (for example, it causes eggshell thinning in birds of prey). The long-term chronic health effects of DDT on humans include immune system depression and estrogen-like alterations during reproductive development. DDT and its metabolite DDE are listed as possible human carcinogens, particularly as regards hormonal cancers, such as breast cancer. Humans are mainly exposed to DDT through their food; in fact DDT has been detected in food and breast milk all over the world.

Mirex is an insecticide used against fire ants, western harvester ants and yellow jacket wasps in the United States, leaf cutter ants in South America, harvester termites in South Africa, mealy bugs in Hawaii, and termite control in China. Mirex is also used as a fire retardant in plastics, rubber, paint, paper and electrical goods. Mirex is one of the most stable and persistent POPs. The chemical is toxic to plants (affecting their development and growth), aquatic organisms (crustaceans are the most sensitive), fish (affecting their behavior) and birds. Mirex is listed as a possible human carcinogen. Humans are exposed to mirex through their diets, particularly meat, fish and wild game, although intake levels are generally below residue tolerances.

Toxaphene is an insecticide used to protect cotton, cereal grains, fruits, nuts and vegetables and also used to combat the ticks and mites that are parasitic to livestock. Toxaphene, made up of at least 670 chemicals, is non-toxic to plants, highly toxic to fish and has been noted to cause reproductive disorders in birds. Toxaphene has been listed

as a possible human carcinogen. Humans are exposed to the chemical through their diets, but levels detected in food are usually very low.

In 2009, three congeners (**α -HCH**, **β -HCH** and **γ -HCH** or **lindane**) of **hexachlorocyclohexanes (HCHs)** were designated as new POPs under Stockholm Convention. HCHs are insecticide, and have been produced in huge amounts in the world, including 4 million tons of technical HCHs and 11,400 tons of γ -HCH isomer in China, and 287,000 tons of technical HCHs in Japan. γ -HCH is the active ingredient of the mixture and has been produced and commercialized in some countries including those in Europe. It is also used for scabby or rice control in humans as well as pets. Technical HCH mixture, on the other hand, contains α -HCH isomer as a major component and was synthesized in other countries including Japan and China. α -HCH is most volatile among the isomers, and known to be transported for long distance to arctic region or high mountains where it deposits and contaminates the environment. On the other hand, β -HCH resists metabolism and tends to be accumulated in higher levels in organisms than other isomers.

Chlordecone is an organochlorine pesticide, structurally very similar to mirex (two chlorines are replaced with ketone in chlordecone), and has been used mainly for agricultural insecticide, miticide and fungicide. Its use started in 1958 for variety of purposes, including insecticides to control banana root borer, Colorado potato beetle, potato and tobacco wireworm, as well as larvicide of fly and fungicide against apple scab and powdery mildew. Its production reached to 1,600 t (total between 1951 – 1973) in US and majority of chlordecone as well as its derivative, Kelvan, were exported to Europe, Asia, Latin America and Africa. Chlordecone was listed in Annex A of the Stockholm Convention at its 4th COP in 2009. (UNEP/POPS/POPRC.3/20/Add.10 “Revised risk profile on chlordecone”).

Endosulfan is another organochlorine insecticide, composed from two isomers (α -, and β -) (UNEP/POPS/POPRC.5/10/Add.2 “Risk profile on endosulfan”). It has been sold from mid 1950's in 60 countries in the world, and has been used for variety of crops, including soy, cotton, rice, tea, vegetables, fruit, nuts, berries, grapes, etc. In US, it was registered in 2006 as veterinary insecticide to control ectoparasites of beef and lactating cattle as a ear tag. Its annual production reached to 10,000 t in 1980. In recent years India was the largest production country (9,900 t/a during 2001-2007; more than 4,000t was exported in 2007) followed by Germany (c.a. 4,000t/a), China (2,400 t), Israel, Brazil and Korea. Endosulfan was listed in Annex A of the Stockholm Convention at its 5th COP in 2011.

2.1.2 Other agricultural chemicals including current use pesticides

There is information concerning arctic pollution caused by the current use pesticides through their long- range transport (Hoferkamp et al., 2010). The list includes chlorothalonil, chlorpyrifos, dacthal, diazinon, dicofol, methoxychlor, pentachloronitrobenzene (PCNB), trifluralin, PCP and Lindane.

Chlorothalonil is a polychlorinated aromatic compound first produced in 1966 in US. It has been used as fungicide, bactericide and mildewcide for peanuts, potatoes, tomato and golf courses, and its annual usage in US averaged 6,800 t (US EPA, 1999: EPA 738-R-99-004” Reregistration Eligibility Decision (RED) Chlorothalonil”). **Dacthal**, or dimethyl tetrachloroterephthalate, is a herbicide developed by American Vanguard. HCB and 2,3,7,8-TCDD were detected as impurities in dacthal by US EPA, and the registrant subsequently altered their manufacturing process to reduce their contamination (EPA 738-R-98-005; Reregistration Eligibility Decision (RED) DCPA).

Chlorpyrifos is an organophosphate insecticide with three chlorine atoms on the pyridine ring. It was introduced commercially in 1965. In the organism, it is metabolized by mixed-function oxidases in the liver, and becomes highly reactive chlorpyrifos oxon by oxidative desulfurization. This oxon form binds with acetylcholine esterase strongly and inhibits its activity. Its annual use was estimated around 2,200 – 3,200 t for agricultural, and 680 – 1,040 t for industrial purposes, respectively, in US (EPA 1982). Currently China is reported to become the largest production base of Chlorpyrifos in the world with total production capability exceeding 100,000 t (AgroNews 2012). **Diazinon** is another organophosphate insecticide developed in 1952. 4,670 t of diazinon was produced in US in 1990 (ASTDR 1990 “Diazinon”). It was once used broadly in non-agricultural indoor and outdoor uses. However, recently the use was limited to agricultural use in US, and its use is expected to decrease gradually.

Dicofol is an organochlorine pesticide, particularly for controlling mites, which is produced by the chlorination followed by hydrolysis of DDT. Like in the case of DDT, dicofol has two major isomers, p,p'- and o,p'-isomer. Annual domestic agricultural use of dicofol was reported to be 390 t in US (between 1987-96; US EPA 1998). Due to the presence of unreacted DDT and other derivatives in the final product, a Dicofol Specific Review was initiated in 1984, which concluded that dicofol-containing use will be cancelled in US if the impurity levels exceed 0.1 % by July 1, 1987. Use of DDT as intermediate for dicofol production was first registered as the specific exemption of the production and use of DDT under Stockholm Convention. As at 17 May 2009, there were no Parties registered for the specific exemptions for this purpose. In accordance with Article 4 of the Convention, no new registrations may be made with respect to such exemptions. Dicofol is nominated as a candidate of additional POPs under the Convention in 2013. Another organochlorine insecticide, **methoxychlor**, has structurely similar to DDT with two hydroxyl groups on the benzene rings instead of chlorine atoms. It was used to protect crops, livestock and pets against fleas, mosquitoes and other insects. In 1975, 2,500 t of methoxychlor was produced in US, but the level became an order of magnitude lower in late 1980's. It has shown to have acute toxicity as well as endocrine disruptive activities, and US EPA decided that methoxychlor is not eligible for reregistration in 2004.

PCNB is a fungicide produced from nitrobenzene or PeCB. It is used to control diseases on vegetables, field crops, turf, seeds etc. EPA estimated usage of PCNB in US around 350 – 450 t/a, mainly for cottons, potatoes and turfs. **Trifluralin** is an organofluorine chemical with trifluoromethyl moiety on dinitro-N,N-dipropylaniline

moiety. It is produced in US, Italy, Australia, Brazil etc. with total amount of 20,000 – 25,000 t/a . Trifluralin was banned in 2009 in EU (UNECE). (BiPRO GmbH, 2010).

PCP has been used as herbicides and other agrochemical purposes. The identified main sources into the environment are: treatment of wood (sapstain control agent), impregnation of heavy-duty textiles and fibres (fungicide), use and disposal of treated wood and textiles (including imported goods), contaminated sites (former PCP production and wood preservation plants) and treatment of contaminated soil and groundwater, natural sources or burning processes. PCP is nominated as additional POPs under the Stockholm Convention and is being reviewed by POPs Review Committee.

2.1.3 PPCPs or other biologically active chemicals of concern (Boxall et al., 2012)

Potential environmental impacts of antibiotics (such as triclosan), or pharmaceutical compounds used in house as well as in poultry industries have been attracted attention in recent decade. These chemicals are frequently termed as PPCPs (pharmaceuticals and personal care products) together with musks in detergents, UV protection chemicals for sun-screens, parabens for preservatives, etc. These chemicals are frequently detected in effluents from sewage treatment plants (or waste water treatment plants; WWTPs) and biosolids used for fertilizers.

Triclosan is an organochlorine chemical with antimicrobial activity, and has been used for various purposes including hand-soaps, toothpaste, etc. Triclosan is known to produce non-TEF type dioxins (2,8-DCDD, 2,3,7-TrCDD, 1,2,8-TriCDD and 1,2,3,8-TCDD) by photochemical reactions in the environment. Other chemicals of concern in the effluents of WWTPs, though rather categorized as industrial chemicals, include **benzophenone-3** and **4-methylbenzylidene camphor** (UV filters) (Tovar-Sanchez, A., et al. 2013), **synthetic musks** (Nakata, H., et al., 2012 / Zhang X., et al., 2008), artificial sweeteners (such as **sucralose**), **cyclosiloxanes**, **nano-particles** and other polar organic chemicals including **LAS** (Johnson, A.C., et al., 2008).

2.2. Persistent Toxic Substances - Industrial Compounds

Variety of chemicals have been produced and used in industries as well as in commercial uses. Majority of industrial chemicals concerned from the standpoint of PTS are organohalogen compounds with either of the following properties / uses;

- 1) Stable liquids for heat transfer, insulation, hydraulic liquids, solvents; PCB, HCB, PeCB, SCCP, perfluorinated alkyl ethers, etc.
- 2) Flame retardants; PBDE, HxBB, chlorinated paraffins, HBCD, Decloran plus
- 3) Stable surfactants or dispersants; PFOS and their salts, derivatives, PFOA or other fluorosurfactants, etc.

In addition, other chemicals without halogen atoms are also of concern;

- 4) Other additives to plastics or other personal uses; plasticizers (including phthalate diesters), UV adsorbers, antimicrobes (triclosan etc), musks, nanoparticles

In this section we briefly summarize information regarding industrial POPs chemicals controlled under the Stockholm Convention, including original, newly added POPs, those currently being reviewed under the Convention, and other PTS chemicals.

PCBs are a family of 209 compounds composed of attached benzene rings with varying numbers (from 1 to 10) and locations of chlorine atoms. They are resistant to heat, non-flammable, have a low vapor pressure and a high dielectric constant. PCBs were first manufactured in 1929 for industrial use, primarily as heat exchange fluids and as an insulating medium in electrical capacitors, transformers, hydraulic and heat transfer systems. They have also been used in sealants used for weatherproofing, and in carbonless copy paper, paint additives, adhesives and plastics. After recognition of the toxicity and ubiquitous presence in the environment, PCB production was banned in many countries. However PCBs-containing goods produced before the ban, including electrical transformers and capacitors, are still used in the world. PCBs remain in the environment for decades, where they are available for uptake and subsequent bioaccumulation in organisms. PCBs are also by-products of incomplete combustion and industrial processes. They include 13 compounds which exhibit extremely toxic, dioxin-like properties. PCBs are toxic to aquatic organisms and fish, and cause reproductive failure, immune suppression in a variety of other wildlife species. Acute human exposure to PCBs can produce swelling of the eyelids, pigmentation of the nails and mucous membranes, fatigue, nausea and vomiting. Chronic exposure, including at low levels, can cause alteration to liver enzymes, rashes, acne, developmental, mental and behavioral problems, immune suppression, and possibly cancer. Studies of children in the United States (Michigan State) followed subsequent to exposure to PCBs while in the womb (via placental transfer) and from breast milk, manifested deficits in intellectual function, short-term memory loss, and hyperactivity and behavioral problems. Humans are exposed to PCBs through their diet. Fish and marine mammals, because of their high fat content and elevated position in the food chain, are at risk of PCB contamination. They also constitute a major dietary food for some aboriginal peoples living in the Arctic. Vegetable oils and milk also constitute dietary pathways of exposure.

HCB and **PeCB** were explained in the previous section.

Polybrominated diphenyl ethers (PBDE) have been commercially used as three technical mixtures: tetra- or pentabromodiphenyl ether (tetra-/penta-BDE), octabromodiphenyl ether (octa-BDE), and decabromodiphenyl ether (deca-BDE). The penta- and octa-products contain several BDE congeners, while the deca-product is composed almost entirely of deca-BDE. The former two were designated as tetra/penta-BDE and hexa/hepta-BDE, respectively, under the Stockholm Convention. They had a big share among brominated flame retardants (BFRs), and have been widely used in many products, such as television sets, computers, radios, textiles, new synthetic building materials, and automobiles. Recent major use of cPeBDE and cOBDE were

polyurethane foam (95-98 % of cPeBDE production; 10-18% weight loadings) and ABS (acrylonitrile-butadiene-styrene) polymers (95% of cOBDE production; 12-18% weight loadings), respectively. Cumulative production of commercial PeBDE and commercial OBDE were estimated to be 100,000 t and 180,000 t (latter based on rough estimated figure of 6,000t/a times 30 years) (UNEP/POPS/POPRC.2/17/ Add.1 "cTe/PeBDE", UNEP-POPS-POPRC.3-20-Add.6 "Risk profile on cOBDE"). CPeBDE was produced in Israel, Japan, US and EU, but has been phased out (Japan (1990), EU (1997), US (significant new use rule in 2006)). Similarly the production of cOBDE in Netherlands, France, US, Japan, UK and Israel already ceased. A newly proposed candidate, decabromo-diphenyl ether (DBDE), on the other hand, is still produced and used. 7,500 – 10,000 t/a of DBDE is sold in EU (2010; except those imported in articles or preparations), 25,000 – 50,000 t/a in US (in 2002, 2006), and its production in China was estimated to be 30,000 t/a (2005). (UNEP/POPS/POPRC.9/2 "DBDE"). PBDE are similar in behavior (hydrophobic, lipophilic, thermally stable) to PCB. Growing evidence suggests that PBDE are widespread global environmental pollutants and that they are capable of bio-accumulation in food chains. Several studies have reported their occurrence in a wide variety of environmental compartments, and in human tissues from around the world. PBDEs.

Hexabromobiphenyl is another brominated flame retardant (BFR). 6,000 t of total PBB (Polybromobiphenyl) was produced during 1970 – 1976, and 88 % (c.a. 5,400 t) was thought to be hexabrominated forms (UNEP/POPS/POPRC.2/17/Add.3; Risk profile on hexabromobiphenyl). HxBB was mainly used for ABS thermoplastics for constructing business machine housings, industrial products (for example, motor housing), and electrical products (such as TV, radios).

In addition to PBDE and HxBB, another BFR, **hexabromocyclododecane (HBCD)**, was decided to be listed in Annex A of the Convention at COP-6 in 2013. HBCD is a mixture of several isomers with γ -HBCD as the dominant isomer (70-95%). It has been used for flame retardant of expanded (EPS) and extruded (XPS) polystyrene foam insulation boards in the building and construction industry as major application. HBCD levels in polystyrene foam boards ranged from 0.7 % to 3.0 %. Another use includes polymer dispersion on cotton, or cotton mixed with synthetic blends, in the back coating of textiles where HBCD is present around in concentrations ranging between 2.2 – 4.3 %. Global demand of HBCD was reported around 21,000 – 22,000 t/a (2002~2003). In US, the sum of manufactured and imported HBCD is between 4,540 to 22,900 t. Recent Japanese sum of manufactured and imported HBCD was reported around 700 t in early 1990's, and recently is between 3,400 t (2004) to 2,700 t (2008). In EU, total volume of HBCD was estimated about 11,580 t in 2006. Various toxicological and ecotoxicological data have been reported in the three groups of BFRs, i.e., PBDE, HxBB and HBCD, including endocrine disruptive effects. For example, HBCD is thought to be endocrine disruptors of both the hypothalamus-pituitary-thyroid hormone axis and of sex-steroid regulated processes in mammals.

Short-chain chlorinated paraffins (SCCPs) are part of a family of chemicals referred to as chlorinated paraffins. Chlorinated paraffins are complex mixtures of straight chain chlorinated hydrocarbon molecules with a range of chain lengths (short

C10-13, middle C14-17 and long C18-30) and degrees of chlorination (between 40 - 70 % weight basis). These compounds were first produced as extreme pressure additives around 1930. In 1985, the estimated world production of chlorinated paraffins was ~300,000 tons (WHO 1996). SCCPs comprise the smallest fraction of the global production and have been used for lubricants and coolants in metal cutting and metal forming operations and as secondary plasticizers and flame retardants in plastics. The widespread use of SCCPs is potential sources of environmental contamination, particularly to the aquatic environment. SCCPs may be released into the environment from improperly disposed metal-working fluids containing SCCP or from polymers containing SCCPs. Available data support that SCCPs are not mutagenic, nor genotoxic, and are of low toxicity with general non-specific toxicity following repeated exposure. As SCCPs contain a huge number of isomers, however, further toxicological researches will be needed to assess its potential impact on human beings and wildlife properly (European Commission Joint Research Centre, 1999).

Dechlorane Plus (DP) is an organochlorine flame retardant developed as a replacement for mirex by mirex producer, OxyChem, in US and has been used for more than four decades (Xian, Q. et al., 2011; Feo, M.L. et al., 2012). Annual production of DP in the world was estimated around 5,000 t, among which 450 t was produced in US and 300 - 1,000 t in China. A company, Anpon, in China (located Huai'an, northwest of Shanghai) alone has reached production capacity of 2,000 t per year in 2006. Like other flame retardants, the percentage composition of DP in commercial polymers is rather high (10 – 35 % on weight basis). (Sverko, E., et al., 2011). Other flame retardants with similar chemical structure include dechlorane 602, 603 and 604.

Per/polyfluorinated compounds (PFCs) or fluorosurfactants include per-or polyfluorinated carbon chains with polar group, such as sulfonate, carboxylate, phosphate, phosphite or alcohol. **Perfluorooctane sulfonate (PFOS)** has been sold in the market from 1956 in US. PFOS and its derivatives have been used in a variety of industrial and commercial products, such as stain repellents, aviation hydraulic oils, paper coatings, fire fighting foams, antireflectants and photoresists for semiconductors, metal plating, baits to control leaf-cutting ants, etc. . PFOA or other perfluoroalkyl carboxylates have been used for dispersants for fluoropolymer production, surface coatings, paint mix, and mold release agents. A global monitoring study in the early 2000's showed the widespread presence of perfluorooctanesulfonate (PFOS) and related compounds in wildlife tissues as well as bioaccumulative properties of these compounds. Toxicological studies on PFOS and perfluorooctanoic acid (PFOA) showed adverse effects on intercellular communication, membrane transport, and developmental and neuroendocrine anomalies in laboratory animals.

PFOS has been produced in US for nearly half a century by electrochemical fluorination (ECF) process, which produces variety of branched isomers in addition to linear PFOS. A primary product, containing only 30% of linear isomer, is partially purified (to 70 % linear) and sold in the market. It was estimated that the global PFOSF (precursor of PFOS) production was 13,670 tons in total until phasing out of 3M production in 2003. In Japan, a company produced PFOS by ECF between early 1980's until 2009. Recent annual production was estimated to be 1 - 10 t. In China, PFOS

started to be produced in 2001, and the recent annual production is estimated to be around 200 to 250 t/a.

PFOS is now controlled globally under the Stockholm Convention as listed in Annex B, which, however, means that its production and use continue for various acceptable purposes and specific exemptions registered by the Parties. In US, a stewardship program is ongoing to phase out the use of PFOA and longer perfluoroalkyl carboxylic acids until 2015. Some countries, including US, UK and Germany, set up temporal criteria to start action on the drinking water levels of PFOS and PFOA. Variety of their derivative have been synthesized and used in industries, while their emission sources, environmental fates and behaviors are still to be clarified. Another group of fluorochemicals, so-called fluorotelomer alcohols, such as 8:2 FTOH and 10:2 FTOH, have been used for surface treatment. They are more volatile than carboxylic or sulfonic PFCs, transported long-range through the atmosphere, and known to be converted to PFOA or other perfluoroalkylcarboxylates in the environment.

Contrary to other industrial chemicals such as flame retardants, PFCs are not “bulk chemical”, i.e., usually included in the products far less than 1% in weight basis. However, it should be pointed out that they have been used in many active and advanced industries in East Asian countries, including electronic devices and car production, textiles and leather industries, metal plating, other high quality materials production, and medical sector or other sectors using such high quality / sophisticated products. They show rather unique environmental behaviors due to their high water solubility, which, together with their extreme persistence, give them rather high risks of contaminating water environment.

Organotins are a group of chemicals with different numbers (1 to 4) of alkyl or aryl-group, including methyl, butyl and phenyl groups, attached to tin. Organotins have been extensively used for industrial and agricultural purposes such as PVC stabilizers, fungicides, insecticides, industrial catalysts and wood preservatives. Among them, tributyltin (TBT), its derivative (TBTO) and triphenyltin (TPT) have been widely used as antifouling paints on fishing boats, large ships and vessels, harbor structures, marine platforms and aquaculture nets. The primary source of TBT is leaching from sea ship hulls. Related activities that cause emissions of TBT are sea ship traffic, docking activities and dumping of dredged material. Scratched paints containing TBT or TPT contaminate the local areas around the docks and harbors. In addition, sources include industrial discharges from production/formulation of all organic tin compounds, atmospheric deposition of organic tin compounds, TBT used for wood conservation application, leaching, dumping of conserved wood as waste, antiseptic or disinfecting use of TBT and disposal of harbor sediments contaminated with organic tin compounds (OSPAR 2000). Considerable quantities of TBT were released into the marine environment and as a consequence, widespread pollutions in marine environment occurred. TBT pollution in the aquatic environment has been of global concern because of its extreme toxicity and ecotoxicological hazards, and then restriction on its use has been implemented in many developed countries in the mid to end 1980s. The International Maritime Organization (IMO) has launched the Antifouling System (AFS)

treaty in which TBT-based paint is completely banned from 2003 and no residue of TBT is allowed on ship hulls from 2008.

Considerable scientific efforts to synthesize information on **Mercury** have been conducted to support another international legally binding instrument, Minamata Convention for Mercury, established in autumn 2013. Global mercury emission to the air from anthropogenic source is estimated to be 1960 tons in 2010, one third of which comes from artisanal and small scale gold mining (Global Mercury Assessment, UNEP 2013). Coal combustion is estimated to input 475 tons of mercury in 2010, the majority of which is from power generation and industrial use. In regional scale, East and South East Asia are estimated to account for 40% of the global anthropogenic emission followed by South Asia (8%). There still remain considerable uncertainties as for these emission estimates (for example, total emission estimates varied between 1,010 and 4,070 tons in 2010). Also it should be pointed out that current anthropogenic source is estimated to share only 30 % of the total emission, and majority of the rest is thought to be re-emissions of previously released mercury. It is estimated that mercury levels in surface 100m of the ocean doubled in the last 100 years due to historical use of mercury. Annual mercury emission to the global aquatic environment is likely to be at least 1,000 tons. The contribution from the natural geological process is estimated to share 10 % of the total. Chloralkali process to make chlorine gas and sodium hydroxide by the electrolysis of brine as well as battery uses are among the most significant use of mercury in the world (Concord East/West Sprl (2004)). In Europe, 7,600 tons of liquid mercury is currently used for 34 electrolysis plants in 15 countries, which account for 31% of total chlorine production in Europe (in homepage of Euro Chlor: <http://www.eurochlor.org/chlorine-industry-issues/mercury.aspx>). A voluntary phasing out program of mercury cell technology in European Chloroalkali industries until 2020 is now on-going. In Japan, mercury cell process was phased out in 1986 and majority of sodium hydroxide is synthesized by ion exchange membrane method. The situation is similar in China, where mercury cell process accounted for c.a. 10 % of all the electrolysis plants in 1975, but was decreased to 2 % in 1995 (Qi, et al. (2000)). It is now reported to be phased out in China (Manabe, 2011).

Methyl mercury, more toxic than inorganic mercury, may be volatilized or emitted into the air from combustion sources such as incinerators and power plants. Municipal solid-waste incinerators and coal-burning power plants are both substantial sources of methyl mercury, for mercury is a contaminant in coal while unintentional methylation process may likely occur in incineration. Although inventories have estimated inputs of these constituents, estimates of associated methyl mercury formation have not been made. Methyl mercury is also known to be produced by biological activity from inorganic mercury, though global significance of this latter route is not clear. For humans, marine seafoods, particularly fishes and marine mammals of higher trophic levels, are known to be major consumption route of mercury, particularly methyl mercury, and some countries set fish consumption advisories to reduce exposure levels and risks of methyl mercury. In Japan, Ministry of Health, Welfare and Labor announced advisories for pregnant women as for elimination of seafoods (fishes and marine mammals) with higher levels of mercury during pregnancy stage.

Organo-lead, including alkyllead, was once used mainly as anti-knocking agents in gasoline. Historically lead has been used for variety of purposes, including white paints and face powders, anti-rust paints for steels, solders, crystal glass production, etc. Lead is known to have nervous toxicity, particularly for children, and its control has been of concerns in many countries in the world. Lead has four stable isotopes, and isotope signatures have been used as specific indicators to identify major exposure sources, to conduct source apportionment, and to trace movement of lead in the environment.

2.3. Persistent Toxic Substances – Unintentional By-Products

Some of the PTSs are both intentional and unintentional production sources while others, notably dioxins and furans, have only unintentional sources. Unintentional sources include either the production of other chemicals or combustion/high temperature processes.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) are ubiquitous contaminants in environmental media and humans. PCDD/Fs are mainly generated by combustion process of solid waste incinerators and steel industry. They are also known to be by-products of synthesizing various chemicals, including 2,4,5-T, PCP, CNP productions and Chloro-alkali industries (Hites, R.A., 2011, Sakurai et al. 1998, Masunaga et al., 2001). Detailed studies have been conducted to clarify the production mechanisms and to develop techniques to reduce their productions / emissions, and the relevant information as well as estimation methods of their emissions from different sources have been compiled under the Stockholm Convention.

PCDD/Fs are toxic to fish, causing behavioral changes and death (early life stages are particularly sensitive). They have also been implicated in a diversity of developmental and digestive disorders in birds and other wildlife. In humans, chloracne is the most consistent health effect observed with exposure to dioxins. Other health effects include fatigue, depression, personality changes and altered cellular and hormone levels (which can include immune, enzyme, reproductive and developmental disorders). The fetus (via the placenta) and breast-feeding infants are at higher risk of thalamic, pituitary and thyroid regulatory system problems. Exposure to PCDD/Fs is also thought to exacerbate endometriosis in women (a painful, chronic gynecological disorder in which uterine tissues grow outside the uterus) and has been linked to impaired glucose tolerance and diabetes. The 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (2, 3, 7, 8-TCDD) congener is classified as a human carcinogen and is a multisite carcinogen in experimental animals, according to the World Health Organization's International Agency for Research on Cancer (IARC). The US EPA in its draft reassessment has classified 2, 3, 7, 8-TCDD as a hormonal carcinogen. Humans are exposed to dioxins through their diet, namely the fatty portion of animal products. Furans, along with dioxins, are common by-products of PCB manufacture, waste incinerators, and auto emissions. Furans have many of the same toxic effects on the health of wildlife and humans as do dioxins; however, the IARC of the World Health Organization (WHO) notes that scientific evidence suggests that furans are not classifiable as to their carcinogenicity to humans. Humans are exposed to furans in their food, again, mainly

through the fatty portion of animal products. The mechanisms of their toxicities have been extensively studied in recent decades, including identification of their target receptor, Ah-Receptor (AhR), and other genes / proteins involved in the process as well as induced by the dioxins (Chopra & Schrenk, 2011, Yoshioka et al., 2011). AhR induces cytochrome P450 1A1, one of a series of enzymes hydroxylating hydrophobic xenochemicals to provide them anchor for adding hydrophilic moieties, like glucuronate or sulfate, and to promote their excretion to the outside of the body. Dioxins themselves, however, are not metabolized by CyP1A1, and the failure to eliminate this group of chemicals may be related to their strong toxicity. Further research, however, is needed to understand their toxicity mechanisms well.

There have been an increasing number of observations, which appears to indicate that dioxins may have been present in the environment for considerably longer than the onset of industrial activity (Hashimoto et al, 1990 and Alcock et al., 1998), and that they may be formed through non-anthropogenic activities. Dioxins were detected in a sediment core around the age of 8 thousand years, much earlier than the industrial ages, obtained from the bottom of Pacific Ocean (Hashimoto et al, 1990). The researchers believe this is consistent with the emission of trace quantities of PCDD/PCDF from natural forest fires prior to the human activities. These studies provide a strong indication that natural processes can form PCDD/PCDF. There is little doubt though, that the vast majority of PCDD/PCDF is formed through anthropogenic activity. Brominated and mixed (chloro/bromo-) dioxins are also known to be produced by the incineration of wastes including, for example, organobromine compounds. In a real incineration procedure, variety of dioxins with both chlorine and bromine substitutions are expected to be produced, though limited data have been available in the literature due to lack of available standards for the research of such a huge amount of complex mixture of chemicals.

PCB, HCB and PeCB are known to be produced in high temperature processes such as incineration. Their emissions to the environment depend on the incinerating conditions, composition of materials to be incinerated, and absence/presence and type of flue-gas treatment plants. Ministry of the Environment, Japan, has been conducting extensive survey to quantitate total unintentional emission of PCB and HCB as well as dioxins/furans, and compiled the data. Based on their report, it seems generally that unintentional production / emission of these three groups of chemicals show similar trends with dioxins, and that BAT/BEP developed to decrease dioxins emission will be applicable to the decrease of PCB, HCB and PeCB. Differences in their physicochemical properties, such as volatility, however, affect the efficiencies of filters to remove emission of each chemical. See also section 2.1 and 2.2 for their intentional production

Polycyclic aromatic hydrocarbons (PAHs) are most ubiquitous contaminants in the environment. These compounds are generally molecules made up of hydrogen and carbon atoms with two or more fused benzene rings in linear, angular, or cluster arrangements. Two general types of PAH have been characterized as follows; (1) fused-ring compounds such as alkylated naphthalenes, phenanthrene, and benzo[a]pyrene and (2) linked-ring compounds such as biphenyls. Together, PAH comprise a homologues

series of fused aromatic ring compounds increasing environmental concern. PAHs and their derivatives have attracted attention according to their potential health hazard to human as well as wildlife. PAHs are of extreme ecotoxicological importance since they have been found to be responsible for such toxic effects as DNA adducts and carcinogenesis. The investigation of these compounds has been great scientific interest because they are potentially carcinogenic, mutagenic, and teratogenic to aquatic organisms. Not all PAH are potent carcinogens and mutagens, but some of them can initiate carcinogenesis and mutagenesis after metabolic activation.

Although PAHs are included in oils, combustion sources are thought to account for over 90% of the environmental burden of PAHs. In particular, stationary point sources account for around 90% of these inputs (Howsam and Jones 1998). Inputs to the atmosphere are dominated by emissions associated with residential heating (coal, wood, oil and gas burning) and industrial processes (coke manufacture etc.). Automobile emission and wild fires are also sources to the atmospheric PAHs. Non-combustion processes such as the production and use of creosote and coal-tar, and the remediation of sites contaminated with these substances, though poorly quantified, are potentially significant primary and secondary sources. Nations undergoing rapid industrialization may well prove to be an increasingly significant source of PAH in global terms with the increase in number of mobile and industrial sources. In marine environment, the contamination sources of PAHs have two main pathways, i.e. atmospheric deposition from combustion process and oil spillage.

PAHs with three or less number of aromatic rings are present mainly in gas phase while those with five or more numbers are mainly in particle phase. A variety of derivatives of PAHs are also known to be present, including methylated or other alkylated PAHs, nitro-PAHs, chloro-PAHs amino-PAHs and oxy/hydroxy-PAHs. The first group is found in oils or other geological samples, and has been used as markers to reveal underground thermal history after their formation as well as identifying their oil production areas. They are also used as a characteristic marker for oil combustion process. The latter groups, particularly nitro-PAHs, are produced in high temperature processes, such as automobile engines, and they are used as markers to identify major sources of airborne particles. Extensive researches have been conducted to utilize ratios or presence / absence of specific PAHs as well as their isotope signatures for diagnostic purpose to identify major emission sources of PAHs in the environment. Examples of PAHs source indicators and their diagnostic ratios are summarized in Table 2-1.

Table 2-1 PAHs diagnostic ratios for the identification of emission sources (from Yan et al. (2005); Kumata et al. (2006); Tobiszewski & Namiesnik (2012))

Indicators	Marker	Diagnostic ratio for each source type				
		Petrogenic	Pyrogenic/combustion			Non-combustion (Al smelter)
			Petroleum combustion	Dieasel combustion	Coal combustion	
FLA / (FLA + PYR)	petrogenic / petroleum burning / biomas or coal burning	< 0.40	0.40 – 0.50		> 0.50	> 0.50
ANT / (PHE + ANT)	petrogenic vs pyrogenic	< 0.10	> 0.10		> 0.10	> 0.10
BaA / (BaA + CHY)	petrogenic vs pyrogenic	< 0.20	> 0.35		> 0.35	> 0.35
BaP / (BaP + BeP)	fresh (0.5) vs aged (< 0.5) particles					
RET / (RET + CHY)	wood burning	?	0.15 – 0.50		0.30 – 0.45	0.83, 0.96
IcdP / (IcdP + BghiP)	petrogenic / petroleum burning / biomas or coal burning	< 0.20	0.20 – 0.50		> 0.50	> 0.50
2meNP / PHE	fossil fuel vs combustion	2.0 – 6.0	< 1.0			
1,7-dmPHE / (1,7- + 2,6-dmPHE)	fossil fuel s biomass combustion	?	0.4		0.65 – 0.68	0.9
ΣmePHE / PHE	petroleum vs diesel combustion		< 1.0	> 1.0		
BbF / BkF						2.5 – 2.9
BaP / BghiP	traffic (> 0.6) vs non-traffic (< 0.6) emission					
ΣLMW / ΣHMW	petrogenic vs pyrogenic	> 1.0	< 1.0			
pPAHs / (p + C1)PAHs	petrogenic vs pyrogenic	< 0.50	> 0.50			
nPAHs/pPAHs	Combustion temp (ratios are higher in higher temp combustion)					
¹⁴ C / ¹² C	fossil fuel vs biomass		< 10 ⁻¹⁵		10 ⁻¹²	
FLA: Fluoranthene	BaP: Benzo(a)pyrene	1,7dmPHE: 1,7-dimethylphenanthrene			BbF: Benzo(b)fluoranthene	
PYR: Pyrene	BeP: Benzo(e)pyrene	2,6dmPHE: 2,6-dimethylphenanthrene			BkF: Benzo(k)fluoranthene	
ANT: Anthracene	RET: Retene	ΣmePHE: total methylated phenanthrenes			C1-PAHs: C1-alkyl PAHs	
PHE: Phenanthrene	IcdP: Indeno(123-cd)pyrene	ΣLMW: sum of low molecular weight PAHs			nPAHs: nitro-PAHs	
BaA: Benzo(a)anthracene	BghiP: Benzo(ghi)perylene	ΣHMW: sum of high molecular weight PAHs				
CHY: Chrycene	2meNP: 2-methylnaphthalene	pPAHs: parent PAHs (no side chains)				

2.4. Regionally Specific PTS

Information on the production or usage of a particular chemical in the region and the comparison with its global production will be useful to consider regional priority of chemicals in PTS list in NOWPAP region. Some of the data compiled in the homepage of the Stockholm Convention on each chemical were compiled in the previous section. Other information on the historical, present usage or sales of selected persistent pesticides in each NOWPAP country were found in National Implementation Plan (NIP) of several countries under the Stockholm Convention, and also published in scientific literatures, such as Voldner and Li (1993, 1995; global toxaphene, DDT, γ -HCH & HCHs), Li et al. (1996, 1997, 1999; global technical HCHs and α -, β -, γ -HCH), Li & Macdonald (2005; global HCHs), Li et al. (2001; HCH in China, 2004; HCHs in former Soviet Union), Li et al. (1999; DDT in China, 2006; DDT in former Soviet Union), Barrie et al. (1997), Breivik et al. (2002; global PCB-153), Jia et al. (2009; endosulfan in China). Emission estimate of PFOS and other PFCs have been published by Murakami et al (2008; Japan), Murakami & Takizawa (2010; Japan and global estimate), Kim et al. (2011; Korea), Kim (2012; Korea), Lim et al. (2011; PFOS in China), Zhang et al. (2012; PFOS in China), and Xie et al. (2013; PFOS in China). Several reviews are published on BFRs, including Tanabe (2008; PBDE and HBCD in Japan), Ma et al. (2012; PBDE in China), Chen et al. (2012; PBDE in China). Recently Wang et al. published a review article on the inventory of POPs in China (Front. Environ. Sci. Engin. 2012, 6(1): 2–16).

Table 2-1. Global cumulative usage of selected pesticides for various periods of time (Barrie et al. 1997)

Pesticides	Usage (tonnes)	Period	Source
DDT	1500000	1948-1993	Voldner and Li 1995
Technical HCH	550000	1948-1993	Voldner and Li 1995
Technical lindane	720000	1948-1993	Voldner and Li 1995
Toxaphene	450000	1948-1993	Voldner and Li 1993
Technical HCH	40000 29000	1980 1990	Li et al. 1996
Technical lindane	5900 4000	1980 1990	Li et al. 1996
α -HCH	28000 20400	1980 1990	Li et al. 1996
γ -HCH	11900 8400	1980 1990	Li et al. 1996
Interpolated			
DDT	2600000 990000	1950-1993 1970-1993	Voldner and Li 1995
Toxaphene	1330000 670000	1950-1993 1970-1993	Voldner and Li 1993

Table 2-2. Current use pesticides and their production (Hoferkamp et al., 2010; others)

chlorothalonil	5000-7300 t/year in US
chlorpyrifos	3600-5000(or 2900-4200) t/year in US
dacthal	200 t/year in US
diazinon	1820-3200 (or 4670) t/year in US
dicofol	5500 t/year globally 390 t/a in US
methoxychlor	193-2500 t/year in US
pentachloronitrobenzene (PCNB)	350-450 t./year in US
trifluralin	8700-10500 t/year in US (20000-25000 t/y in the world)
PCP	8500-50000 t/year in US
(Lindane	3220 t/year globally)

While the production of legacy POPs and other OCPs have been decreasing / ceasing in recent decades in US / Europe, some of the chemicals production have been moving to Asia. For example, China is now reported to be the largest production base of Chlorpyrifos, an organophosphate insecticide with chlorine atoms. Other major pesticides of high exporting value produced in China include glyphosate, imidacloprid, paraquat, atrazine and 2,4-D (AgrNews, 2012). China is also known as the biggest production country of chlorinated paraffins, and also PFOS.

PFOS seems to be an interesting example of PTS of regional concern in NOWPAP. Majority of PFOS had been produced in US and Europe until 2002. After phasing out of its production, global demand of PFOS is now supplied by China. PFOS has been used in many advanced industries, including electronic devices production and high quality textile production, which have been developing and are very active in East Asian countries. This may be at least part of the reason why PFOS emission inventories or its environmental levels in East Asian countries are among higher groups in the world. PFOS is also known to be highly soluble in water, and is unique to show distinct environmental behavior and strong potential to contaminate water environment. There are also a series of perfluorochemicals with different structures which have been produced and used for similar purposes. They are frequently used as derivatives rather than free chemicals, and analysis of their total levels (including derivatives) needs further research. Further research will also be needed to assess their health and / or environmental effects as a whole.

Another group of chemicals of potential concern include unintentionally produced chemicals, particularly as by-products during the synthesis of other chemicals. Dioxins, for example, were produced in the synthetic process of several OC chemicals or chloro-alkali process as stated above. Recently several incidences of unintentional PCB or other organochlorine production have been reported, including detection of unreacted DDT in dicofol (Qiu et al., 2005), unintentionally produced PCB and HCB in chlorinated paraffins (Takasuga et al., 2012), and PCB contamination in several pigments and silicone glue (Anezaki & Nakano, 2013). East Asia is now major

producers and users of various halogenated chemicals, and potential impacts of their impurities, in addition to the chemicals themselves, need further attention and research.

The western coast of the northern part of NOWPAP seas can be divided into four regions according to the pollution loads: (1) Amur Lagoon, (2) northern region, (3) central region, and (4) southern region of Primorsky Krai. Water composition in the Amur lagoon is influenced to a great extent by the Amur River. In the lagoon waters, there is a high concentration of detergents, petroleum hydrocarbons and heavy metals.

In recent years, the development of oil industry in the territory of the Northern Sakhalin and its shelf has caused serious concerns regarding the state of marine ecosystems. Crude oil and petroleum are the main emergent substances in this region. Southern-western coastal waters of Sakhalin are the active shipping area with polluted by diesel waste, heavy metals and detergents.

In the northern region - from the Zolotoy Cape to Povorotny Cape - the major sources of pollution to coastal waters are ore-mining and ore-chemical production. The largest operations are located near Rudnaya and Zerkalnaya Bays. Pollutions include large quantities of heavy metals (Pb, Zn) and As, as well as other chemicals in dissolved and suspended forms.

In the southern region –Peter the Great Bay – large volumes of wastewater get into marine environment untreated. Sewages contain many domestic and industrial pollutants, including pesticides. Razdolnaya River entering the Bay brings various pesticides coming from agricultural regions of Primorsky krai. Detectable concentrations of DDT, HCH and PCB were revealed in bottom sediments of estuaries of several rivers running into the Bay.

In the southern–western region in the Tumen River mouth the detectable level of DDT and HCH was recorded. The impact of the tailings discharged into the Tumen River on the marine biota is considerable.

Another natural resources production area is Bohai Bay, which is located near the south-western edge of NOWPAP region. Bohai Bay is reported to be the largest oil and gas production base offshore in China. In Japan, a small scale oil production was once conducted from Niigata to Akita prefectures, both of which faced to central NOWPAP area, but stopped operation years ago. Maricultures are active within bays or Seto Inland sea areas as well as Pacific side of northern Japan, while they are not so actively conducted along NOWPAP area. Agricultural activities as well as industrial and other activities from ordinary life may have potential sources of environmental impacts to the NOWPAP marine environment.

In summary, regionally specific PTS may be grouped in the following lists;

* Residues and other secondary emissions from legacy POPs, i.e., those produced in the past and contaminated the terrestrial, coastal and off-shore environment. This group includes PCB, DDT and other OCPs, and organic tins.

- * Current production or usage of chemicals in or nearby the region. Particularly those produced or used relatively in large amounts, such as Chlorpyrifos or other current use pesticides, chlorinated paraffins, PFOS and other fluorinated chemicals, brominated or chlorinated flame retardants, etc., may need further attention to evaluate potential of their adverse effects to human life and environment properly.
- * Unintentionary produced chemicals. Some are produced in incineration or other high temperature processes, such as dioxins and PAHs, their derivative etc. Other compounds as by-products in the chemical production processes, on the other hand, also need attention. Chlorinated aryl chemicals, such as PCB isomers and polychlorinated benzenes, tend to be produced in various processes.
- * Large oil and gas production activity in the north-eastern and south-western edges of NOWPAP region. These facilities may have a potential to cause large pollution in / around the area with chemicals including PAHs.

In addition to the production amounts in NOWPAP region, long-range transport potential of chemicals should be taken into consideration for selecting regionally specific PTS. This aspect will be discussed further in section 3.3.1.

3. Characteristics of PTS sources, transport and ecotoxicological effects in the NOWPAP region (by the published data)

3.1. General information on PTS sources

PTS chemicals may be categorized into intentional and unintentional ones. Lifecycle of an intentional chemical includes its production, storage, transport to its usage sites, usage, and waste treatment process (dumping, incineration, recycling, etc.). Environmental emission may occur in each step. Unintentional ones, on the other hand, may be emitted into the environment at the time of production, or may be included in another intentional product and will contaminate the environment / human beings when the product is used.

10 intentional ones among the original 12 POPs are sometimes called “legacy POPs” due to the fact that majority of their production occurred in the past and stop now, and their past production and usage cause present contamination in the global environment / human beings. Among the new 11 POPs so far added to the Annexes, Lindane (γ -HCH), α -HCH, β -HCH and chlordecone are also in the category of legacy POPs while the other 7, including four brominated flame retardants, HxBB, Te/PeBDEs, Hx/HpBDEs, HBCD, an organochlorine pesticide, endosulfan, and a fluorosurfactant, PFOS (including its salts and PFOSF), have been used until recently, or even now. In the latter chemicals, except for the agrochemicals, emission from the production and usage may play major roles in the environmental emission of the chemicals, while the secondary emission from the contaminated soils, coastal sediments etc. as well as those already in the environment and moving around the globe are of primary concerns in the rest of POPs, i.e., “legacy POPs”. Another significant difference exists between the agrochemicals or other bioactive chemicals, which are intentionally used in open environment, and industrial chemicals, which tend to be used in closed condition or working / indoor environment or in commercial goods for personal uses. Industrial chemicals tend to have point sources, such as factories, waste dumping sites etc., though some recent POPs, such as PFOS, have been used in many different purposes, including personal goods, and thus may have diffusive or non-point sources, too. Brominated flame retardants are another group of chemicals with non-point sources due to their broad use in commercial goods and building materials of houses. They are also characteristic to have indoor exposure as major exposure occasion in contrast to legacy POPs which have been exposed mainly through food consumption, particularly fishes or other aquatic organisms. More detailed information of sources in each country will be given in the following sections. Major sources of POPs, i.e., those listed in Annex A to C of the Stockholm Convention, have been investigated in each Party and reported in the NIP (National Implementation Plan) under the Stockholm Convention. This will provide us with a solid basis for the compilation of PTS sources information. It should be noted, however, that the information in NIP is generally country basis and not always compatible with the geographical restriction of NOWPAP region. In addition to them, the information on some other chemicals may be available in PRTR databases in several countries. PRTR includes air and water emission data from each factory / office and thus will be useful to make a detailed map of emission sources in the region, though its quantitative precision is supposed to be not high due to voluntary nature of the reported

data from each factory / organization. In some countries, use of agrochemicals, such as pesticides, herbicides, etc., for agricultural purposes have been compiled in local district basis. FAO once made a compilation of usage of pesticides in each country of the world. This does not seem to be updated, however, and the reliability of the existing data is not clear. A tool-kit for estimating emission of unintentionally produced POPs is available for dioxins and furans to support NIP compilation, though this is meant to provide a simple and rough estimate of the production. There are also a number of scientific publications on the estimation of major emission sources of POPs and other chemicals. In the following section general description of the topics as well as the information in each country will be summarized.

3.2. Generation, use and discharge/emission

<Russia>

Contamination of the environment with PTS may come from point sources (industrial discharges and wastewater treatment plant effluents) or, more frequently, from diffuse sources (atmospheric transport and deposition), the major pathway for transfer of persistent organic pollutants to remote sites.

Russia has some shortage of reliable monitoring data on the PTS, programs on emission control, and adequate data quality control. Environmental management of chemicals and relevant research began some time ago. Studies of PTS concentrations in the environment and in human populations have been carried out periodically. Reliable data is very limited, but now Russia has established environmental standards to cover PTS.

Many industries in Russia continue to use technologies installed when the plants were originally built. Industry began to change rapidly in the 1990s. Industrial production in Russia has declined, many old industries have been closed or renovated and this process is resulting in new, profitable and more environmentally friendly operations. In 2000 -2012 years some new enterprises of oil and gas industry have been built in the region. These plants are able to produce PTS as components of wastewaters and emissions.

Some PTS entering the marine ecosystems in the Russian part of NOWPAP region are of terrestrial origin, and thus can be described as from land based sources. Three general terrestrial patterns are identified: 1) atmospheric; 2) via rivers; 3) direct flow into the sea via dumping, sewages and storm water runoff. Atmospheric pollutants include materials that are dropped with rain and snow.

Typical sources of coastal water pollution are domestic wastewater, industrial and agricultural wastewater, and natural loads. There are two types of discharge of wastewaters: point and non-point. Point sources include constantly existing streams and sewage outlets where the direct measurements of the discharge are possible. The non-point sources include temporary streams, farmland and urban surface runoff, livestock production. Both point and non-point sources are present in the Russian part of

NOWPAP region. Most wastewater sources have not been treated well before discharge; however, certain amount of sewage directly discharged into the sea.

The discharge of wastewaters within Primorsky Krai – the major Russian provinces faced to the NOWPAP area is provided by different kind of economical activities. The electricity and heat production is a main activity in terms of wastewater discharge. Municipal water usage, treatment and discharge are second ones. Other activities generate and discharge less than 15% of total amount of wastewater. The agriculture, coal production and transport become most significant source of pollution, at the excluding of power generation and municipal water usage.

Based on 2002 -2010 data, the air in Primorsky Krai and other territories of region was mostly contaminated by NO_x and benzo(a)pyrene.. The main sources of air pollution are emissions from industrial enterprises (including thermal power plants) and from automobiles. PTS concentrations in the air are not control.

Data on PTS in river and marine waters are limited. The use of data on PTS concentrations in bottom sediments and in mollusks might be an alternative way to assess the impact of land based sources on coastal marine areas. Data on PTS concentrations in sediments and marine organisms are more readily available. Elevated PTS concentrations (DDT, HCH and PCB) have been detected in a wide range of environmental media and aquatic biota. Other PTS such as aldrin, dieldrin, endrin, chlordane, mirex, toxaphene and heptachlor have not been used in the Russian Federation.

Organotins are the component of anti-fouling paints which have been used in ships, fishery nets and in various coastal constructions. Organotins are toxic substances which are able to accumulate in bottom sediments around dockyard or other harbor facilities. Biological effects of organotins appeared in imposex formation in marine organisms, gastropod especially. Active marine transport in the coastal waters of Primorsky krai (Peter the Great Bay and others) and in adjacent sea implies the occurrence of organotins in Russian area of NOWPAP region. However, we do not know any relevant data on organotins level in marine environment in this area.

The discharge of wastewaters is the main source of PTS entering the coastal waters in the Russian part of NOWPAP region. The volume of wastewater generated and discharged in 2002 in Primorsky Kray was 398 million m³, and reached up 407.3 million m³ in 2007 (Natural Resources and Protection of Environment..., 2007), or 1.17 to 1.00 million tons/day, that is rather stable. Thus the distinct trend of decrease was observed (Figure 3-1).

This volume of wastewaters looks not so big in accordance with relatively low absolute population in the part of Russia under consideration. But amount of waste waters generated by capita reaches up in the Primorsky Krai 266 tons/person/year that is twice comparing with Korea and China. It means that local hot spots are likely possible at the Russian part of NOWPAP area despite the low population density. Sewage from the region's largest city, Vladivostok, accounts for 84% of this amount. Expert

assessment adds an additional 138 million m³/year of waste and storm water from the Vladivostok area and 21million m³/year from the rest part of region as storm water run-off. An assessment of annual direct input can be made accounting for the concentrations of some chemical substances in waste and storm water run-off.

Thousand tons

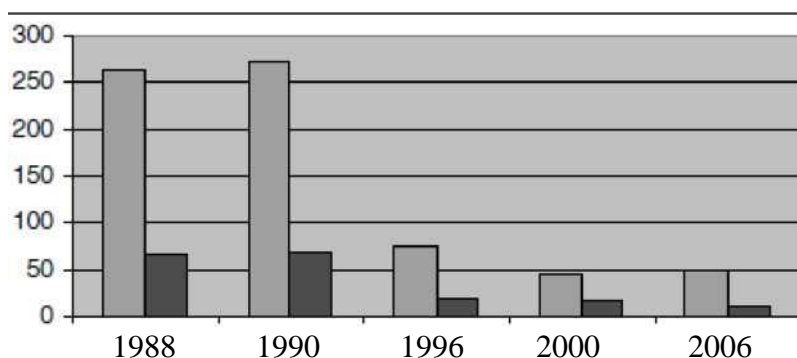


Figure3-1. Annual amount of wastewaters discharged to Amursky bay (grey bar) and Ussuriisky bay (dark bar) from Vladivostok and its suburbs in 1988-2006 (Nigmatulina,2007).

The annual discharge of domestic wastewater in Primorsky Krai in 2007 was about 0.132 bln. tons, and about 41% of this amount is discharged untreated and 19% is only partially treated. The annual discharge of industrial wastewater in Primorsky Krai in 2007 was about 0.25 bln. tons, with 94% of this volume discharged untreated. Fortunately, 93% of this untreated industrial wastewater is cooling water from electric power stations that release pretty low levels of contamination. Information on direct input of contaminants in Russia is gathered from official data on municipal and industrial waste volumes and on expert assessment. The annual discharge of wastewaters in Primorsky krai in 2008 – 2010 are presented in Figure 3-2.

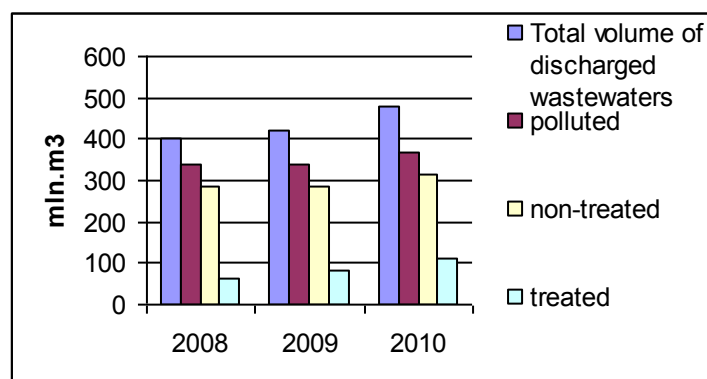


Figure 3-2. Wastewater discharge, million m³/year, in Primorsky krai in 2008-2010 (Report..2012)

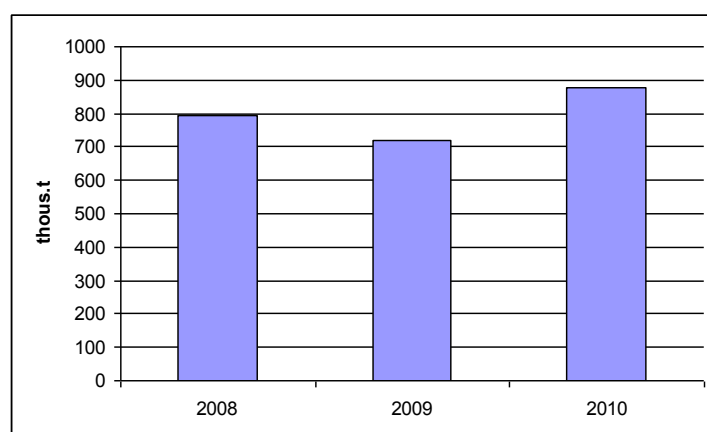


Figure 3-3. Total amount of contaminants, thous. t, discharged with wastewaters in Primorsky krai in 2008-2010 (Report...2012)

Last years the total volume of wastewaters and amount of contaminant increased slightly, it reflects the industrial development in Primorsky krai (Figure 3-3).

Wastewater volume does not exceed 1-2% of river runoff, but contribution of pollutant inputs due to wastewater reaches up 20% for BOD and 46-50% for ammonia and petroleum hydrocarbons. Second point is a very contrast spatial distribution of wastewaters discharge: The Vladivostok-Artem-Ussurisk agglomeration locates on the south of Primorsky krai gives 88% of wastewater inputs of pollutants (Table 3-1).

Table 3-1. Wastewater discharge from the different industry to the Amursky and Ussuriisky bays in 2007 (Nigmatulina, 2007)

	Amursky Bay		Ussuriisky Bay	
	Total volume, thous.m ³ /years (number of enterprises)	%	Total volume, thous.m ³ /years (number of enterprises)	%
Municipal water usage	52011 (13)	88,5	13528 (9)	82,3
Power generation	2286 (8)	3,9	436,4 (1)	2,7
Military	59,7 (2)	0,1	225 (4)	1,4
Railway transport	415 (5)	0,7	--"--	--"--
Auto transport	28 (2)	0,1	--"--	--"--
Industry enterprises	2693 (22)	4,6	2017 (16)	1,3
Agriculture	1320 (16)	2,2	228 (5)	1,3
Total	58815 (68)	100	16437 (35)	100

PTS concentration in wastewater and wastes are not analyzed specifically, but these chemicals can be generated in each industry and entering the river and marine environment.

Official data on the waste dumping at the Russia within NOWPAP area are absent. The main part of dumped waste consists of dredged sediments. Negative influence of this material on the coastal waters connected with elevated concentration of pollutants because dredging operations at Russian Far East are carried out in the harbor areas with usually contaminated bottom sediments. There are experimental data on polluted grounds dumping impact on ecological conditions in coastal waters around Vladivostok. The grounds were excavated in the highly polluted Golden Horn Bay in 1970-1983 and moved to Amursky bay or Ussuriisky bay, where the dumped sediments could be transported on vast distance from the site of dumping under influence of water dynamics with accumulation of pollutants both in deeper part of the bays and in their coastal zones. Inputs of sediments with high concentrations of pollutants, petroleum hydrocarbons mainly, is considered as a cause of the rise of negative processes in bottom water layer. Petroleum biotransformation with microorganisms leads to appearance of various toxic substances in seawater which affect marine organisms (Mishukov et al., 2009).

Municipal and industrial wastes in Russia are kept on the landfill directly or after incineration. Emission of gases from landfill may be sources of PTS.

Dioxin (PCDD) and furan air concentrations are determined on the Asian part of Russian Federation (RF) territory (ATR), as compared to the European part of RF (ETR). Dioxin emission was 225 g TEQ in ATR and 839 g in ETR in 2010 (State report 2011).

At the same time air pollution and air transfer are the important sources of PTS drop to marine environment. Air pollution in Russia in 2005-2010 has not increased significantly. Roshydromet monitoring services control benzo(a)pyrene (BaP) emission in major cities. In Primorsky kray BaP level exceeded MPC in 5 cities – Vladivostok, Nakhodka, Ussuriisk, Spassk, Partizansk. (Fig.3-4, Table 3-2).

The main sources of air pollution are emissions from industrial enterprises (including thermal power plants) and from automobiles. Emission of power stations is more than 50% of total emission. Annual emission of auto transport in 2010 was 176,8 thous. t, or 76% of industrial emission (Report...2012).

Among POPs, dioxins, furans, PCB, HCB have unintentional sources of air pollution. Major sources of dioxin emission and contamination are known to be processes like waste incineration, metal production, bio-fuel incineration and uncontrolled combustion, for example fires at landfill sites. The European regulations stipulate that air emissions should be less than 0.1 ng TEQ/Nm³.

Dioxin emission has been evaluated in European part of the territory of Russia (ERT) only. Total drop of TCDD and furans in 2008 was estimated as 1958 g TEQ. Of this

amount 1057 g were caused by Russian and foreign anthropogenic sources, and 901 g (46%) due to natural sources, fires mainly. Dioxin drop from Russian sources to the

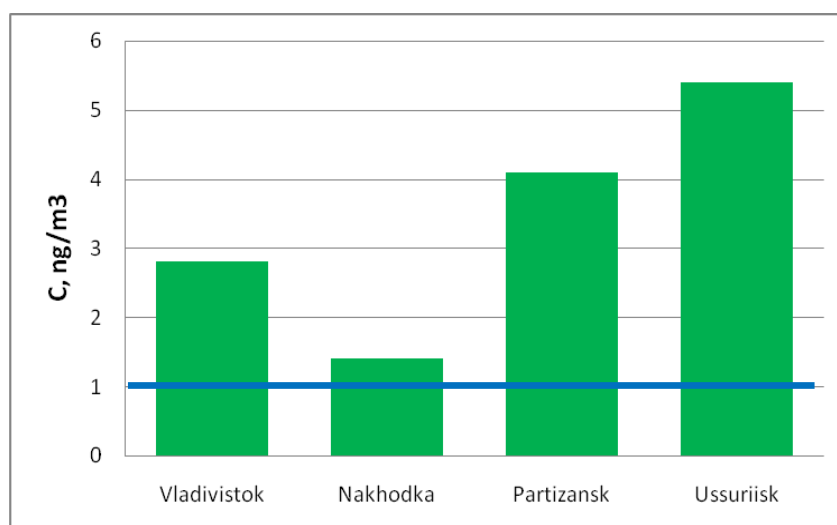


Figure 3-4. Benzo(a)pyrene concentration (C, ng/m³) in the air of industrial cities of Primorsky krai in 2010 (Report...2012). MPC of benzo(a)pyrene in Russia is 1 ng/m³.

Table 3-2. Emission of toxic substances (thous.t) to atmosphere from industrial enterprises in Primorsky krai (Report...2012)

Substances	2009	2010
Total	226,1	232,8
Solid particles	83,7	86,1
Toxic hydrocarbons	2,5	3,1
Organic volatilities	-	3,2

Asiatic part of territory of Russia was 221 g TEQ, and to European part of territory of Russia – 664 g (State report ...2011).

<China>

In China, POPs monitoring in recent years found that the concentration of residual pesticide POPs is relatively high in water bodies of a small number of estuaries, and that the concentration of pollution caused by POPs is relatively high in the soils of wastewater irrigated farms, vegetable plots and sites of pesticide POPs production and storage. Relatively high concentrations of Dioxins were detected in the organisms, sediments and soils around a few lakes in central and east China, and the sediments in

some maritime zones of the East China Sea and Yellow Sea. In sodium pentachlorophenol contaminated areas and schistosomiasis affected areas, Dioxins levels in human blood samples and human breast milk samples were found to be higher than those in persons in other areas. But due to lack of the systematic monitoring and risk assessment, it's still hard to determine impacts of POPs on China's ecological environment and public health (National Implementation Plan (NIP) of China, 2007).

Pesticide POPs in Annex A of the Convention

Pesticide POPs in Annex A of the Stockholm Convention include: Aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene. There are 45 enterprises in China that produce the pesticide POPs from Annex A of the convention (including primary production and formulation plants), which are located in 18 provinces and municipalities of China (Fig 3-5).

Production and use of toxaphene and heptachlor were stopped in the 1970's, and the production and use of hexachlorobenzene were stopped in 2004. Currently, chlordane and mirex are still in production and use, mainly for termite prevention and control in buildings.

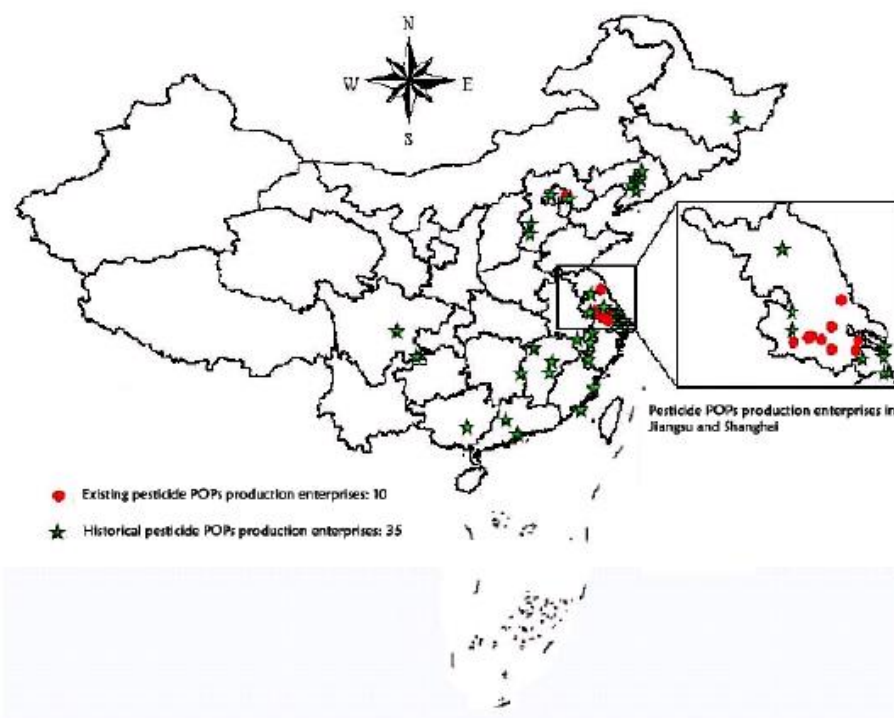


Fig. 3-5 Distribution of enterprises producing pesticide POPs in Annex A

By the end of 2004, China had produced a total of 110,000 tons of pesticide POPs from Annex A of the convention, of which about 30,000 tons were directly used in field as agricultural pesticides for pest prevention and control, in termite prevention and

control and in disease control, and about 80,000 tons of hexachlorobenzene were used as raw materials in the production of pesticides (sodium pentachlorophenate (Na-PCP) and pentachlorophenol (PCP) and some was exported. Table 1 presents the production and use situation of enterprise producing pesticide POPs listed in Annex A of the Convention. Table 2 gives the basic situation of other pesticide POPs that were never produced or the production of which has stopped (NIP of China, 2007).

Table 3-3. Production situation and uses of pesticide POPs in Annex A at the end of 2004

Type	Production capacity (tons/year)	Output (tons/year)	Import/export (tons/year)	Number of production enterprises	Highest historical output (tons/year)	Accumulated output (tons)	Uses
Chlordane (Crude oil)	1,760	363	0	5	843(1999)	-9,000	Termite control
Mirex	677	15	0	3*	31(2000)	-160	Termite control

Table 3-4. Basic situation of other pesticide POPs that were never produced of the production of which has stopped

Type	Status	Highest historical annual output (tons, year)	Accumulated output (tons)	Usage field in the past
Hexachlorobenzene	Used to produce, stopped in 2004	7,365(1990)	>79,278	PCP raw materials
Toxaphene	Used to produce, stopped in the 1980s	3,740(1973)	20,660	Agriculture (grain and cotton production)
Heptachlor	Used to produce, stopped in the 1980s	11(1968)	<100	Railway crossties
Aldrin	Used in research, never produced in scale			
Dieldrin	Used in research, never produced in scale			
Endrin	Never researched, produced or used			

Especially, the Chlordane distribution related to the NORWAP region in China are given in Tab 3-5.

Tab. 3-5 Chlordane use distribution from 1997-2001

Province	Annual Consumption (tons)					Five years accumulated consumption (tons)
	1997	1998	1999	2000	2001	
Liaoning	1	0	0	0	0	1
Jiangsu	86.2	111.1	103.4	96.4	78.8	475.8
Shandong	0.4	0.4	0.4	0.3	0.3	1.8

PCBs from Annex A of the Convention

The production of PCBs oils began in 1965 in China and there were 4 production enterprises. The production was gradually stopped from 1974 to the 1980's. According to preliminary investigation and analysis, the accumulative production output was about 7,000 to 10,000 tons. PCBs oils can be used to produce many kinds of PCBs-containing products. PCBs usage is divided into three categories (according to the extent of contact of PCBs in products with the outside): closed use (such as capacitors, transformers and current stabilizers), semi-closed use (such as heat transmission oil, hydraulic oil and vacuum pump oil) and open use (such as printing ink, dope and fireproofing paint). There were 11 enterprises producing the aforementioned PCBs-containing products before 1980, of which 3 produced PCBs-containing electrical capacitors, and 8 produced PCBs-containing paint. All of them stopped production in the beginning of the 1980's.

Preliminary investigations show that out of all PCBs produced in China, about 1000 tons were for open use such as paint additives, about 6000 tons were used as an impregnate for electrical capacitors, and the rest needs further verification. The capacitors were YL, YLW series power-factor correction capacitors, CL series serial capacitors, and RLS and RLST series electrical heating capacitors. According to technical requirements on PCBs-containing capacitors in the 1970's, it is estimated that each capacitor contains 10-15 kilograms of PCBs oil and hence the accumulative output of PCBs-containing capacitors was about 500,000.

During the 1950's and the 1980's, China used to import PCBs-containing electrical equipment from other countries without being informed, most of which were specific transformers and capacitors for large facilities. The imported PCBs-containing electrical devices were mostly distributed in large enterprises and the rest were distributed in the electrical power sector. At present, it is beginning to be found that there were PCBs contained in about 500 capacitors (already discarded) and about 50 transformers (already discarded) in the electrical power sector; but the data for most imported PCBs-containing electrical devices, possibly in large enterprises in the non-power sector, are not available. Distribution of identified enterprises producing PCBs

oils, PCBs-containing electrical equipment and PCBs-containing paint can be seen in Fig. 3-6 (NIP of China, 2007).

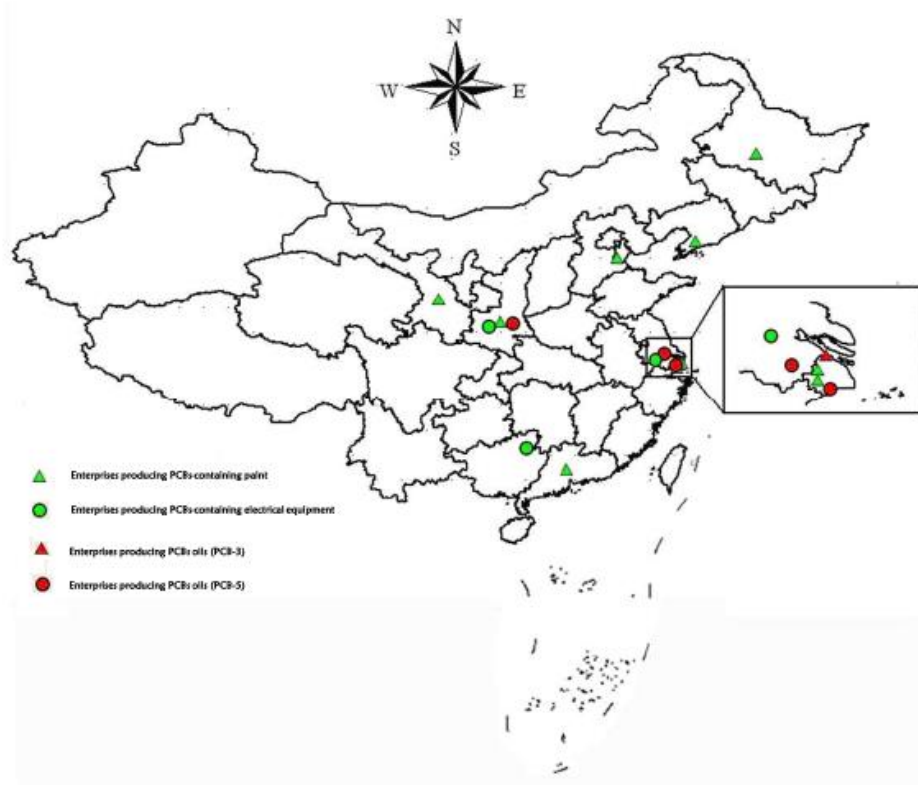


Fig. 3-6 Distribution of identified enterprises producing PCBs oils, PCBs-containing electrical equipment and PCBs-containing paint

PCBs-containing devices in use include PCBs-containing capacitors and transformers. Existing investigation results show that PCB-Containing electrical devices in use in China are capacitors, most of which exist in different types of large enterprises and institutes of the non-power sector. At present, there are about 460 PCBs-containing capacitors found in use in the power sector of the whole country. Because of the extent of sectors involved, the large number of enterprises, the weakness in management, and the long time period, investigations have encountered great difficulties concerning PCBs-containing capacitors in the non-power sector of China. Investigations in Liaoning, the demonstration province, show that there are about 554 PCBs-containing capacitors in use in the non-power sector in the province, the distribution of which is shown in Fig. 3-7.

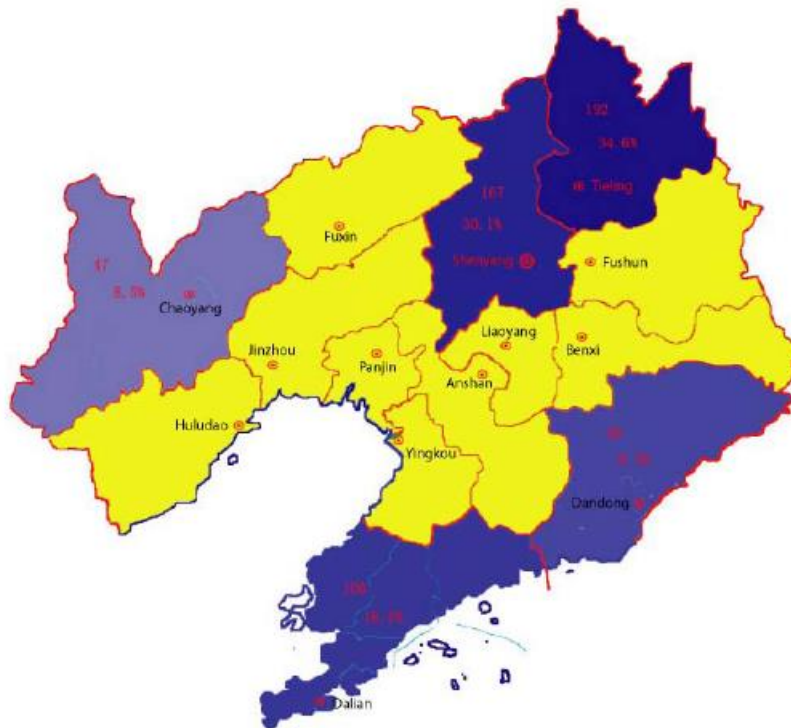


Fig. 3-7 Distribution of PCBs-containing capacitors in use in the non-power sector in Liaoning Province

Chemicals from Annex B of the Convention, DDT

China began producing DDT in the 1950's, and there used to be 11 production enterprises. The highest annual output was 21,164 tons and the cumulative output by 2004 was 464,000 tons. Figure 2-10 shows DDT production over the years. Since the State Council decided to stop DDT production in the whole country in 1983, there remain only two enterprises producing technical grade DDT and one enterprise producing DDT preparations. Since 1995, the output of technical grade DDT in China has been maintained at the level of 5,000-6,000 tons/year, and the output in 2004 was 3,945 tons.

China stopped large scale production and agricultural application of DDT in the 1980's. In the disease control field, DDT was used to kill mosquitoes and pests in the malaria prevailing areas (mainly in the south of the Yangtze River) by the indoor residential spraying method. But since 2001, DDT has not been used in normal disease control. In 2004, DDT was used as the intermediate in dicofol productions, which accounted for more than 73% of the total national use amount. Some was exported for disease vector control, accounting for about 23% of the total, and a little was used in antifouling paint, accounting for about 4% of the total.

Currently, there are 3 to 5 enterprises producing technical grade dicofol, one of which basically produces dicofol with self-produced DDT in a closed system. The

annual output of dicofol of the whole country is about 3,000-4,000 tons. Besides that, there are about 19 antifouling paint production enterprises using DDT as the additive, with the annual average consumption of about 250 tons.

From 1998 to 2004, there were some DDT exports each year, but there was no DDT import. DDT was mainly exported to Africa and Southeast Asia for malaria prevention and control (NIP of China, 2007).

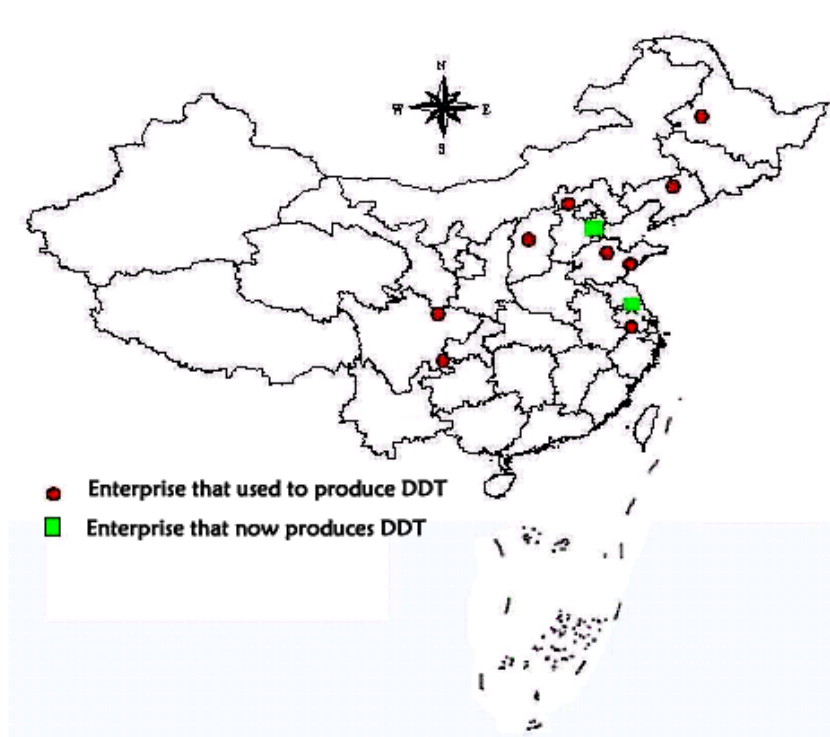


Fig. 3-8 Distribution of DDT production enterprises

The chemicals listed in Annex C of the Convention, Dioxins

Due to great discrepancies of industrial enterprises in scale, technology, management, pollution control facility, environmental protection awareness, etc. , and release status of each source, monitoring data on Dioxins releases and pollution research, are quite insufficient in China.

Research showed that the local combustion might be the main contributor of PCDD/PCDFs sources in Anshan, Liaoning Province. Polyurethane foam (PUF)-disk based passive air sampling were used to collect samples in a big steel industrial park of Anshan, Northeast China from June 2008 to March 2009 (Li et al, 2011). The levels, seasonal variations and potential sources of PCDD/Fs, PCBs and PBDEs in the atmosphere around the steel industrial complex were investigated, and potential contribution of these three groups of persistent organic pollutants (POPs) from iron and

contribution of these three groups of persistent organic pollutants (POPs) from iron and steel production was also assessed. The air concentrations of $\Sigma 17\text{PCDD/Fs}$ (summer:0.02-2.77 pg m^{-3} ;winter:0.20-9.79 pg m^{-3}), $\Sigma 19\text{PCBs}$ (summer:23.5-155.8 pg m^{-3} ;winter:14.6-81.3 pg m^{-3}) and $\Sigma 13\text{PBDEs}$ (summer:2.91-10.7 pg m^{-3} ;winter:1.10-3.89 pg m^{-3}) in this targeted industrial park were relatively low in comparison to other studies, which implied that industrial activities of iron and steel had not resulted in serious contamination to the ambient air in this area. On the whole, the air concentrations of PCDD/Fs in winter were higher than those in summer, whereas the concentrations of PCBs and PBDEs showed opposite trends. The results from principal component analysis indicated that coal combustion might be the main contributor of PCDD/F sources in this area.

The sources of other PTS

The sources of other PTS and POPs were discussed in some literatures. Distribution of PAHs in surface seawater of Qingdao coast area and their preliminary apportionment were studied (Li et al, 2012). Total 15 PAHs concentrations have been quantified by solid phase extraction-high performance liquid chromatography with fluorescent detection. The results showed that the concentrations of total PAHs correlated strongly with dissolved organic carbon concentrations ($R=0.9447$) in surface seawater. The two ratios of paired PAH isomeric compounds, fluoranthene to fluoranthene plus pyrene, and anthracene to phenanthrene plus anthracene, for source apportionment suggested that various petroleum related sources, such as oil spill and petroleum combustion, were the major origin at most sampling sites, except in clean areas where PAHs were predominantly derived from coal and wood combustion. Contents and distribution characterizations of PAHs, PCBs, and OCPs in the sediments collected from the southern Shandong Peninsula coastal area were discussed using gas chromatography-mass spectrometry (GC/MS) analysis method (Wang, 2010). Results showed that the concentration of PAHs in the surface sediment decreased gradually from the inshore area to the offshore area. According to the ratio of P/A and FL/PY, the release from fuel combustion was one of the most major source of PAHs in this area. The concentrations of PCBs and OCPs in the surface sediment also decreased from the inshore to the offshore area. The HCHs data showed the area was polluted by agricultural and industrial activities at the same time. There were only a few DDTs imported into the area in the recent years, and DDTs were decomposed by aerobic microorganisms in surface sediment.

Scientific reports have been published recently on the estimation of PFOS production, usage and environmental emission in China (Lim et al., 2011, Zhang et al., 2012, Xie et al., 2013). Estimation of changes of annual PFOS production in China are shown here (all re-drawn based on the data reported in the reports). Although there are some inconsistencies as for the recent trends of PFOS production, all estimated c.a. 250 t/a of PFOS production in middle 2000's, and a total cumulative production of 900 to 1,800 tons until now.

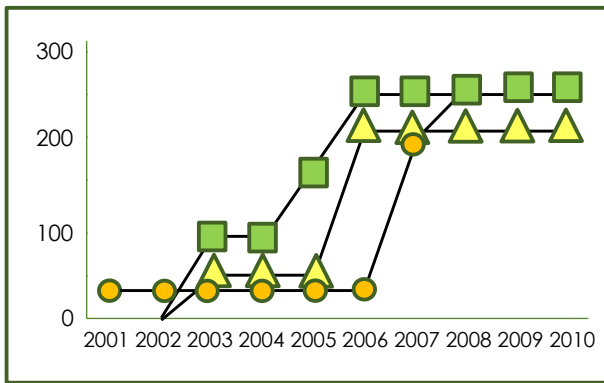


Figure 3-9 PFOS production estimate (based on Lim et al., 2011)

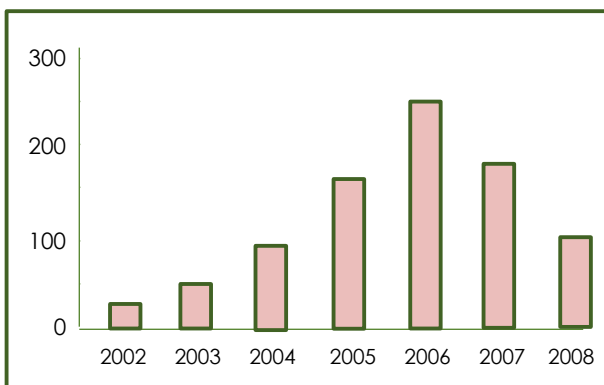


Figure 3-10 PFOS production estimate (based on Zhang et al., 2012)

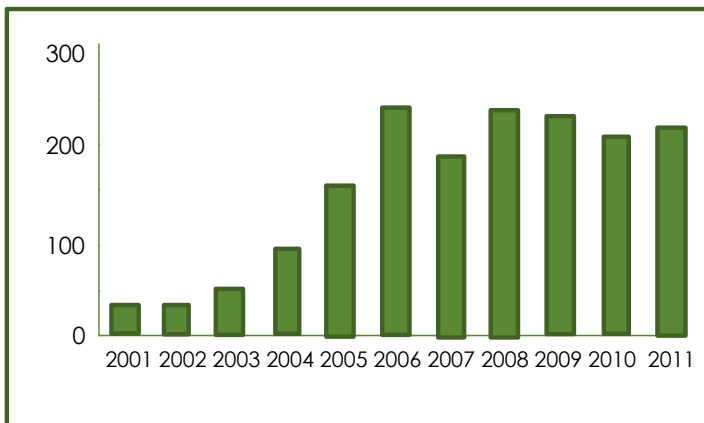


Figure 3-11 PFOS production estimate (based on Xie et al., 2013)

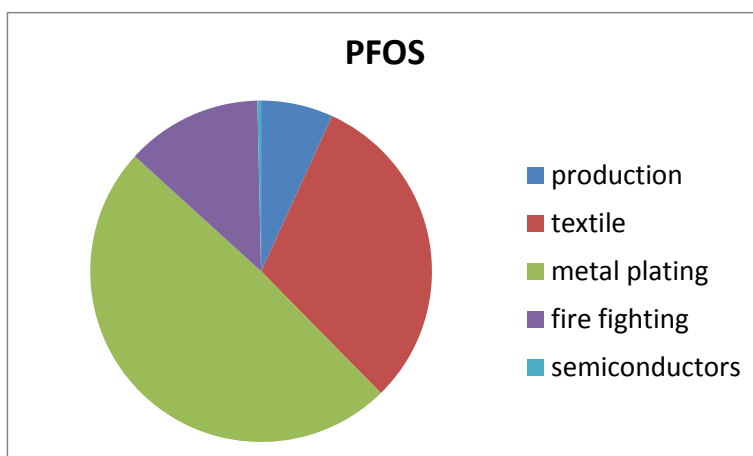


Figure 3-12 Emission estimate of PFOS from each industrial sector in China (based on reported data in S. Xie et al. 2013)

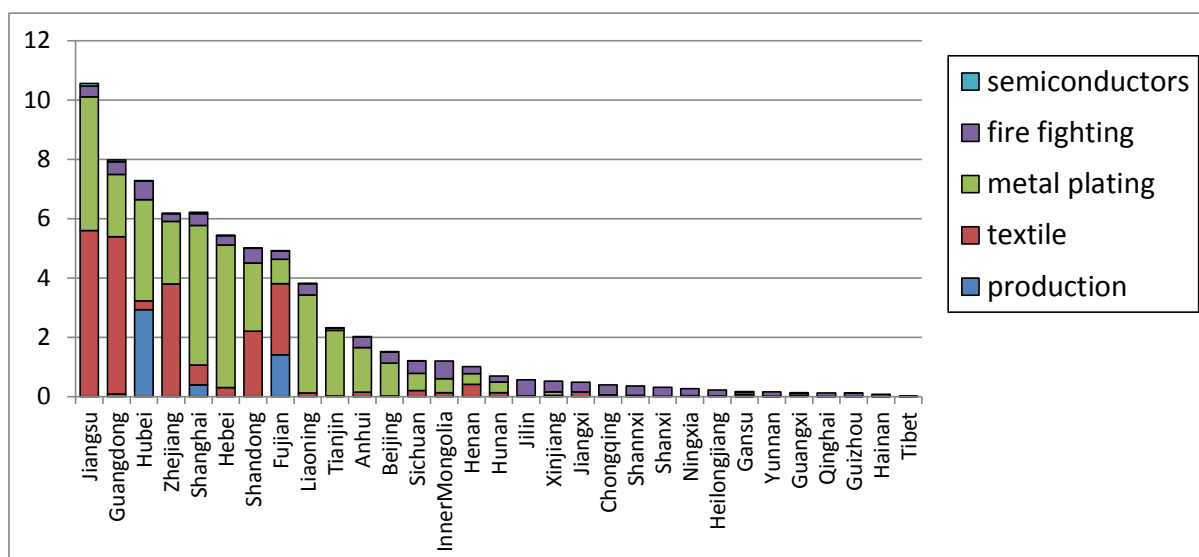


Figure 3-13 Emission estimate of PFOS from each industrial sector in various provinces in China (based on reported data in S. Xie et al., 2013)

<Korea>

The Korean Ministry of Environment has launched a nationwide inventory project, to identify the sources of PCDD/F and dioxin-like PCB emissions into the atmosphere. In 2001, the annual emission of PCDD/Fs and dl-PCBs from various sources was estimated to be 1219–1233 g/year as the World Health Organization (WHO)-toxic equivalent (TEQ) values in 1998. The main source of dioxins in Korea was found to be municipal solid waste incinerator, which account for about 85% of the total TEQ emissions. The second most important source is the steel industry, with a contribution of about 9.2% of the total TEQ emissions. The dl-PCBs contributed about 8.3–10.8% of the total emissions of these compounds. Therefore, the major source of PCDD/Fs in Korean environments could be summarized with emissions from incinerators and steel industry (Moon et al., 2008a).

In South Korea, approximately 4300 tons of PCBs were used until the 1990s and approximately 3600 tons of various OCPs were used for agricultural purposes until the 1980s (Kim and Smith, 2001). Although Korean government prohibited production, use and application for all the OCPs under Stockholm Convention, these contaminants are still present in coastal environments (Hong et al., 2006; Moon et al., 2009a; Choi et al., 2010a; Moon et al., 2010a; Park et al., 2010; Choi et al., 2011a) and are found in humans (Moon et al., 2012a). Among OCPs, HCB was not used for agricultural purposes in South Korea and the occurrence of HCB seems to be associated with long-range transport from neighbor countries (Japan and China) and incineration activities.

Brominated flame retardants (BFRs) are not produced in Korea but are imported from various countries (KEI, 2001). The use of flame retardants has been steadily increasing, by approximately 10% per year for the last two decades (KEI, 2001). Total consumption of BFRs, within the total flame retardant market, was approximately 56% (KEI, 2001). The consumption of BFRs in Korea in 2002 was 49,050 tons (KISTI, 2002); deca-BDE accounted for a major proportion (25%; 12,324 tons), while penta-BDEs and octa-BDEs collectively accounted for only a minor proportion (0.2%; 84 tons) of the total BFR market (KISTI, 2002). According to a report by Watanabe and Sakai (2003), total deca-BDE consumption in Asia was 24,050 tons in 2001, indicating that about 50% (12,324 tons) of the total deca-BDE demand in Asia was in Korea. The rapid growth of the electronics market in Korea could explain the increase in demand for PBDEs.

There has no consumption data available on PFCs in South Korea. However, the consumption pattern would be similar to worldwide production trends. The worldwide production of perfluorooctane sulfonyl fluoride (PFOSF) was estimated to be 96,000 tons during the period 1970–2002, and the current inventory of PFOS in ocean surface waters is estimated to be 235–1770 tons (Yamashita et al., 2005).

According to the investigation of Korean Ministry of Maritime Affairs and Fisheries (MOMAF) from 1999 to 2001 (MOMAF, 2003), the production of tin based antifouling paint stayed a plateau from 1998 (4,139 ton) to 2000 (4,279 ton) and then began to decrease in 2001 (3,596 ton) after partial ban of the use of trialkyltin based paint on ship < 400 ton in Korea. By contrast, production of tin-free antifouling paint steadily increased from 8% of total amount of production in 1998 (373 ton) to 38% in 2001 (2,229 ton). Owing to the recommendation from the International Maritime Organization (IMO), the Korean government decided the restriction on use of TBT-based antifouling paints in March 2000 and then their use was totally banned in November 2003.

<Japan>

In Japan, 59,000 t of PCB was produced until 1972, among which 54,000 t was estimated to be used domestically (5,300 t was exported while 1,000 t was imported in the period). Domestic use included 37,100 t of transformer or condenser oils, 5,400 t of non carbon duplicating papers, 8,600 t of heating oils and 2,900 t of other purposes. After ban of PCB production and new usage, the Law concerning special measures

against PCB waste was established, and government asked companies to register and keep PCB containing transformers or other electric equipment while collected and stored other PCB containing goods. Decomposition of PCB oil (5,500 t) was first conducted by incineration (1987~1989). Due to increased concerns about harmful by-product formation, non-incineration processes, including chemical dechlorination (sodium dispersion method), plasma melting decomposition method, hydrothermal oxidation decomposition method and catalyst hydrothermal dechlorination method, had been developed and employed for the decomposition of PCB from 2004. Five facilities have been constructed at Kitakyushu, Toyota, Tokyo, Osaka and Hokkaido for the process. During the long-term storage, part of the stockpile (0.1 ~ a few %) was lost due to bankrupts or other reasons. Additionally, 30 among 3,495 transformers and 88 among 37,652 condensers in the affected Tohoku areas were lost by the great East Japan earthquake and Tsunami in March 2011.

All the POPs agricultural chemicals are now banned in Japan. After the ban, these chemicals were buried underground until the destruction methods are established. Ministry of Agriculture, Forestry and Fisheries conducted survey of buried agrochemicals in 2001, and identified 4,400 t of POPs agricultural chemicals all over Japan. Among them 2,200 t was decomposed until 2008, and 1,800 t was decomposed until 2012. Now 400 t is kept under control. Majority of POPs agricultural chemicals, however, were already used in the environment.

Table 3-6. Amounts of POPs agricultural chemicals used in Japan (MOE 2002)

Name	total usage amounts (year range)	additional information
Aldrin	2,500 t (1958-1972)	all imported
Dieldrin	673 t (1958-1972)	all imported
Endrin	1,500 t (1958-1972)	all imported
DDT	45,000 t (~1970)	total domestic production
	21,800 t (1958~1970)	domestic use as agrochemicals
	21,700 t (1957-1971)	for pest control
Chlordane	240 t (1958-1970)	all imported (as agrochemicals)
	~11,900 t (1979~1986)	termite control
Heptachlor	1,500 t (1958~1972)	all imported
Mirex	never registered as agrochemicals	might be used as flame retardants
Toxaphene	never registered as agrochemicals	

Table 3-7 Emission estimates of other POPs

HCB	840 t (-1982)	Sakai et al., 2001
	1.9~68 t/a (1965: total)	impurities in PCP, PCNB, TCTP
	0.9~10 t/a (1995: total)	
Dioxins/furans	120 t	Masunaga et al., 2001
	200 t	impurities in PCP
	162 kg	impurities in CNP
		impurities in other herbicides

In 1990's, unintentional production of chlorinated dioxins and furans from incinerators and other high temperature processes became major environmental concern in Japan. Act on special measures against Dioxins was established in 1999, and extensive efforts have been conducted to identify major emission sources, quantify their levels, find and develop BAT/BEP, and reduce emissions. Emissions of dioxins/furans/dl-PCBs were estimated based on measured data of selected incinerators and other high temperature processes every year. Also extensive monitoring of atmosphere, water, soils and sediments have been conducted to assess effectiveness of measures and countermeasures against dioxins. Furthermore dioxins monitoring in human samples and selected wildlife have been conducted and reported by the government. The results of changes in emission inventories and environmental monitoring data are summarized in figure.

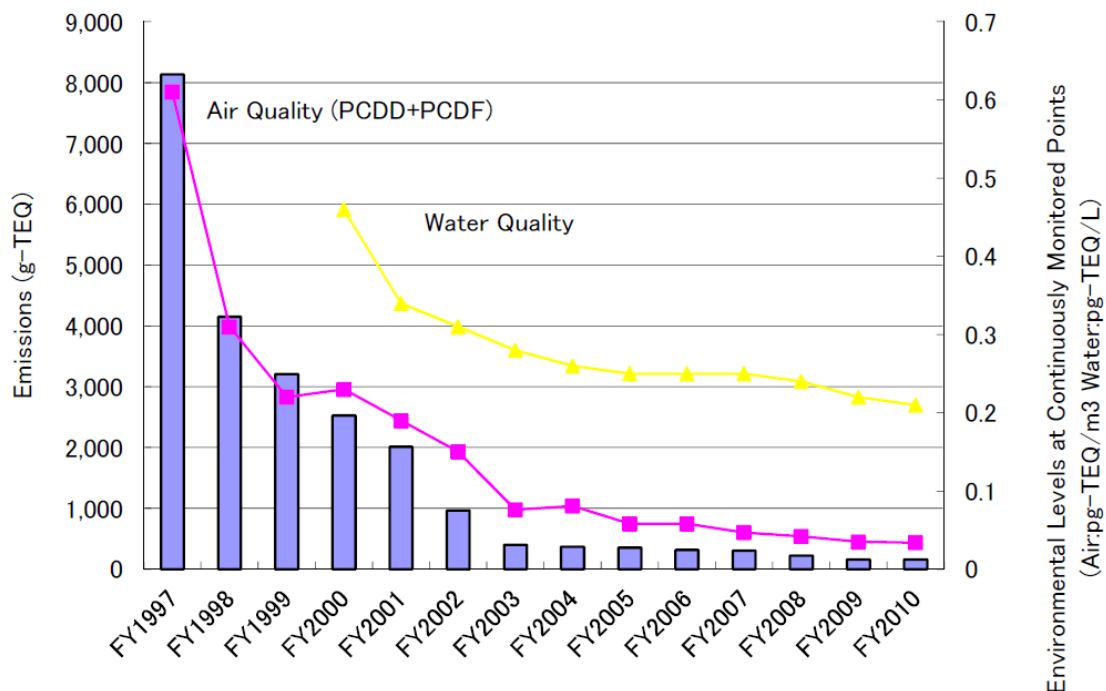


Figure 3-14 National dioxin emissions and environmental levels in air and water
Bar graph represents estimated emission inventories of dioxins.

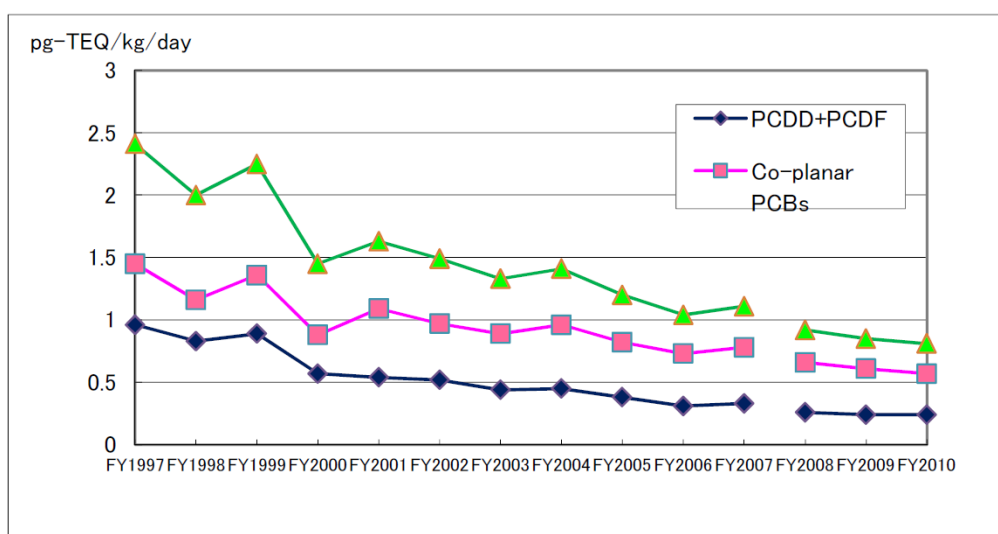
Atmospheric levels of dioxins are affected primarily by the emission inventory of dioxins to the atmosphere. As shown above, there has been quantitatively good correlations between estimated emissions (bar graphs; based on monitoring data of selected incinerators and other high temperature processes) and averaged atmospheric levels of dioxins, indicating that Japan could capture the pollution status precisely and quantitatively, and that dioxin management in Japan has been conducted successfully and efficiently to reduce the emission of dioxins to 158 ~ 160 g-TEQ, i.e., 1/50 of the 1997 levels during the last 13 years.

Table 3-7 National dioxin emission inventories in Japan

Sources of Dioxin Emissions	Total Amount of Dioxins Emission (g-TEQ/year)														
	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	
1 Fields of waste disposal	7205~	3355~	2562~	2121~	1689~	748~	219~	215~	213~	193~	182~	132~	102~	95	
	7658	3808	2893	2252	1801	771	244	237	237	218	200	137	103		
	"water"	5.3	5.3	5.3	2.5	1.5	0.87	0.60	0.65	0.36	0.78	1.6	0.6	0.7	
General waste incinerators	5000	1550	1350	1019	812	370	71	64	62	54	52	42	36	33	
	"water"	0.044	0.044	0.035	0.035	0.019	0.008	0.004	0.002	0.001	0.003	0.002	0.001	0.0021	
Industrial waste incinerators	1505	1105	695	558	535	266	75	70	73	63	60	42	33	29	
	"water"	5.3	5.3	5.3	2.5	1.5	0.86	0.60	0.65	0.36	0.78	1.6	0.6	0.7	
Small-scale waste incinerators	700~	700~	517~	544~	342~	112~	73~	81~	78~	76~	70~	48~	33~		
	1153	1153	848	675	454	135	98	103	102	101	88	53	34	33	
2 Fields of industry	470	335	306	268	205	189	149	125	110	93	100	80	54	61	
	"water"	6.3	5.8	5.8	5.0	1.8	1.2	0.93	1.0	1.0	0.75	0.8	0.5	0.3	0.6
Electric steel-making furnaces	229	140	142	131	95.3	94.8	80.3	64.0	49.6	39.5	50.2	33.0	20.1	30.1	
Sintering furnaces for iron and steel industry	135	114	101	69.8	65.0	51.1	35.7	30.4	29.3	21.2	20.5	22.5	9.1	10.9	
Facilities for recovering zinc	47.4	25.4	21.8	26.5	9.2	14.7	5.5	8.1	4.1	8.2	1.8	3.1	2.1	2.3	
	"water"	0.0036	0.0036	0.0036	0.0036	0.0036	0.0026	0.0066	0.0047	0.0018	0.00065	0.0014	0.0006	0.0004	
Facilities for manufacturing aluminum base alloy	31.0	28.8	23.1	22.2	19.7	16.3	17.4	13.0	15.2	12.9	15.6	11.3	14.6	8.7	
	"water"	0.34	0.068	0.093	0.056	0.082	0.024	0.029	0.011	0.008	0.027	0.023	0.009	0.008	0.011
Facilities for recovering copper	0.053	0.053	0.048	0.038	0.013	0.088	-	-	-	-	-	-	-	-	
Pulping process with bleaching	0.74	0.71	0.74	0.73	0.90	0.65	0.46	0.62	0.58	0.50	0.58	0.27	0.19	0.24	
	"water"	0.74	0.71	0.74	0.73	0.90	0.65	0.46	0.62	0.58	0.50	0.58	0.27	0.19	0.24
Other facilities	26.5	25.6	17.8	17.9	15.3	11.0	9.9	9.1	10.8	10.2	11.1	9.6	7.5	8.5	
	"water"	5.2	5.0	5.0	4.2	0.85	0.52	0.44	0.38	0.42	0.22	0.19	0.20	0.13	0.32
3 Others	4.8~	4.9~	4.9~	4.9~	4.7~	4.3~	4.4~	4.2~	4.2~	4.0~	4.2~	3.6~	2.4~	2.5~	
	7.4	7.6	7.7	7.6	7.5	7.2	7.3	7.2	7.2	7.0	7.3	6.3	4.0	4.3	
	"water"	1.2	1.2	1.2	1.2	1.0	0.53	0.56	0.37	0.47	0.24	0.29	0.20	0.14	0.23
Crematories	2.1~	2.2~	2.2~	2.2~	2.2~	2.3~	2.3~	2.4~	2.4~	2.5~	2.6~	2.2~	1.2~	1.2~	
	4.6	4.8	4.9	4.8	4.9	5.1	5.1	5.3	5.3	5.4	5.7	4.9	2.8	3.0	
Cigarette smoke	0.1~	0.1~	0.1~	0.1~	0.1~	0.1~	0.1~	0.1~	0.1~	0.1~	0.1	0.07	0.06	0.058	
	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2					
Automobile exhaust	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.3	1.2	1.2	1.2	1.1	1.0	1.0	
Sewage treatment plants	1.1	1.1	1.1	1.1	0.99	0.51	0.54	0.36	0.46	0.23	0.28	0.19	0.13	0.23	
	"water"	1.1	1.1	1.1	1.1	0.99	0.51	0.54	0.36	0.46	0.23	0.28	0.19	0.13	0.23
Solid waste final disposal sites	0.093	0.093	0.093	0.056	0.027	0.021	0.020	0.018	0.012	0.014	0.010	0.010	0.006	0.006	
	"water"	0.093	0.093	0.093	0.056	0.027	0.021	0.020	0.018	0.012	0.014	0.010	0.010	0.006	0.006
Total	7680~	3695~	2874~	2394~	1899~	941~	372~	344~	327~	289~	286~	215~	155~	158~	
	8135	4151	3208	2527	2013	967	400	369	354	317	307	223	157	160	
	"water"	12.8	12.3	12.4	8.7	4.4	2.6	2.1	2.0	1.8	1.8	2.7	1.3	1.1	1.5

Note 1: Emissions from 1997 to 2007 used WHO-TEF(1998), and emissions after 2008 used WHO-TEF(2006) where possible.

Note 2: "Water" in the table means the amount emitted into water.



(Toxic Equivalency Factors (TFEs) used to calculate the figures in the table have been changed since FY 2008.)
 Source: Ministry of Health, Labour and Welfare: Total Diet Study for Dioxins.

Figure 3-15 Chronological changes in daily intake of dioxins from food

The following Table 3-9 compiles recent reported data on the estimation of PFOS and other PFCs emission inventories in Japan and Korea together with the world emission. It was estimated that global PFOS production reached its maximum (around 4,400 tons) in 2000 (3M, 2000).

	Japan ¹⁾	Korea ²⁾			Europe		Whole globe ⁵⁾	
	2005	Domestic	Industrial	Wastewater	Ref ³⁾	Ref ⁴⁾	2000	2004-2006
PFOS	3.6	0.05	0.12	1.63		21.3		14-84 ⁶⁾
PFHxA		0.29	0.39	0.61	2.8			
PFHpA	2.6	0.05	0.05	0.08	0.86		1	
PFOA	5.6	0.24	0.1	0.28	14.3	31.3	200	50-100
PFNA	2.6	0.03	0.02	0.04	0.26		25	(6-13) ⁷⁾
	1) Murakami et al., Environ. Sci. Technol., 42, 6566 (2008)							
	2) Kim et al., J. Hazard. Materials 201-202, 82 (2012)							
	3) McLachran et al., Environ. Sci. Technol., 41, 7260 (2007)							
	4) Pistocchi, Loos, Environ. Sci. Technol., 43, 9237 (2009)							
	5) Prevedouros et al., Environ. Sci. Technol., 40, 32 (2006)							
	6) Paul et al., Environ. Sci. Technol., 43, 386 (2009)							
	7) Murakami, Takizawa, J. Japan Soc. Water Environ., 33, 103 (2010)							

In Japan, PFOS was produced by a company located along central NOWPAP from early 1980's until 2009. Recent data on the production and import of PFOS is compiled in the following table (Ministry of the Environment, 2009).

Table 3-10 Data on PFOS and their salts in Japan (unit: tons/year)

Year	Production	Import	Domestic shipment		Export
			Total	AFFF	
2000	no data	no data	no data	5.9	no data
2001	no data	no data	no data	3.7	no data
2002	7.1	3.1	8.8	3	0.1
2003	14.5	—	8.7	2	0.7
2004	8.5	—	9.2	1.1	0.1
2005	5.7	—	7.9	0.85	<0.1
2006	6.5	0.2	6.7	0.4	<0.1
2007	8	0.3	8.5	0.23	<0.1
2008	5.5	0.3	6.2	0.18	<0.1

AFFF: aqueous fire fighting foams.

Also the information on the current major usage / emission industries is compiled and reported by Japanese government.

Table 3-11 Major usage / emission industries of PFOS and their salts in Japan

Purposes																												
Major usages in Stockholm Convention Parties	* Water / oil repellants * Surfactants																											
Past major domestic usages in Japan (2006–2008) according to METI	<table border="1"> <thead> <tr> <th rowspan="2">Purposes</th> <th colspan="3">Shipment ratios</th> </tr> <tr> <th>2006</th> <th>2007</th> <th>2008</th> </tr> </thead> <tbody> <tr> <td>Antireflectants / photoresists for semiconductors</td> <td>67%</td> <td>76%</td> <td>88%</td> </tr> <tr> <td>Chemicals for metal plating</td> <td>21%</td> <td>14%</td> <td>6%</td> </tr> <tr> <td>AFFF</td> <td>5%</td> <td>< 1%</td> <td>3%</td> </tr> <tr> <td>Films or print papers</td> <td>< 1%</td> <td>5%</td> <td>0%</td> </tr> <tr> <td>Others, including : Aviation hydraulic oils : Textile Industries : Etching for metals / semiconductors : Industrial polishes, abrasives : Insect baits to control ants</td> <td>6%</td> <td>5%</td> <td>4%</td> </tr> </tbody> </table>	Purposes	Shipment ratios			2006	2007	2008	Antireflectants / photoresists for semiconductors	67%	76%	88%	Chemicals for metal plating	21%	14%	6%	AFFF	5%	< 1%	3%	Films or print papers	< 1%	5%	0%	Others, including : Aviation hydraulic oils : Textile Industries : Etching for metals / semiconductors : Industrial polishes, abrasives : Insect baits to control ants	6%	5%	4%
	Purposes		Shipment ratios																									
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Films or print papers	< 1%	5%	0%																									
Others, including : Aviation hydraulic oils : Textile Industries : Etching for metals / semiconductors : Industrial polishes, abrasives : Insect baits to control ants	6%	5%	4%																									
Essential uses under Chemical Substances Control Law in Japan	Photoresist for semiconductors Etching agents for ceramic filters and compound-semiconductors ($\geq 3\text{MHz}$) Photographic film for industries (use of PFOS-containing AFFFs)																											

As explained later, production, import and usage of industrial chemicals in Japan are controlled by the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. (Chemical Substances Control Law). All the chemicals listed under the Annexes A and B of the Stockholm Convention have been designated as Class 1 Specified Chemicals under the law; i.e., their production, import and usage are basically banned in Japan except for essential uses and specific exemptions registered by the government against the Convention. As listed in the above table, major PFOS usages in recent years include active ingredients in AFFF (2/3 ~ 3/4 of the total PFOS) followed by metal plating. Majority of PFOS stockpile in the present Japan, on the

other hand, was estimated in the form of AFFF. Based on the governmental survey, stockpiles of PFOS as in the form of AFFF in each industrial sector are as follows;

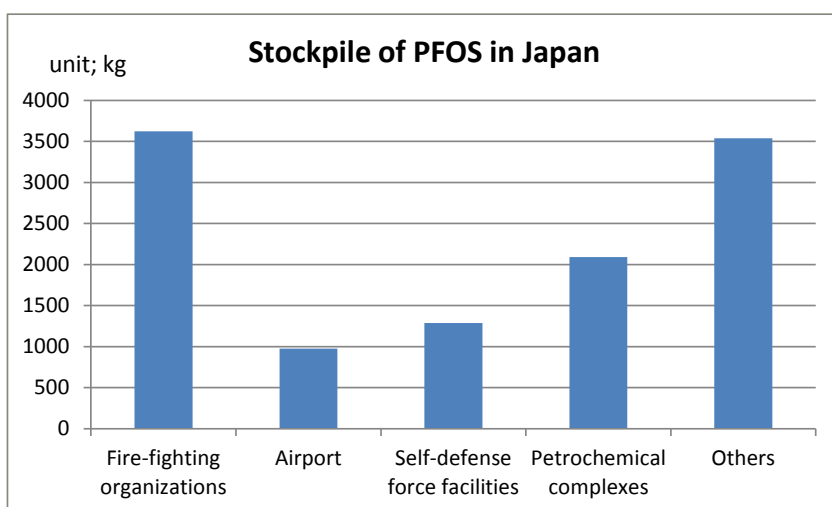


Figure 3-16 Estimated stockpiles of PFOS in the form of AFFF in each sectors

The data on PFOS stockpile in each sector on prefecture basis is available and is shown in the following Figure 3-17.

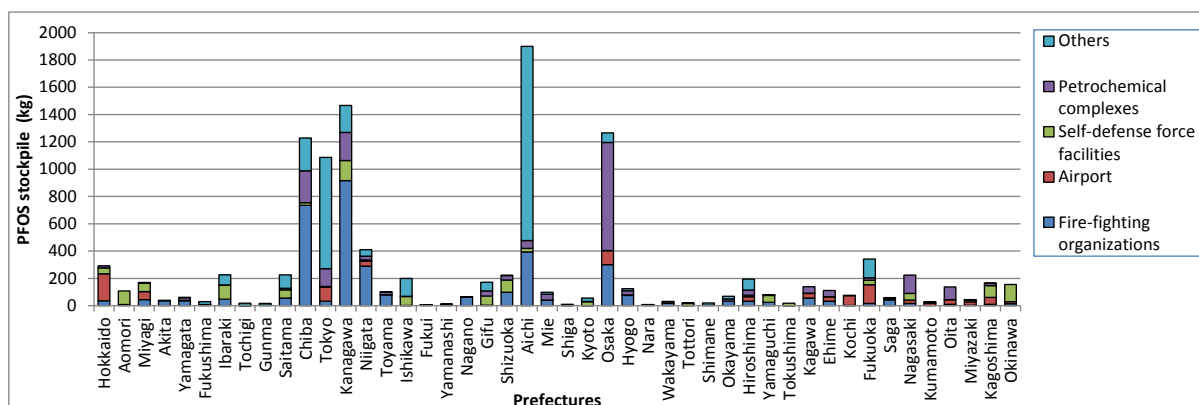


Figure 3-17 Estimated PFOS stockpiles in each prefecture (data from the Ministry of the Environment)

As shown in the figure, more than 1 ton of PFOS as in the form of AFFF is stocked in several prefectures including Metropolitan Tokyo where fire-fighting organizations or petrochemical complexes are found to be large stock places of PFOS. Majority of “others” are in fact car parks under the ground or in the building located particularly in densely populated areas, which use AFFF in their fire extinguishing facilities. Decomposition of PFOS stockpile, including those in AFFF, started by establishing decomposition methods and setting criteria to confirm both good decomposition efficiencies and safe operation of the facilities.

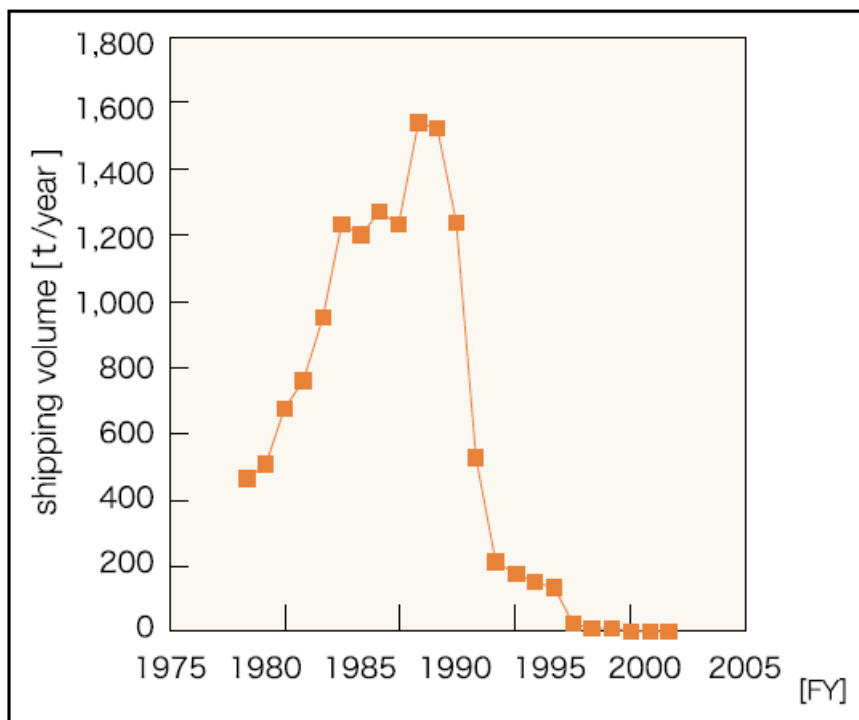


Figure Estimated TBTs shipment in Japan (Ministry of the Environment (2009))

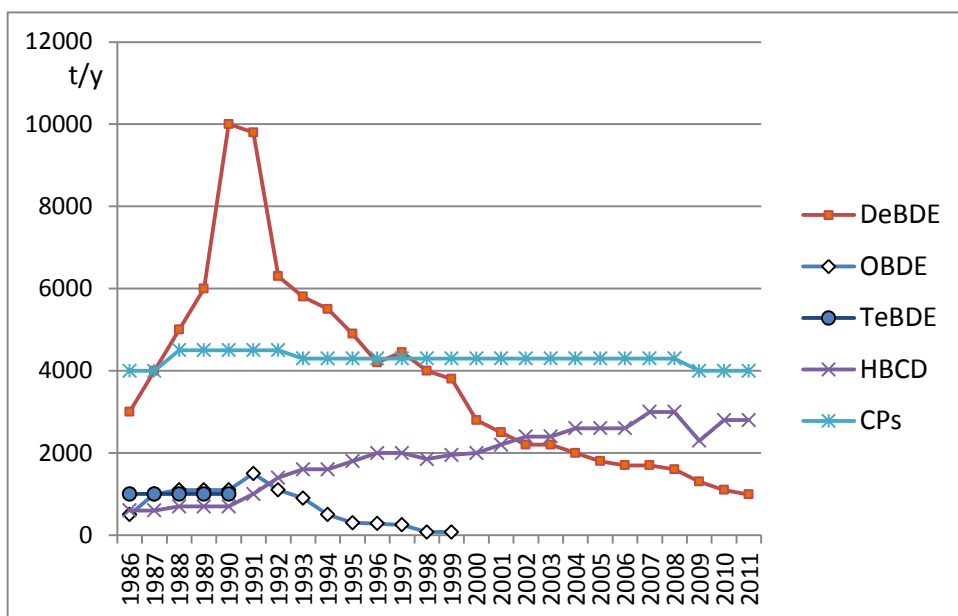


Figure Estimated demands of brominated flame retardants (TeBDE, OBDE, DeBDE, HBCD) and chlorinated paraffins (CPs) in Japan (Ministry of the Environment (2013))

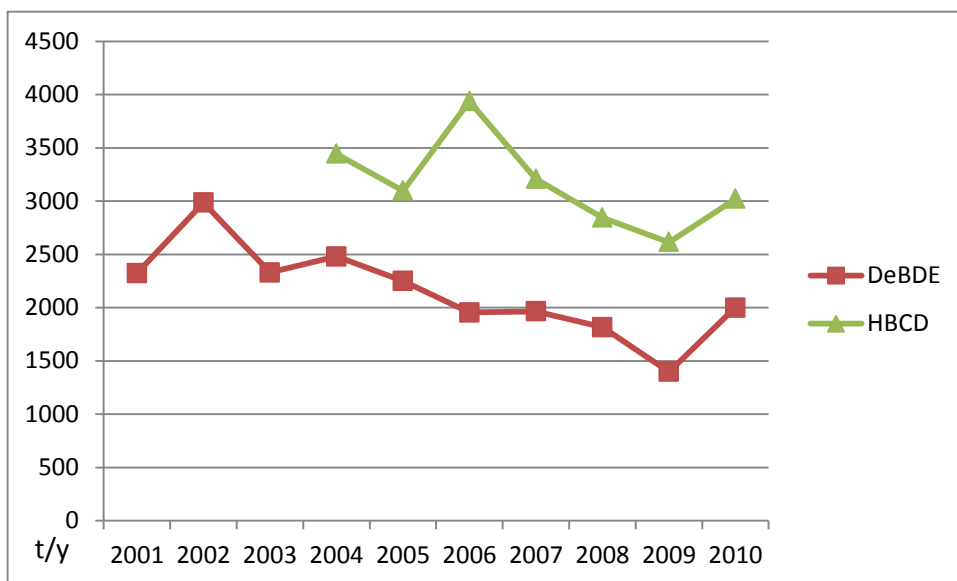


Figure Estimated (production + import) of DeBDE and HBCD in Japan (based on the data from Ministry of Economy, Trade and Industries, cited in Ministry of the Environment (2013))

Detailed study on the emission inventory of mercury in Japan was recently published (Nansai et al (2012)).

3.3. Regional features of PTS transport including modeling approaches

Long-range transport of chemicals in the regional or global scale is primarily controlled by their physical / chemical properties, though human economic activities, i.e., import and export of chemicals, goods or wastes containing substantial amounts of target chemicals, also affect the spread of chemicals significantly. First, grouping of chemicals according to their physicochemical properties will be described followed by the major transport processes in the environment through air, water and biota as well as economic activities.

3.3.1 Long-range transport potential of chemicals in air and water

Chemicals, if persistent enough, distribute to various environmental media, such as air, water, soil, sediments and biota, according to their physicochemical properties, and tend to spread into the global environment on the movement of air or water. Persistent chemicals will be generally categorized into three groups, i.e., Fliers, Swimmers and Hoppers (sometimes separated into single Hoppers and multiple Hoppers), according to their partition properties among air, water and soil (or biota) (Wania 2003, Lohmann et al, 2007). Among them, most important group from the standpoint of transboundary pollution is Hoppers, i.e., those having limited volatility and staying on the surface of soils or water with occasional evaporation into air and

travel for some distance until condensation or wash out, like in the case of jump of grasshoppers (Grasshopper effect; Wania & Mackay, 1996). The ambient temperature at which the “condensation point” is reached differs for the various compounds involved, indicating a global fractionation or global distillation. Among Hoppers, more volatile chemicals, such as HCB and α -HCH, tend to stay in air and travel for a longer distance until their deposition on cold environment, such as Arctic / Antarctic or high mountains. Their behavior is like movement of water vapor from their sources (kitchen or bath) to a cold, northside window in a winter house. Their environmental levels generally show small temporal / spatical variations except for the areas around the strong emission sources. Other Hoppers with low volatility, such as DDT or dioxins, tend to be absorbed on fine particles, and move for a shorter distance with particles. Chemicals with high volatility (Fliers), like flon, for example, are always in gas phase even in cold environment and travel globally, but may not affect health of human or wildlife significantly due to lower chance of contamination through food chains because of their low levels in water or terrestrial environment. Similarly those with higher solubility into water (Swimmers) were thought to have limited chance of contamination through food chains due to their lower lipophilicity. However, PFOS (Perfluorooctane sulfonate) was suspected to have potentially significant effects to the health of human and wildlife due to its high bioaccumulation properties inspite of its high water solubility and low lipophilicity, and was nominated and agreed to the additional POPs under the Stockholm Convention.

Other group of chemicals interested from the point of long-range transport include unintentionally produced chemicals such as PAHs (polycyclic aromatic hydrocarbons) and dioxins. They are produced in high temperature chemical reaction processes, such as incineration and smelting, and include low volatility compounds mainly attached in the particles. They may be spread widely into the environment on the strong upper flow of air produced, for example, in the large forest fires. A finer fraction of atmospheric particles with diameters less than 2.5 micrometers (PM_{2.5}), which are produced mainly through combustion of coals, gasolines, diesels and other incineration processes, has attracted attention in recent days due to their potential health effects through inhalation. They tend to be produced in densely populated areas and affect the local environment. They can be transported in long distance, however, due to their small sizes and thus are also important from the standpoint of long-range transport of pollution. Among them, black carbon, or soot, has attracted attention not only from their health effects but also their potential effects to climate change.

An idea of long-range transport potential (LRTP) of a chemical has been proposed to show how long a particular compound will be transported in the environment, and characteristic travel distance (CTD) has frequently been used to express the property quantitatively. CTD is calculated as a distance of a chemical decreasing to 1/e of the original concentration during transport in a media (air or water) under a hypothetical condition in each model. Although CTD is expressed as a number with distance unit (km), it does not have a meaning in the real environment and is model-dependent, i.e., CTD values are generally not comparable quantitatively among different models. Orders of CTD distances among chemicals, however, are reported to be generally consistent among the models, and CTD will be useful as a guide to categorize chemicals

into several groups with different transport potentials. Calculated CTDs for group of chemicals reported in the literatures are compiled in the following tables (note that each of the tables is calculated based on different models).

Table 3-12 Calculated CTD (unit; km) of selected POPs (T. Harner et al., 2012)

Chemical	CTD (air)	CTD (water)
Hexachlorobenzene	230000	700
Pentachlorobenzene	120000	200
PCB-180 (hepta homolog)	17000	340
α -HCH	7800	830
PCB-28 (tri homolog)	5100	190
γ -HCH	4200	220
BDE-99	3700	540
DDT	3600	490
β -HCH	3100	430
Hexabromobiphenyl	3000	540
Toxaphene	2800	1600
2378-TCDD	1600	130
Dieldrin	1100	580
chlordanes	1100	300
chlordecone	710	1700
Aldrin	60	130
PFOS**	10	63 000

Table 3-13 Calculated CTD (km; air) of current use pesticides (Hoferkamp et al., 2010)

chlorothalonil	430
chlorpyrifos	4420
dacthal,	2690
diazinon	130
dicofol	640
methoxychlor	55
pentachloronitrobenzene (PCNB)	12100
trifluralin	110
PCP	1320

As explained previously, HCB is known to be transported truly long distance, in global scale, from their sources. In fact, HCB levels in the air samples collected in all over Japan showed strikingly narrower spatial variations compared with other chemicals (see later chapter on environmental monitoring data). Pentachlorobenzene also shows a similar level of estimated CTD, and thus thought to have similar long range transport potential to HCB. They are true global pollutants and their movements far exceed the size of NOWPAP region, suggesting that their levels in NOWPAP region may reflect current global pollution status with variations reflecting the effects of sources within the region. PCB isomers, α -HCH and some other chemicals including PCNB show

relatively large CTDs, too, and thus are expected to be transported in transregional / global scale. The proportion of the effects of sources outside of the region is different in different chemicals depending on their source distribution. It was reported that major emission sources of PCB-28 and PCB 153 are located in Europe and North America and their transboundary transports significantly affect their levels in East Asia, while α -HCH and β -HCH were mainly originated from the sources within the region (Woehrschimmel et al., 2012). Due to its high LRTP and water solubility, however, α -HCH shows large mobility once emitted in the environment. Recent report on the HCH levels in surface sea water collected by a ship of opportunity shows much higher levels of α -HCH in northern side of circum polar front of North Pacific Ocean than southern side, indicating the result of long range transport of α -HCH from its usage area to the cold polar region during a few decades after its banning (Kunugi et al., 2010). Other OCPs (organochlorine pesticides) and brominated flame retardants as well as dioxins and furans, all having smaller CTDs, tend to be present in particulate rather than in gas phase, and thus show shorter transport capabilities and tend to reflect local pollution status more strongly.

3.3.2 Other factors to be considered in the environmental transport of PTS

Generally, chemicals are transported on the flow of air, surface water or ground water in terrestrial environment, and sea current in marine environment. Outline of the transport processes including information of winds, rivers and sea currents in NOWPAP region were summarized in the previous sections. Here we add some more processes to be considered for the construction of models, particularly for some types of chemicals.

Many of the PTS tend to be adsorbed on particles or sediments once in water phase; their movement in terrestrial environment is supposed to be affected by the movement of soil / sediment particles on storm water, and thus rather difficult to simulate quantitatively. Eventually, however, they are transported and deposited in coastal environment. Coastal sediments are thus thought to be a temporal sink and secondary sources of many of PTS, including organotins, i.e., tributyltin (TBT) and triphenyltin (TPT), which once used extensively as antifouling reagent in the bottom of the ship or on fishing nets. Although TBT and TPT are already banned under the Convention of International Maritime Organization (IMO), past usage of these chemicals sometimes caused severe coastal pollution, particularly in places nearby docks and ports, where coastal sediments were contaminated with fragments of paints including these antifouling reagents.

The chemodynamics of PTS in open ocean environment may include several different processes; i.e., transport through air and deposition (dry and wet) to the surface, partition between air, water and biota (and particles), horizontal transport with water (sea current), seasonal vertical mixing in mixing layers, sedimentation to deep water by biological processes, and vertical transport with water. Importance of Sea Surface Microlayers (SML) for the partitioning and transport of some chemicals / heavy metals have been pointed out, although quantitative treatment of the effects of SML to PTS awaits further researches. Sea ice coverage may also affect environmental behavior of PTS. Considerable attention has been paid recently on the potential effects of global

warming / climate change on the environmental chemodynamics of POPs, including re-emission of deposited POPs to the air by the ice melt processes in Arctic region (UNEP/AMAP expert group, 2010). It is pointed out that vertical cycling of sea water in NOWPAP region has been slowed down in recent several decades, possibly because of global warming. As a thermohaline process, this is affected strongly by sea surface temperatures (SST) and salinities in winter in a region near Russia where a deep water is thought to be produced. Changes in temperature and precipitation in both inside and outside of NOWPAP region may potentially affect the deep water production process and hence vertical cycling processes.

Other transport processes to be considered include those accumulated in migrating organisms. Some birds species and fishes migrate long distances within or across NOWPAP borders. Part of the PTS accumulated in their body during their stay in more polluted areas may be excreted in less polluted areas and cause detectable levels of pollution. Potential transport of POPs by whales between Northern and Southern hemispheres were calculated by Wania and their data was the basis for the explicit description of the process under the Stockholm Convention (Wania, 1998).

Another transport mechanisms which might cause significant pollution in other countries are those related to human economic activity, i.e., trade of chemicals, products containing target chemicals, and recycling / reuse of used goods and waste materials. In order to prevent spread of pollution through the trade of new industrial products, several international activities, such as Basel, Rotterdam and Stockholm Conventions and OECD-based activities, have been conducted, and harmonization among the activities are being pursued. Chemicals already banned / restricted internationally, for example POPs, should be notified at the time of trading, thus synergies among the three conventions, i.e., Stockholm Convention (protect human health and environment from POPs), Rotterdam Convention (prior informed consent of trades including hazardous chemicals) and Basel Convention (regulations on import / export of hazardous wastes), have been strengthened. Recycling activities have been developed from both environmental and economical reason, and now play significant roles in various industrial sectors. Global trade of plastic wastes showed significant flow of these wastes to East Asia (Terazono et al., 2004). Waste treatment / dumping processes as well as recycling / retrieval of resources from the wastes may cause emission of pollutants. The process is particularly problematic in developing countries, due to inferior facilities for conducting such processes, lack of suitable waste treatment system for preventing emission of pollutants, and lack of information on the chemicals included in the wastes / goods. TV, PC and other electric equipments contain various resources, such as gold, as well as flame retardants, plasticizers and other plastic additives, some of which have been banned / being phased out due to potential adverse effects to human beings and the environment. In addition, recycling / retrieval processes themselves may produce unintentional chemicals, such as dioxins. Emission of PTS from the treatment of electric wastes, a so-called E-waste issue, has attracted attention in recent decades though the emission inventory from the processes are still difficult to compile. Among the new POPs, PFOS is even more difficult to control because it is present only on the surface of materials / goods, occupying only small proportions (on total weight basis), thus usually not explicitly stated in MSDS or other component list. Furthermore, it is

not only present as free form but also combined with polymers, which are difficult to detect / quantitate in the present analytical methods.

Among PTS, PFOS is exceptional in its high water solubility, and thought to be transported mainly on the movement of water for a long distance as shown in Table 3-12. Although considerable researches have been conducted recently to identify major sources of PFOS, there still remain large uncertainties as for the emission inventory. There are several reasons for the difficulties; 1) PFOS had been largely produced outside of the NOWPAP region until recently and the major inventory in NOWPAP region consists of users and waste dumping sites, both of which are difficult to identify and estimate their emission levels, 2) PFOS has wide application for various purposes in variety of derivatized forms, many of which are difficult to identify by the current analytical procedures, and 3) PFOS has non-point sources (diffuse sources) and tend to contaminate ground water once emitted. The production is now limited in China, and its usage has been banned / strictly controlled after listing to Annex B of the Stockholm Convention. However, the past usage still affect the environment of each country considerably through various routes as shown above. In addition to waste dumping sites, sewage treatment process was also reported to cause secondary pollution through the usage of PFOS-contaminated sewage as fertilizers in agricultural fields(REFs).

3.3.3 Outline of researches on PTS models

Development of models have been helping us to understand chemodynamics and predict environmental transport and fate of chemicals including PTS (Wania & Mackay, 1996; Wania, 1998; Wania, 2003). These models are basically grouped into two categories, i.e., Lagrangian models based on the fluid dynamic description of the movement of chemicals, and Euler models by separating environment into boxes in which partitions of chemicals between different environmental media are calculated (Hollander et al., 2008). The latter approach is also called multimedia model or fugacity model and has been used by many researchers due primarily to much smaller demands to computer power than the former approach (Mackay, 2001). In fact these two types of models are frequently combined together to properly calculate partition and movement of chemicals in the environment in global and regional scales. In addition, various researches have been reported to compile or estimate emission inventory data for particular chemicals, which are needed to develop models (Lohmann et al., 2007).

Extensive researches have been conducted on the development and application of models to describe environmental fates of chemicals, including their comparison (Scheringer, 2009; Hollander et al., 2008; Fenner et al., 2005). LRTP of mono- to decabrominated diphenylethers was evaluated by using four different models (Wania & Dugani, 2003). By the comparison with PCB congeners as benchmark chemicals, a reasonable result consistent with the field monitoring observation was obtained; i.e., lower-brominated congeners have a LRTP comparable to that of PCBs known to be subject to significant LRT, whereas the highly brominated congeners have a very low potential to reach remote areas. Part of quantitative differences among models could be explained by the differences in the assumed height of the air compartment, which influences the relative importance of atmospheric degradation and deposition processes.

An improved design of atmospheric monitoring method for global as well as regional scale POPs monitoring is proposed based on discussion among field scientists and modelers (Hung et al., 2013).

In addition to the development of atmospheric transport models and multimedia fugacity models, modelling researches have been actively conducted in water environment, where integration of bioaccumulation through the foodweb into multimedia partition is a key issue. Marinov et al. (2009) reported development of PAHs models in marine environment. They compared the model results with monitoring data and found essentially good relationship. They pointed out, however, that the validation of the observed dynamics would require far more complete and extensive datasets than those available in literature. One of the key issues is reliable estimate of bioaccumulation process through the foodweb. Experimentally, BCFs (bioconcentration factors), in which exchanges through only respiratory or dermal processes are evaluated, have been most often measured while BAFs (bioaccumulation factors), which include exchanges through all processes including feeds and thus are expected to represent the natural situation more appropriately, are reported to be measured only 0.2% of current use organic chemicals. BMFs (biomagnification factors), which represent accumulation potential through food consumption, is another important factor to be clarified (Arnot and Goba, 2006). Walters et al. (2011) recently reported bioaccumulation status of PCBs in a lake to investigate relationship between water-octanol partition coefficients and organism trophic position as revealed by the stable nitrogen analysis ($\delta^{15}\text{N}$). TMFs (Trophic magnification factors) derived from stable isotope analysis have been increasingly used to quantify biomagnification of organochlorines in the environment. Based on the detailed field studies as well as standardization of TMFs values, the authors demonstrated usefulness of TMFs by showing remarkably consistent K_{ow} effect on TMFs.

Detailed bioaccumulation studies of PTS from water and sediments to fishes were conducted under controlled experimental condition using microcosm and were reported. Uptake efficiency of dissolved PFOS at the respiratory surface of a marine benthic fish, marbled flounder, was estimated to be 3.2% of that of oxygen, and the half life of PFOS in the whole body to be 29 to 31 days (Sakurai et al (2013)). PFOS in suspended and bottom sediments was also found to contribute to body burden of the fish, and the authors recommended further investigation for revealing uptake mechanisms. The same group also reported the results of respiratory uptake kinetics of 99 PTS, including PCB, DDT and PAHs, and reported respiratory uptake rate constants, ranging from 2,000 to 42,000 $\text{L kg-lipid}^{-1} \text{d}^{-1}$, and respiratory uptake efficiencies (E_w), ranging from 0.060 to 1.3 (Kobayashi et al. (2013)). They reported that, except for PAHs, E_w tend to increase with the increase of octanol/water partition coefficients up to $\log K_{ow} = 5$, however that the value of K_{ow} was found to be significantly lower (about one-third) than those reported in the literatures for the chemicals with $\log K_{ow}$ between 3 and 5.

3.4. Current status and temporal trends of PTS concentration in the environment

A large amount of information on the environmental levels of variety of chemicals have been accumulated in NOWPAP region. Here summaries of relevant information in each country will be compiled.

<Russia>

Recent years major marine monitoring researches in the Russian area of NOWPAP region took place in the coastal waters of Primorsky krai, in Peter the Great bay namely. This bay locates in the north-western part of the central part of NOWPAP region. The density of population and industry along the coastal line of the bay is the highest in the Russian Far East, so the bay is the most polluted area on the Russian coast of NOWPAP region. The main areas of monitoring program include the inner bays and bights, Amursky bay and Ussuriisky bay which are situated around Vladivostok, and Possyet Bay which is located in the south on the borders with North Korea and China (Figure 3-18).

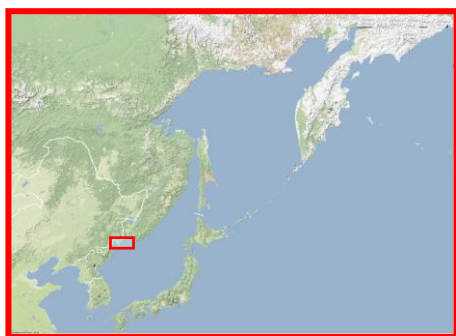


Figure 3-18. Peter the Great Bay

Total amount of DDT and HCH in seawater and bottom sediments in 1990-2010 was determined in three areas around Vladivostok: Zolotoy Rog Bay (Golden Horn Bay, this is the most polluted harbor near Vladivostok), and Amursky and Ussuriisky bays which are located around Vladivostok (Figure 6).

Total pesticide concentration in sea water varied from year to year, but in general decreased, especially when compared with the middle of the 1990-s. Organochlorine concentrations in bottom sediments collected around Vladivostok were analyzed in 1996 - 1998 (Tkalin et al., 1997, 2000). Sediment samples were taken by van Veen grab and only the surface layer (about 2 cm) was used for analysis. Pesticides concentrations were determined using a Varian 36100 GC and a Saturn 4DMS/MS. Data are presented in Table 3-14.

Table 3-14. Concentrations of organochlorine pesticides in bottom sediments (ng/g dry weight) in Peter the Great Bay (around Vladivostok) (Tkalin et al., 1997; 2000)

Area, year	Sum of HCHs	Sum of DDTs
1994	<0,20 – 5,50	0,80 - 22,70
1996	0,28—5,70	<0,50 -26,10
1997	0,19 – 4,77	0,01 – 4,31

In 1997 α HCH/ γ HCH ratio did not reveal specific feature, but α HCH dominated in general in Amursky bay. DDT/DDE ratio changed from 0,19 to 4,3. Authors suggest that sources of DDT and technical – grade γ HCH still existed in this area, despite an official ban on the use of these chemicals. Probably DDT and HCH were used unofficially for pest control on ships or for technical and domestic purposes. Regular data on pesticide concentrations in bottom sediments are available since 2004 only. Total concentration increased in 2008 (Fig. 3-19).

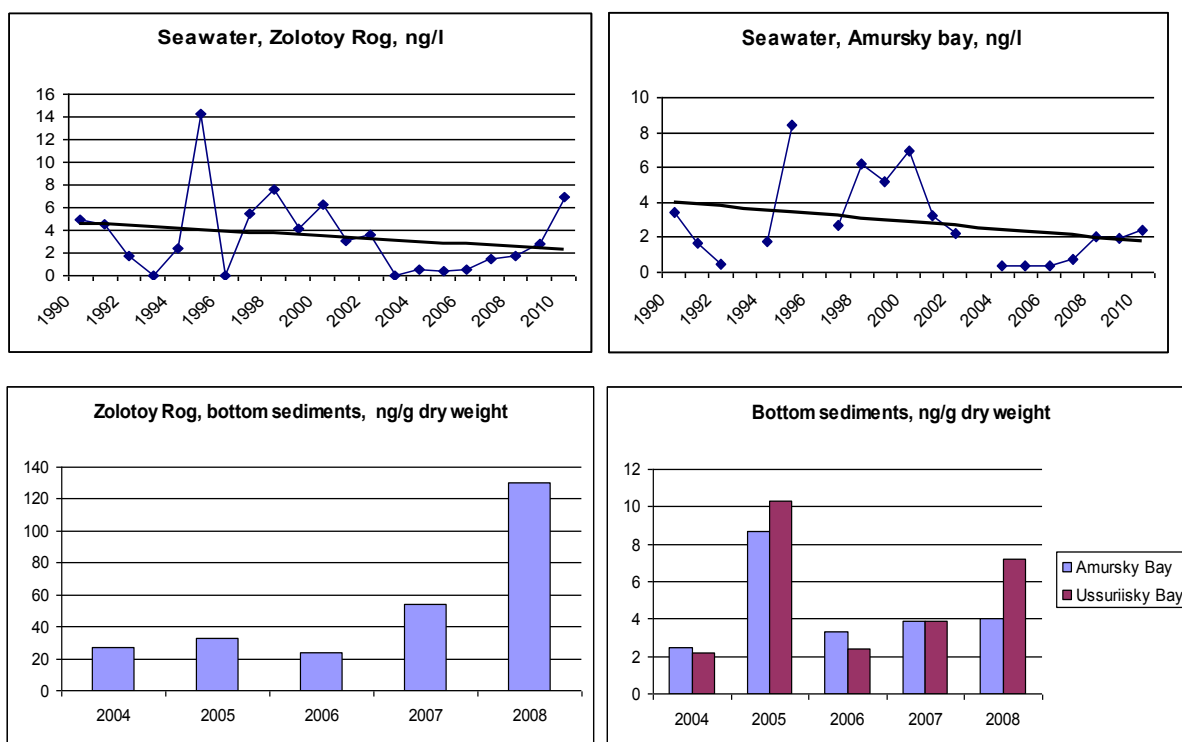


Figure 3-19. Total PTS concentrations (HCH + DDT) in seawater and bottom sediments in interior bights and bays of Peter the Great Bay, Sea of Japan (the Russian area of NOWPAP region) (Lukyanova, Chernova, unpublished data)

Nevertheless, Environmental Monitoring Center (EMC) of Primorsky Territorial Office on Hydrometeorology and Environmental Monitoring (Primhydromet) has informed the local community that pesticides concentration doesn't exceed maximal

permitted concentrations (MPC) adopted in Russia. MPC for seawater in fishery areas in the Russian Federation for DDT, HCH and PCB is 10 ng/l. Ecological standards for these chemicals in bottom sediments in Russia are not developed yet. Average concentration in bottom sediments in unpolluted areas of Peter the Great Bay is 2,5 ng/g wet weight.

In 2010 pesticide concentrations in sea water in the Bay were similar or slightly lower than in 2009 (State report..2011). Pesticides concentrations in bottom sediments remained at the same level as 2009 but DDT concentration increased (Table 3-15). High levels of DDT and γ HCH testify “New” pesticides input to the costal areas.

Table 3-15. Pesticides concentrations in marine environment in Peter the Great Bay in 2010 at various locations (State report..., 2011).

Pesticides	Seawater, ng/l	Bottom sediments, ng/g
α HCH	0,9	3,9 – 18,2
γ HCH	14,5	7,9 – 16,0
DDT	1,0 – 4,0 – 29,0	35,4 – 57,9
DDE	1,0 – 5,0 – 29,0	25,5 - 33,6
DDD	1,0 -2,5 – 34,0	16,7 – 55,4

In the river waters studied in Primorsky Krai the OCP concentrations of group DDT (sum of DDT and its metabolites DDD and DDE) were less than 35 ng/l, and group HCH (sum of hexachlorcyclohexan isomers: Eldrin etc.) were less than 4 ng/l (State report... 2011).

Regular monitoring of PCBs in marine environment in Russia is not carried out. In 2010 several samples of bottom sediments collected in estuarine zones of Peter the Great Bay were analyzed. Many rivers with different levels of anthropogenic pollution flow into the Bay. According to the hypothesis of biogeochemical barriers it is supposed that major amount of pollutants including PCBs precipitates in estuaries. Therefore, pollutant concentration in estuaries may be a maximum over neighboring areas. DDT and PCB concentrations in bottom sediments in estuaries of three rivers flowing into the Bay were similar. The highest PCB concentration (32 ng/g dry weight) was determined in the estuary of Razdolnaya River, which flows through the urban areas (Table 3-16).

Table 3-16. PTS concentrations in the bottom sediments (ng/g dry weight) of estuaries of the rivers flowing into Peter the Great Bay (2010) (Lukyanova et al., 2013)

PTS	Gladkaya River	Sukhodol River	Razdolnaya River
PCB	6.9	11.5	32.6
HCH ($\alpha + \beta + \gamma$)	0.5	0.48	2.1
DDT+DDD+DDE	6.3	12.9	44.7

Detail analysis of the samples revealed domination of γ HCH and p,p'-DDT in bottom sediments (Table 3-17). Data obtained continued input of OCP to coastal zone in Russian area of NOWPAP region.

Table 3-17. PCB and organochlorane pesticides concentrations in bottom sediments from estuaries of some rives flowing into Peter the Great Bay, pg/g dry weight (Lukyanova et al., 2013)

	Gladkaya River	Sukhodol River	Razdolnaya River 1	Razdolnaya River 2
Sum mono- chloro-biphenyls(CB)	33	< 5	83	32
Sum di -CB	189	< 5	1559	916
Sum tri-CB	839	201	800	240
Sum tetra-CB	2191	3066	11658	6276
Sum penta - CB	3002	6762	15425	7762
Sum hexa - CB	604	1400	3043	2046
Sum hepta - CP	26,9	70,7	55,9	34,4
Sum octa - CP	1,0	6,8	9,1	4,6
Sum nona - CP	< 0,1	< 0,7	< 0,3	< 0,3
Total Sum PCB	6886	11505	32633	17311
HCB	63	26	753	434
α -HCH	30	63	154	183
γ -HCH	380	307	1374	1570
β -HCH	67	50	350	334
d-HCH	31	23	128	98
o,p'-DDE	67	42	209	189
p,p'-DDE	410	447	1560	1431
o,p'-DDD	232	561	1061	982
p,p'-DDD	2026	3135	8912	6702
o,p'-DDT	783	2300	5765	6558
p,p'-DDT	2778	6423	27225	24585

Qualitative analysis of PCBs showed that in general the congener profiles in the samples closest to the composition of the commercial mixture Aroclor-1254: pentachlorobiphenyls dominated, taking in samples of 43-59% (Table 3-17). However, in contrast to Aroclor 1254, a high proportion of tetrachlorobiphenyls was observed in Sukhodol and Razdolnaya rivers - 27 and 36% respectively, (in the Aroclor 1254 - 15%). Low-chlorinated congeners (mono-, di-and trichlorobiphenyls) are presented in all samples. Their combined share in Gladkaya river was 15%, Sukhodol river - 1.8%, Razdolnaya river- 6.9-7.5% (in Aroclor 1254 - <1%). This facts indicates the presence in the samples a certain number of other commercial PCB mixtures - Aroclor 1248. As Sovol P-53, which is similar to Aroclor 1254, is most used in Russia, data testify a fairly fresh, though minor, PCBs input in a river from the any local sources. This congeners profile is typical for Sukhodol River. Samples from two other rivers are more different in congener profile of Aroclor 1254, which indicates a long presence of PCBs in the

environment, in which their transformation was aimed at reductive dechlorination of congeners (as a result, low-chlorinated congeners are beginning to dominate). This process usually takes place in bottom sediments as a result of activity of anaerobic microorganisms occurs relatively slowly, so it takes a long time

PAH analysis in seawater and bottom sediments provide from time to time. BaP concentration in the water of the Amur Bay (Peter the Great Bay) was on average $0,4 \pm 0,2$ ng /l on the depth 1 m from the bottom (Anikiev et al, 1987). The influence of local pollutant sources (Razdolnaya river, Vladivostok city) affects only the nearest zones. In the center of the anti-cyclonic circulation at low speed flows BaP concentration reached 0.7 ng /l, while the other six stations it was approximately 0.3 ng l.

Similar situation was observed in August, 2005. Seawater samples were collected in the surface lay. The minimal BaP concentration was detected in exterior open part of the bay near Reineke Island (<0.1 ng/l). Higher concentration of BaP (0.55 ng/l) was found in the surface water in polluted area near Vladivostok (Cherkashin et al., 2008). Ecotoxicological experiments show that existing concentration is not likely to have a negative impact on survival prelarvae Japanese anchovy for short periods (96 hours). However, in case of emergency oil spills PAH concentrations might be higher and exceed the estimated experimental values of the maximum non-lethal concentrations for ichthyoplankton.

Table 3-18. Persistent Organic Pollutants in marine organisms from the Russian zone of NOWPAP region, ng/g wet weight (2011) (Popkov, 2011).

Site of sampling	Species	HCH $\alpha + \beta + \gamma$	DDT+DDD+ DDE	PCB
Peter the Great bay	Flounder <i>Liopsetta pinnifasciata</i>	n.d.	13	18
Peter the Great Bay	Pollock	8	18	17
Central part of NOWPAP	Shrimps	n.d.	n.d.	13
Central part of NOWPAP	Snow crab	n.d.	14	17
Central part of NOWPAP	King crab	n.d.	n.d.	n.d.
Central part of NOWPAP	Greenling	n.d.	129	22
Central part of NOWPAP	Pollock	n.d.	124	29
Central part of NOWPAP	Flounder <i>Pleuronectes microcephalus</i>	n.d.	133	23

n.d. – not detectable

Regular state monitoring of pesticides content in commercial fish and shellfish is carried out since 2010. Monitoring program based on the Federal Law “On the food safety” (2008), the Act of the Government of the Russian Federation “State monitoring of the quality and safety of water biological resources” and the Order of Federal Fisheries Agency “Monitoring of marine biological resources and environment quality in fisheries areas”. Data for the NOWPAP region are presented in Table 3-18.

HCH, DDT and PCB concentrations in marine organisms didn’t exceed sanitary norms for seafood established in the Russian Federation - 200 ng/g wet weight. This monitoring program began since 2010, and it will be continued in future.

The total amount of DDT and its metabolites and isomers of HCH was detected in organs of the sea gulls, fishes, mollusks and marine plants from the various sites of the Peter the Great Bay in 1998-2010 (Figure 3-20). Mussels and flounders were used as the main bioindicators.



Figure 3-20. Map of sampling sites in the Russian area of NOWPAP region.

According to the well-known program Mussel Watch mussels are the most suitable bioindicators of marine pollution in coastal areas all over the World Ocean. In the middle of 1990s DDT and HCH concentrations were detected in soft tissue of

mussels *Crenomytilus grayanus* and *Modiolus kurilensis* collected in Peter the Great Bay near Vladivostok (Table 3-19) (Tkalin et al., 1997, 2000)

Table 3-19. Concentrations of organochlorine pesticides (ng/g dry weight) in the mussels from Peter the Great Bay (Tkalin, 1997, 2000)

Mussels, station	p,p'-DDT	p,p'-DDD	p,p'-DDE	Σ DDT	α-HCH	β-HCH	γ-HCH	Σ HCH	Total
M. kurilensis, Reineke Island ¹	0.42	2.76	6.24	9.42	0.57	0.26	0.52	1.35	10.77
M. kurilensis, Skrebtsova Isl. ²	0.12	10.15	9.74	20.01	0.83	0.83	0.77	2.43	22.44
C. grayanus Reineke Island ¹	0.25	1.93	2.10	4.28	0.29	0.59	0.25	1.13	5.41
C. grayanus Peschany Cape ²	0.53	1.80	3.39	5.72	0.31	0.22	1.76	2.29	8.01

Reineke Island¹ – reference area, Skrebtsova Isl.² – polluted area.

In the early 2000s the total pesticides concentration in soft tissues of mussels collected near Vladivostok (Amursky and Ussuriisky bays) varied from 1 to 30 ng/g wet weight. In liver of flounders from the same areas level of HCH isomers ranged from 30 to 45 ng/g as well as the concentrations of DDT and its metabolites varied from 10 to 170 ng/g in certain years. The highest total pesticide concentration was determined in the liver of the sea gull - 4500 ng/g wet weight.

Organochlorine pesticides (OCP) concentrations in soft tissues of mussels *Crenomytilus grayanus* from the Amursky and the Ussuriisky bays increased from 5 to 10 times from 1996 to 2004 (Tkalin et al., 1997; 2000; Boyarova et al., 2004). (Figure 3-21).

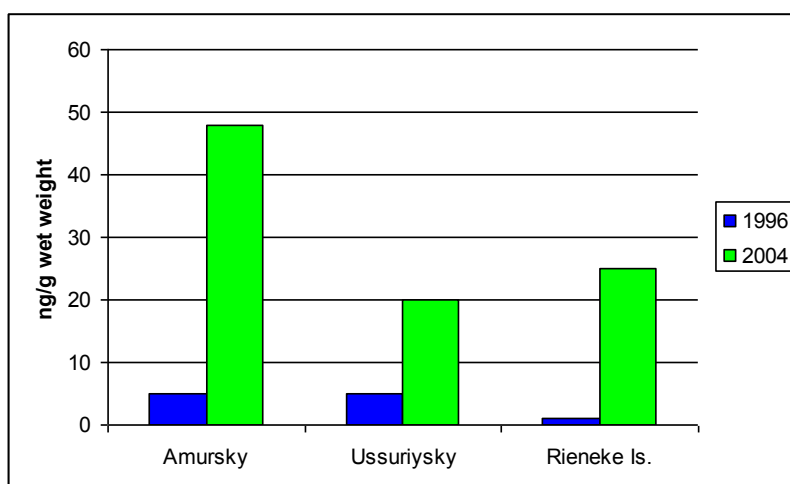


Figure 3-21. Changes of organochlorine pesticides (OCP) (HCH+DDT) concentrations (ng/g wet weight) in soft tissues of mussels *Crenomytilus grayanus* from Peter the Great Bay (Boyarova et al., 2004).

The highest pesticides concentrations - 310 ng/g wet weight - were determined in mussels from the Possyet bay in the south-western part of the Peter the Great bay, near the border with North Korea and China (Lukyanova et al., 2001; Boyarova, Lukyanova, 2006).

Results comparison with the data of Mussel Watch Program on pesticides content in mussels collected in the Asia-Pacific region (Monirith et al., 2004) shows that total pesticides content in mussels collected in Peter the Great Bay is lower than in mussels collected in Hong Kong, China and Vietnam. But there is one feature. Normally HCH level in soft tissues of mussels from Peter the Great Bay was higher then DDT concentration, on the contrary in mussels collected in the other Asia-Pacific countries where DDT is dominating pesticide (Figure 3-22).

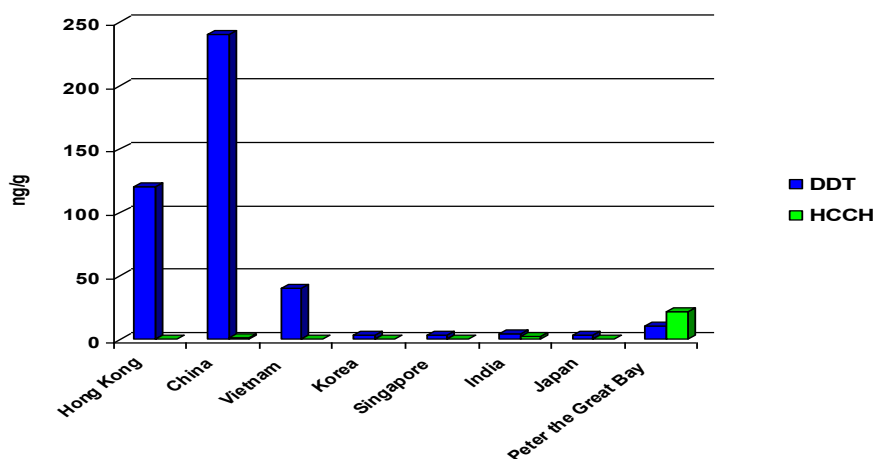


Figure 3-22. Data of Mussel Watch program on OCP content in mussels from the Asia-Pacific region and from the Peter the Great Bay (Monirith et al., 2003; Lukyanova et al., 2007; Lukyanova, Boyarova, 2009).

Fish are important protein source in human nutrition. Seafood safety is necessary for human health. Maximal total pesticides concentrations were determined in fish muscle from the Possyet bay. DDT level was higher than HCH. Total concentrations in fish from the other sites of Peter the Great Bay didn't exceed the MPC for the Russian Federation (200 ng/g wet weight) (Figure 3-23). It is well known that maximal amount of pesticides accumulates in fat-rich organs, namely in liver. OCP content in liver of three species of flounders was higher then in muscles: 400-700 ng/g wet weight in liver and 20-50- ng/g in muscle. HCH concentration in liver of bottom fish (flounders) was higher (40-120 ng/g wet weight) then in pelagic fish (herring - 5 ng/g, rudd – 10 ng/g).

OCP concentration in various marine organisms in food net from one location – the Possyet Bay- increased through food chain from seaweeds (2- 5 ng/g) to fish (120 - 600 ng/g) and to seabirds (4500 ng/g). Concentration coefficient (ration of OCP concentration in sea gull liver to OCP concentration in seaweeds) was about 900.

DDT and HCH concentrations in organs of haarder inhabiting estuarine zones of rivers flowing into Peter the Great Bay were much higher than in marine fish (about

1700 ng/g wet weight in liver of haarder and 50-350 ng/g in liver of flounders). Pesticides concentration in liver of haarder in polluted Razolnaya river was approximately two times higher than in fish collected in Arteomovka river where level of pollution was significantly lower (Figure 3-24).

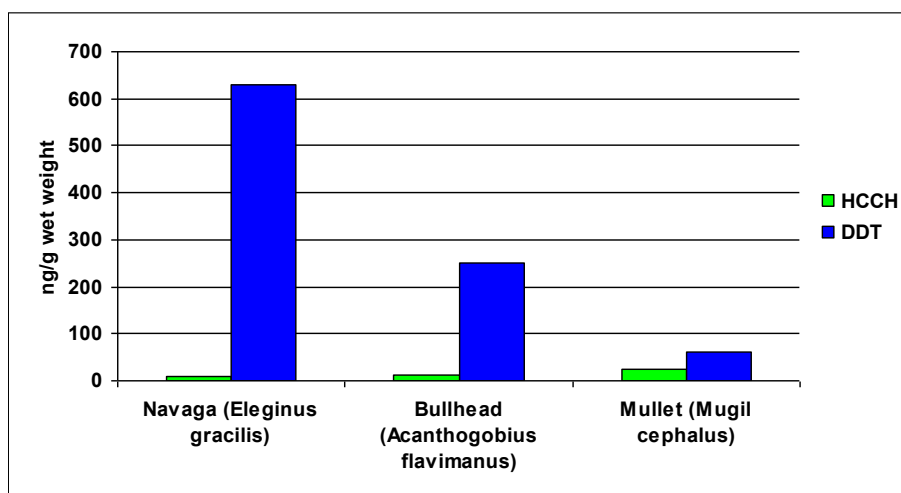


Figure 3-23. Pesticides concentrations in muscles of fish (Possyet Bay) (Lukyanova et al., 2007)

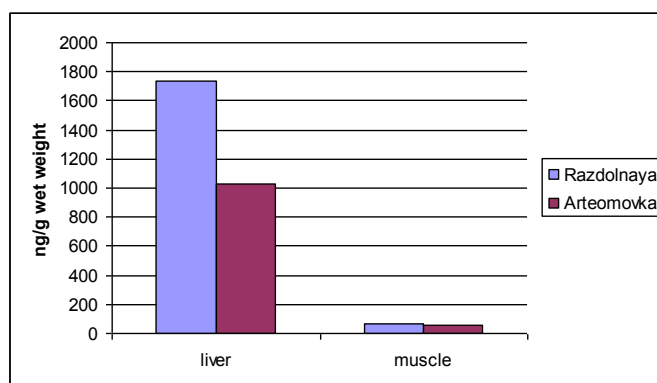


Figure 3-24. OCP concentrations in organs of estuarine fish (haarder *Liza haematocheila*). (Lukyanova et al., 2010).

DDT/DDE ratio in fish from southern part of the Peter the Great Bay (the Possyet bay and Furugelma Island) was ≥ 1 indicating the "new" intake of DDT to marine environment and marine organisms (Figure 3-25).

Hereby, total amount of pesticides in marine environment of Peter the Great Bay decreased last two decades (1990-2010) (Fig.3-19). But data obtained a long-term presence and new input of PTS to marine coastal and estuarine ecosystems of the Russian part of the NOWPAP region. Pesticides accumulation have been found in

various marine organisms. Monitoring programs on PTS (HCH, DDT, PCB) occurrences in marine environment carried out by the Russian Governmental services and agencies in the Russian part of NOWPAP region will be continued.

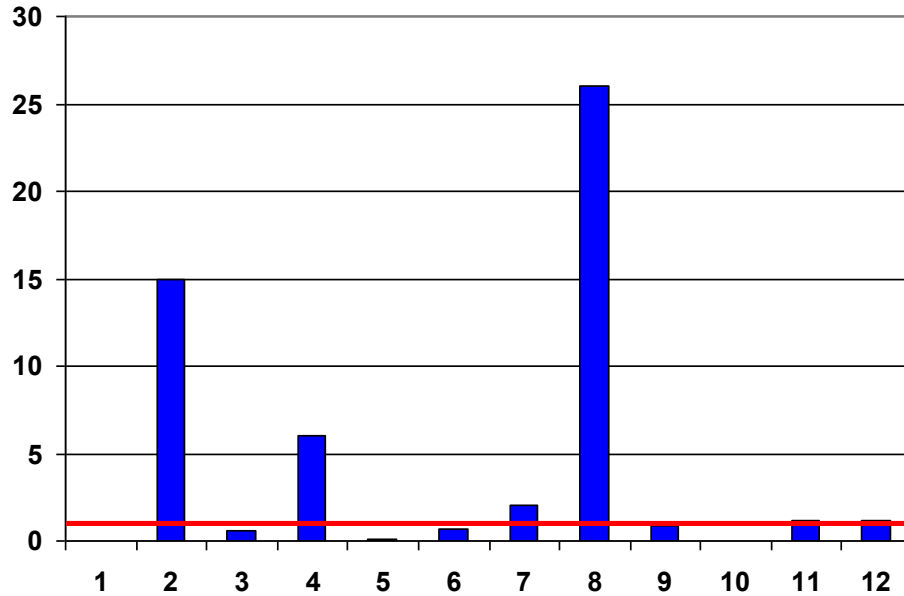


Figure 3-25. DDT / DDE ratio in liver of various fish species from Peter the Great Bay (Lukyanova et al., 2007).

- | | |
|--|--|
| 1 - Herring (<i>C. pallasii</i>) (Tumannaya River mouth) | 7 - Flounder (<i>P. obscurus</i>) (Furugelma Isl.) |
| 2 - Flounder (<i>P. stellatus</i>) (Posyet Bay) | 8 - Flounder (<i>P. stellatus</i>) (Furugelma Isl.) |
| 3 - Flounder (<i>P. obscurus</i>) (Furugelma Isl.) | 9 - Flounder (<i>P. pinnifasciatus</i>) (Amursky bay, 2004) |
| 4 - Herring (<i>C. pallasii</i>) (Amursky bay) | 10 - Flounder (<i>P. obscurus</i>) (Amursky bay, 2004) |
| 5 - Rudd (<i>Tribolodon brandti</i>) (Amursky bay) | 11 - Flounder (<i>P. pinnifasciatus</i>) (Amursky bay, 2005) |
| 6 - Mullet (<i>Mugil cephalus</i>) (Sivuchiya Bay) | 12 - Flounder (<i>P. pinnifasciatus</i>) (Ussuriyskiy bay, 2005) |

<China>

Along Bohai Bay, the characteristics and transport of PTS were studied. In recent years, the rapid economic development in this area, has brought out continuous increasing of the pollution loads in the Bohai Sea, especially as the result of the large coastal reclamation project on Tianjin Binhai New Area. In the period of 2007-2009, the sediment samples in the main rivers, estuaries, intertidal zone, and near shore area of Bohai Bay, were collected, and macrobenthos samples associated with the marine sediments were used to assess the influence of hydrodynamics in the coastal environment on the pattern of trace contaminants and the macrobenthic community (Zheng et al, 2011). Based on data derived from these samples, the levels of PAHs, OCPs, PCBs, and PBDEs in sediments followed the order PAHs>OCPs>PCBs>PBDEs. The higher concentrations of PCBs, OCPs, PAHs and PBDEs were found in the estuarine and near shore environment of the Dagu Drainage River. The spatial distribution of OCPs was different to that of PCBs due to the direction of the velocity field of Bohai Bay in its old and new topography, and the higher water-solubility of OCPs than that of PCBs. The results of the Pearson correlation and the PCA indicate that the medium diameter (MD) of sediments was the predominant factor influencing the distribution of PCBs and OCPs, most sampling sites were characterized mainly by TOC of sediments and biomass of macrobenthos. The results indicate that the distribution of trace contaminants and macrobenthic community in Bohai Bay are mainly affected by the hydrodynamic conditions.

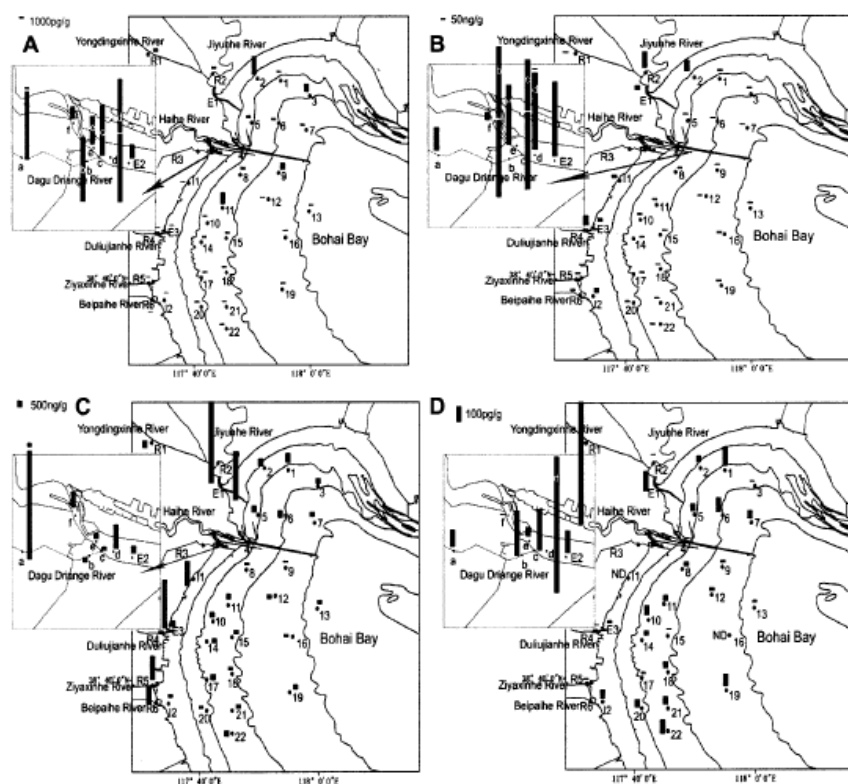


Fig. 3-26 The distribution of trace persistent organic pollutants in sediments from the west coast of Bohai Bay (A PCBs, B OCPs, C PAHs and D PBDEs)

China usually has not organized or conducted systematic monitoring on PTS and POPs yet. But in 2007-2008, national ambient air monitoring programs on POPs are performed. Various methods for sampling and analysis for POPs testing have been applied in different countries or regions. However, in the recent background survey, the sampling, analysis and data treatment were conducted in principle in accordance with "Guidance on the Global Monitoring Plan for persistent Organic Pollutants". Detailed information on air concentrations in the region is shown in Tab. 3-20. Among the 11 sampling sites, 3 sites were at the NOWPAP region. The concentrations of some kinds of POPs at the 3 locations are shown at Tab. 3-21.

Table 3-20. Summary for air monitoring programs

Period	Location	Number of site/sample(/year)	POPs	remarks
2007-2008	11 provinces	2 samples/site	PCB, HCB, Aldrin, Dieldrin, Endrin, DDT, Chlordane, Heptachlor, Mirex, PCDD/PCDFs and dl-PCB	Ministry of Environmental Protection, Chinese Centers for Disease Control and Prevention

Table 3-21. The POPs concentrations in 3 background locations

	Daxinganling, Heilongjiang Province		Qingyuan, Liaoning Province		Changdao, Shandong Province	
	A1	A2	K1	K2	B1	B2
Heptachlor	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND
trans-Heptachlor epoxides(A)	ND	ND	ND	ND	ND	ND
oxychlordane	ND	ND	ND	ND	ND	ND
trans-Heptachlor epoxides(B)	ND	ND	ND	ND	ND	ND
trans-chlordane	ND	ND	ND	ND	ND	4.1
2,4'-DDE	ND	0.07	0.05	0.03	0.03	0.02
cis-chlordane	ND	ND	ND	ND	ND	ND
trans-nonachlor	ND	ND	ND	ND	ND	ND
4,4'-DDE	0.90	0.57	0.41	0.16	0.30	0.21
dieldrin	ND	ND	ND	ND	ND	ND
2,4'-DDD	ND	ND	ND	ND	ND	ND
endrin	ND	ND	ND	ND	ND	ND
4,4'-DDD	ND	ND	ND	ND	0.032	ND

2,4'-DDT	ND	0.21	ND	ND	ND	ND
cis-nonachlor	ND	ND	ND	ND	ND	ND
4,4'-DDT	ND	ND	0.27	0.12	ND	0.12
Mirex	ND	0.02	0.05	0.03	0.03	0.05
PCB-28	8.7	12.6	7.8	4.0	1.9	0.8
PCB-52	2.0	3.8	26.7	17.8	20.4	55.3
PCB-101	0.4	0.6	0.7	0.5	1.1	0.7
PCB-138	0.1	0.1	0.03	0.1	0.03	0.03
PCB-153	0.2	0.3	1.1	1.1	0.5	0.5
PCB-180	0.1	0.1	0.1	0.1	0.2	0.1
HCB	60.2	64.4	1846.5	203.1	138.6	54.3

3.4.1 Pesticide POPs in Annex of the convention

Some researchers have carried out field studies at some places at different time and discovered the existence of pesticide POPs in Annex A in the air, water, soil and foods, but there is no continuous and systematic data. A small number of data show that, comparing with those in sediments and shellfish, POPs concentrations in other media were relatively low.

3.4.2 PCBs from Annex A of the convention

China has not conducted systematic monitoring of PCBs in the environment and has only conducted research monitoring in some areas. Some of the monitoring results are shown in Table 3-22. Research shows that PCBs exist in sediments of a few estuaries and marine coastal areas.

Tab. 3-22 Demonstration data of PCBs concentrations in environmental media in research reports of some areas

Place	Time	Testing method	Sampling/sample number	Environmental media	PCBs concentrations	Reference literature
Taihu Lake	2000	GC-ECD	Not available	Bottom mud	0.983 ng/g	Yang et al., 2003
Qingdao marine coastal area	1997-1999	GC-ECD	9 sampling sites	Surface sediments	0.65-32.9 ng/g dry weight	Zhu et al., 1995

3.4.3 Chemicals from Annex B of the convention

Although DDT was banned as a pesticide in China, it can still be detected in air, water, sediment, field soil, grains, vegetables, fruits, meat, animals and human tissue in many areas. However, most research data show that DDT concentrations are lower than relevant standards. Relevant data are shown in Tab. 3-23 (NIP of China, 2007).

Tab. 3-23 Demonstration data for DDT concentrations in different environmental media in some research documents

Region	Environmental media	Monitoring Method	Number of samples	Time of monitoring	Total DDT level	Reference
					pg/m³	
Atmosphere						
Tianjin	Particle	GC/ECD		2002	1,874	Cheng et al., 2000
Haidian Beijing	Particle	GC/ECD		2002	401-962	Cheng et al., 2000
Taihu lake	Gas	GC/ECD		2002	1,139	Liu et al., 2004
					ng/l	
Water						
Liaohu river	Water			1998-2000	7.04	Zhang et al., 2000
Guanting Reservoir-Yongding River	Water	GC/ECD		2000	ND-46.8	Kang et al., 2003a
Tonghui River	Water	GC/ECD		2003	192.5-2651 31.58-344.9 134.9-3788	Zhou et al., 2005
					ng/g	
Estuary and Marine sediment						
Liaodong Bay, Bohai Bay	Marine sediment	GC/ECD	18	2005	0.3-12.1	Liu et al., 2005
Guanting Reservoir of Yongding River	Sediment	GC/ECD		2001	0.3-1.9	Kang et al., 2003b
Taihu of Yangtze River	Estuary sediment	GC/ECD GC/MS		2000	9.22-27.35	Yuan et al., 2003

DDT concentrations in various foods of China in 2000 are shown in Tab. 3-24.

Tab. 3-24 DDT concentrations in various foods of China in 2000

Variety	Number of Samples	Average Concentration (ng/g)			Original National Standard*(ng/g)	Current National Standard*(mg/kg)
		p,p'-DDT	o,p'-DDT	p,p'-DDT		
Grains	80	4.1	7	14.1	200	0.05
Fruits	88	0.8	1.3	0.8	100	0.05
Meat and its products	40	0.8	2.3	2.7	100	0.05
Content of fat is less than 10% (calculated by original sample)	41	5.6	1.3	1.8	200	0.02
Content of fat is more than 10% (calculated by fat)						2
Fish	30	3.6	0.9	2.5	500	0.5
Eggs	51	2.5	0.5	1.5	1000	0.1
Milk powder	15	0.6	0.6	2.0	Converted to fresh milk	
Milk	5	5.7	25.5	1.3	100	0.02
Vegetable oils	10	0.2	0.5	1.0	500	
Tea-leaf	44	10.8	13.8	31.1	200	0.2

* The source of original standards is the *Standard on HCH and DDT Residue in Foods Such as Grains and Vegetables* (GB2763-81), and the source of new standards is the *Limits of Pollutants in Foods* (GB2763-2005).

Research and monitoring data show that DDT concentrations in environmental media and foods are decreasing constantly in China. Except for sediments and shellfish in few estuary and marine coastal areas, DDT concentrations in other environmental media and foods are lower than national standards. Production and use of dicofol is the main source of DDT pollution.

DDT has been detected in human milk in many areas of China. p,p'-DDT decreased from 1.8 mg/kg in 1982 to 0.24 mg/kg in 1998, and total DDT decreased from 7.71 mg/kg to 2.04 mg/kg. It can be concluded that since DDT was banned, DDT concentrations in human milk have obviously decreased.

3.4.4 The chemicals listed in Annex C of the Convention- Dioxins

Except that the Action Plan on Foods Safety issued in 2003 lists Dioxins capacity in the monitoring plan, and a few research monitoring activities have been carried out on animal foods on this basis, China has not established systematic monitoring of Dioxins in environmental media, health indicators or foods. With little research data, it is very difficult to completely reflect and evaluate the environmental and health risks caused by Dioxins pollution. Some of the research outcomes are listed in Table 3-25.

Tab. 3-25 Sample data on Dioxins concentrations in research reports of some regions

Region	Sample	Dioxins concentration	Monitoring method	Sample situation	Monitoring Time	Reference Literature
Dalian	Human milk	15.84 pg TEQ/g, fat	CALUX method	47 human milk samples	2002	Jin et al., 2003
Shenyang	Human milk	7.21 pg TEQ/g, fat	CALUX method	32 human milk samples	2002	Jin et al., 2003

3.4.5 Other PTS and Emerging POPs in China

A review can be found about the recent research on emerging POPs in China, including PBDEs and PFOS/PFOA, which are newly listed in the Stockholm Convention, as well as Dechlorane Plus and short-chain chlorinated paraffins (SCCPs), which have not been listed in the Convention (Wang et al, 2010).

Tab. 3-26 Summary of Emerging Persistent Organic Pollutions in China

Emerging POPs	Research status	Comparison	Remarks
PBDEs	Relatively well studied in the multimedia environment, human and organisms	In some e-waste dismantling sites, the levels are very high. BDE-209 is usually the dominant	Qingdao Seashore, sediment, 0.12-5.51 ng/g; Coast of Bo Sea, BDE-209 and PBDEs were 2.29 and 0.16 ng/g.
PFOS/PFOA	Some studies have been conducted in various environmental matrices, humans, and organisms	PFOS/PFOA levels in China are relatively low. PFOS is usually the dominant PFC in the environment, except in water	Dalian coastal waters generally much lower than those in American or Canadian
DP	Very few studies have been conducted on DP pollution in China	The DP levels in air in China are comparable to those in air in Great Lakes, USA	Harbin, Heilongjiang Province, 0.35±0.21 pg/m ³
SCCPs	Have developed an method for analysis	SCCP levels have not been reported	

Summary of emerging POPs pollutions in China can be found in Table 3-26. Most research on PBDEs has been conducted in the e-waste dismantling sites in Guangdong and Zhejiang provinces, where PBDEs are at high levels in the environmental matrices and human bodies. PFOS/PFOA levels are relatively low in environmental matrices and human bodies in China, perhaps because of less usage compared with that in North America. Few studies on the pollution status of DPs and SCCPs have been reported in

China. Long-term temporal variations of the levels of such pollutants in China remain unclear because all available data are reported in very recent years. Much work should be done to strengthen the monitoring capacity for emerging POPs in China and to better understand their pollution status (Wang et al, 2010).

<Korea>

Since 1999, National Institute of Environmental Research (NIER) supported by Ministry of Environment (MoE) began nationwide monitoring of POPs in the environment and humans. Since 2001, comprehensive projects have been undertaken to establish the national emission inventory of unintentionally byproducts (dioxins in particular). For marine environment, the National Fisheries Research and Development Institute (NFRDI) supported by the Ministry of Ocean and Fisheries (MOF) has launched the POPs and related compounds (PAHs and butyltins) monitoring in seawater, sediment and bivalves (mussels or oysters) since 2001. Based on the nationwide monitoring program for terrestrial and coastal environments of Korea, a large number of studies have performed to investigate contamination status and temporal trends of POPs and related compounds. For example, several studies have performed to characterize contamination and source of PCDD/Fs in Korean coastal waters and humans (Moon et al., 2005; Moon and Ok, 2006; Moon et al., 2008a, 2008b; Moon and Choi, 2009; Moon et al., 2009b, 2010b, 2010d, 2011b, 2012b; Choi et al., 2010a, 2011a). Many studies on the occurrence of PCBs and OCPs have reported in Korean coastal waters (Kim et al., 2002; Hong et al., 2006; Moon et al., 2008a, 2008b, 2009; Choi et al., 2010; Moon et al., 2010a; Park et al., 2010; Choi et al., 2011) in humans (Moon et al., 2011b). Several studies have reported on PBDE contamination and their consumption pattern in Korean air, sediment and biota (Moon et al., 2007a; 2007b; 2007c; 2008b; 2010a; Park et al., 2010; Moon et al., 2012c; Lee et al., 2013) and humans (Moon et al., 2012a). However, only limited information is available on contamination by PFCs in Korean coastal waters and biota (So et al., 2004; Yoo et al., 2008; 2009; Moon et al., 2010c). Based on the nationwide monitoring program, several studies have reported on contamination status and temporal trends of BTs in seawater, sediment and biota including marine mammals (Choi et al., 2009a, 2009b, 2010a, 2010b, 2011a, 2012b, 2012, 2013a, 2013b). In addition, several publications on distribution, sources and toxicological effects of PAHs were reported for Korean coastal waters during last decades (Yim et al., 2005, 2007; Moon et al., 2006; 2008b, 2010e, 2011a, 2012d, 2012e).

The average concentrations of PCDD/Fs in ambient air samples from the 37 sites ranged from not detected (ND) to 617 fg I-TEQ m³, with an average of 28 fg I-TEQ m³ (Figure 3-27). Compared with rural sites, atmospheric PCDD/Fs concentrations were obviously elevated at residential/industrial sites. Although some industrial sites showed higher levels of PCDD/Fs and PCBs than the residential and background areas, the PCDD/F and PCB levels in the South Korean atmosphere were similar to that of other countries and much lower than the Korean atmospheric PCDD/Fs standard (600 fg TEQ m³). Spatial distributions of atmospheric PCDD/Fs show that the levels of atmospheric PCDD/Fs were found to be the highest in the north-west area of South Korea, which are close to Seoul, the biggest city of South Korea.

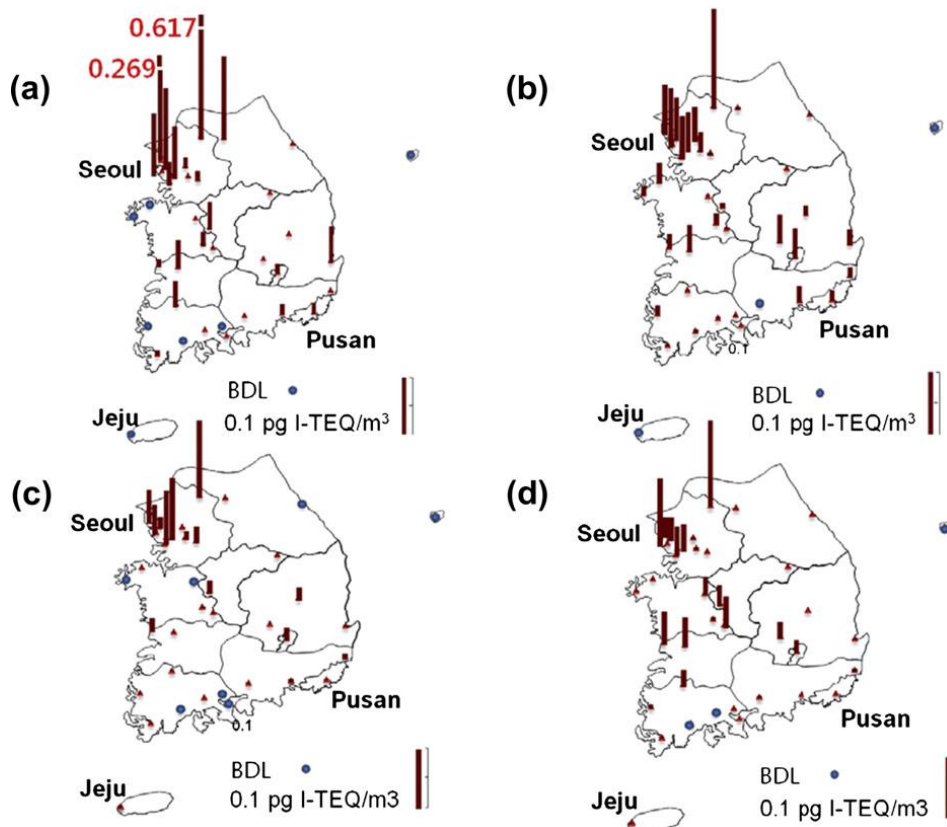


Figure 3-27. Spatial distribution of PCDD/Fs in atmosphere in South Korea (a) winter, (b) spring, (c) summer and (d) autumn (Shin et al., 2011).

The concentrations of DL-PCBs ranged from ND to 16 fg WHO-TEQ m³, with an average of 8 fg WHO-TEQ m³ (Figure 3-28). At most sites DL-PCBs were not detected due to a low contribution to TEQ value than PCDD/Fs. Spatial distributions of atmospheric PCBs are also characterized by the highest levels of DL-PCBs in the north-west area of South Korea. The TEQ values of DL-PCBs in ambient air samples from industrial and residential sites showed a good correlation with those of PCDD/Fs. The coefficients of determination during winter period were 0.88 (industrial) and 0.92 (residential), respectively. However, samples from rural sites did not show any significant correlation.

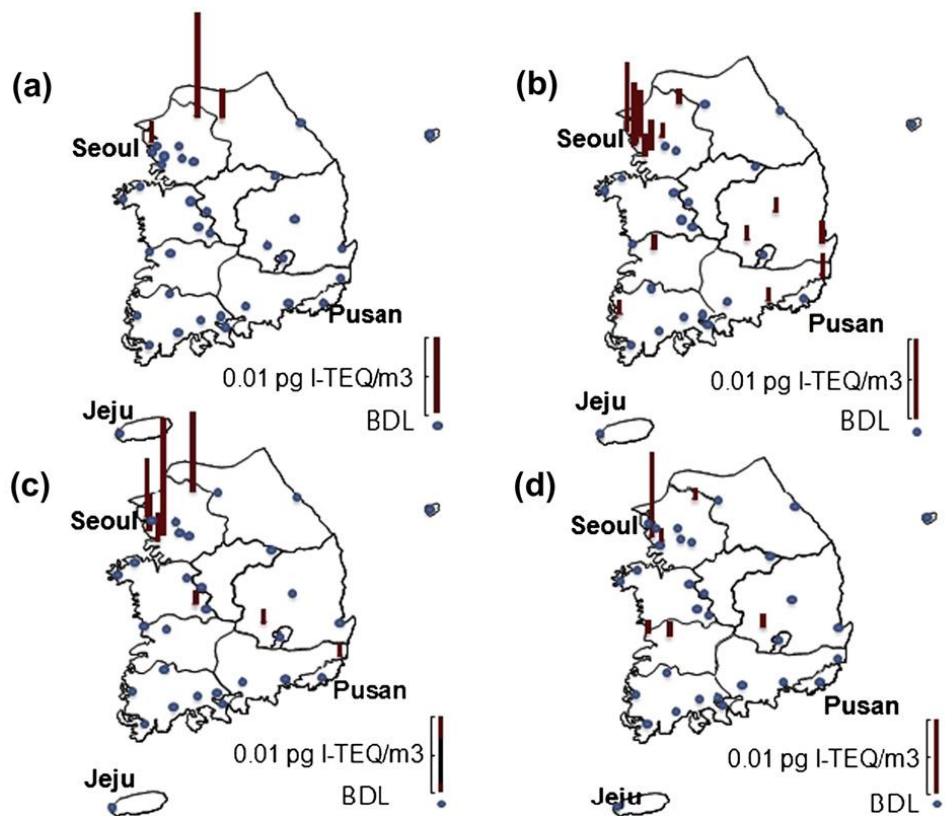


Figure 3-28. Spatial distribution of dioxin-like PCBs in atmosphere in South Korea (a) winter, (b) spring, (c) summer and (d) autumn (Shin et al., 2011).

Figure 3-29 shows a temporal trend of atmospheric levels of PCDD/Fs in South Korea from 1998 to 2007. The first reliable official monitoring programs of air PCDD/Fs and DL-PCBs in South Korea have been started from 1999 and 2002, respectively. For PCDD/Fs, mean concentrations decreased from 425 to 28 fg I-TEQ m³ from 1999 to 2007 which accounts for a 93% reduction in air levels. The Korean government has regulated PCDD/F emissions from MSWIs since 1997 (>50 ton/h, old 0.5 ng I-TEQ m³, new 0.1 ng I-TEQ m³) which resulted small size incinerators became the major point source of PCDD/Fs emission in Korea (Shin et al., 2011), and reinforced the regulation in 2004 (>25 kg/h, old 10 ng I-TEQ m³, new 5 ng I-TEQ m³), resulting in a total decrease of PCDD/Fs emissions. Meanwhile, biannually national dioxin emission inventories of the atmosphere were announced from 2005. In January 2007, South Korea became an official signatory of the Stockholm Convention. For the effective implementation of the Stockholm Convention, the Korean government promulgated a special law on POPs management in 2008 and regulated PCDD/F emissions from other industrial sources (such as metallurgy and non-metallic industries etc.) from 2009. As a result, the contribution to atmospheric PCDD/Fs from incinerators has decreased from 88% to 49% during 2001 and 2007. In 2007, the amount of PCDD/F emissions to the atmosphere in South Korea was estimated to be 188 g, which means a decrease of 81% compared to 2001 (1004 g/year). Those decreasing amounts of

atmospheric emissions of PCDD/Fs and PCBs mostly contributed to the decreasing trend of atmospheric levels. As a whole, the law reinforcement and implementation of best available techniques/best environmental practices (BAT/BEP) at the emission sources resulted in the reduction of PCDD/Fs from those facilities.

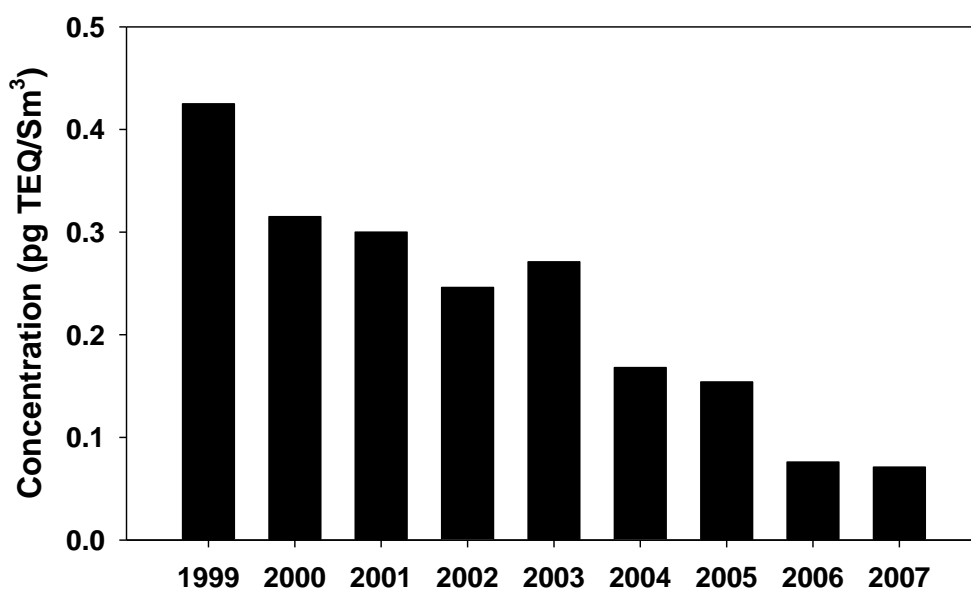


Figure 3-29. Temporal trends of PCDD/Fs concentrations (pg TEQ/m³) in ambient air from Korea during 1999-2007 (Shin et al., 2011).

From marine environment monitoring performed in the NFRDI, the concentrations of POPs and related compounds are summarized in Table 3-27. The concentrations in sediments ranged from nd to 15.03 ng/g dry weight for PCBs, from nd to 3.76 ng/g dry weight for HCHs, from 0.02 to 4.03 ng/g dry weight for DDTs, from 15.58 to 1083 ng/g dry weight for PAHs, from 1.44 to 817 ng Sn/g dry weight for TBT, and from 0.06 to 12.2 pg TEQ/g dry weight for PCDD/Fs. Concentrations of PCBs, HCHs, DDTs and PAHs found in nationwide monitoring program were much lower than those reported in previous studies in several coastal regions (Khim et al., 1999a, b; Hong et al., 2006; Yim et al., 2007; Moon et al., 2008a; Choi et al., 2009a, b). The TBT and PCDD/F concentrations in industrialized bays ranged from nd to 5372 ng Sn/g dry weight (Choi et al., 2009a, b), and from 0.44 to 38.5 pg TEQ/g dry weight (Moon et al., 2008a), respectively.

The higher concentrations of contaminants in several studies (Khim et al., 1999a, b; Hong et al., 2006; Yim et al., 2007; Moon et al., 2008a; Choi et al., 2009a, b) could be attributed to differences in the sampling sites. Sampling in previous surveys was done at sites regarded as “hot spots” to identify sources in each region, while in the present Korean nationwide monitoring study, hot spots were generally avoided. Ranges reported for sediment in the literature are usually broad because of differences in the data calculation methods, sampling periods and influence of sampling sites. The levels

of PCBs and DDTs determined in Korean coasts were apparently lower than those from the Mediterranean Sea (Gomez-Gutierrez et al., 2007), or within the broad range reported in the monitoring of toxic substances in Hong Kong (Kueh and Lam, 2008) and the Baltic Sea (Pikkarainen, 2007). HCH and PAH concentrations in our study were also comparable with those in the Hong Kong marine environment. PCDD/F concentrations in this study were lower than those in Hong Kong coastal waters and the Baltic Sea, and TBT concentrations were higher than those in Hong Kong coastal waters (Pikkarainen, 2007; Verta et al., 2007; Kueh and Lam, 2008). The mean detectable frequencies of PCBs, DDTs, PAHs, TBT and PCDD/Fs revealed ubiquitous contamination of sediments along the Korean coast, ranging from 54% (DDTs) to 100% (PAHs). Among those chemicals, in particular, PAHs and PCDD/Fs with high detection frequencies should be considered as major environmental problems because of the presence of an ongoing source. PAHs originate from a variety of anthropogenic sources including thermal combustion processes, vehicular emissions, and biomass burning (Oros and Ross, 2005).

A waste incinerator is known to be one of the main sources of PCDD/Fs. In Korea, 32 municipal solid waste incinerators and about 1000 various incinerators (small scale < 200 kg/hr and medium scale > 200 kg/hr) are currently in service (Park et al., 2009). Sampling area includes many industrialized bays and special management zones (Ulsan Bay, Busan Harbor, Masan Bay and Incheon coast), which contain large harbors and industrial complexes. A large petrochemical and non-ferrous industrial complex is located in the coastal area of Ulsan Bay in the east coast. Area near Masan Bay in the south coast is home to petrochemical industrial, a steel mill complex, a non-ferrous industrial complex. Industrial source such as steel manufacturers, machine shops, dye houses, pulp factories, and a sewage treatment plant are located around Incheon coast and artificial seawater Lake Shihwa in the west coast. DDTs and PCBs showed moderate detection frequencies, even though the use of DDT and PCBs was banned in 1971 and 1979, respectively. DDTs and PCBs are organic contaminants with a long history due to their physicochemical properties. Ubiquitous contamination of DDT and PCBs in shellfish, cetaceans and sediments has been reported from Korean coastal waters (Choi et al., 2010a; Park et al., 2010). TBT also exhibited a moderate mean detection frequency, despite the complete restriction on the use of TBT-based antifouling paints that occurred in 2003. The reason could be its rapid degradation. The half-life of TBT in sediments from a seawater marina was estimated to be about two years (De Mora et al., 1989). The low detection frequency of HCHs can be attributed to differences in their physicochemical and biochemical properties (Simonich and Hites, 1995). HCHs have higher biodegradability and lower lipophilicity compared with the other contaminants.

Table 3-27. Concentrations of POPs and related compounds in sediments from Korean coastal waters during 2001-2007 (Choi et al., 2011a)

Site Code	Sampling site	PCBs ^a	HCHs ^b (ng/g dry wt)	DDTs ^c	PAHs ^d	TBT (ng Sn/g dry wt)	PCDD/Fs ^e (pg-TEQ/g wet wt)
1	Sokcho coast	0.22 ± 0.36	ND ± 0.00	0.02 ± 0.03	15.58 ± 17.93	4.34 ± 8.85	0.06 ± 0.07
2	Jumunjin coast	0.10 ± 0.14	3.76 ± 0.67	0.04 ± 0.07	34.98 ± 23.68	3.76 ± 7.20	0.09 ± 0.07
3	Jukbyeon coast	0.25 ± 0.45	0.88 ± 1.66	1.61 ± 2.68	29.59 ± 19.68	2.43 ± 5.00	0.17 ± 0.10
4	Hupo coast	0.61 ± 0.72	ND ± 0.00	0.69 ± 0.81	429.77 ± 430.05	5.63 ± 10.55	0.74 ± 0.43
5	Guryongpo coast	ND ± 0.94	ND ± 0.00	0.07 ± 0.11	102.72 ± 176.43	5.36 ± 22.14	0.45 ± 0.54
6	Ulsan coast	14.33 ± 18.23	2.51 ± 4.40	1.02 ± 1.51	1082.26 ± 1211.56	817.24 ± 1573.61	2.75 ± 0.98
7	Onsan coast	3.77 ± 3.70	0.30 ± 0.57	0.59 ± 0.61	239.34 ± 166.66	23.00 ± 20.61	3.64 ± 1.51
8	Busan North Harbor	15.03 ± 8.72	0.56 ± 0.79	4.03 ± 5.60	608.60 ± 459.17	35.17 ± 28.43	3.34 ± 1.68
9	Busan South Harbor	2.92 ± 4.18	1.26 ± 2.35	2.50 ± 4.68	213.93 ± 140.26	45.60 ± 65.96	2.66 ± 2.32
10	Jindong Bay	0.72 ± 0.40	0.05 ± 0.09	1.19 ± 1.18	352.39 ± 236.93	74.02 ± 93.48	6.35 ± 1.79
11	Wonmun Bay	0.91 ± 0.79	0.02 ± 0.05	1.01 ± 0.79	502.27 ± 281.05	44.19 ± 27.52	3.87 ± 0.68
12	Gohyeonseong Bay	0.78 ± 0.55	0.36 ± 0.68	3.56 ± 2.27	501.94 ± 349.80	269.65 ± 150.99	4.47 ± 2.32
13	Haengam Bay	2.13 ± 1.87	0.03 ± 0.06	1.82 ± 3.06	386.52 ± 145.86	42.26 ± 50.39	3.12 ± 1.35
14	East part of Geojedo	0.49 ± 0.31	0.60 ± 1.14	0.16 ± 0.22	705.68 ± 263.78	12.07 ± 12.28	2.20 ± 0.32
15	Masan Bay	0.81 ± 3.43	0.34 ± 0.54	1.21 ± 1.83	413.75 ± 247.46	94.64 ± 134.10	12.22 ± 3.86
16	Gwangyang Bay	1.13 ± 1.79	0.32 ± 0.51	0.29 ± 0.41	299.29 ± 301.61	10.70 ± 12.74	1.74 ± 1.91
17	Gamak Bay	0.56 ± 0.37	0.44 ± 0.76	3.58 ± 5.58	490.20 ± 449.65	74.89 ± 71.31	1.30 ± 0.73
18	Mokpo coast	0.14 ± 0.16	0.47 ± 0.85	0.33 ± 0.57	100.43 ± 88.46	8.73 ± 11.59	0.66 ± 0.26
19	Gochang coast	0.05 ± 0.33	0.31 ± 0.58	0.13 ± 0.13	68.12 ± 33.43	4.47 ± 9.13	0.94 ± 0.73
20	Jeonjupo coast	0.01 ± 0.26	0.35 ± 0.65	0.13 ± 0.14	62.90 ± 35.01	1.47 ± 4.13	1.51 ± 1.67
21	Gunsan coast	0.19 ± 0.29	0.47 ± 0.83	0.72 ± 0.80	117.49 ± 84.77	3.89 ± 7.35	1.25 ± 0.58
22	Cheonsu Bay	0.20 ± 0.36	0.34 ± 0.62	0.26 ± 0.37	150.29 ± 80.48	1.44 ± 2.77	1.27 ± 0.85
23	Garorym Bay	0.20 ± 0.40	0.38 ± 0.70	0.04 ± 0.09	48.36 ± 79.06	7.37 ± 16.48	0.09 ± 0.10
24	Asan Bay	0.43 ± 0.82	0.64 ± 1.20	0.15 ± 0.20	107.05 ± 52.21	15.75 ± 25.55	2.75 ± 2.00
25	Incheon coast	1.05 ± 0.72	0.56 ± 1.03	0.39 ± 0.40	222.85 ± 124.44	7.20 ± 10.22	0.78 ± 0.22
	Min	ND ± 0.94	ND ± 0.00	0.02 ± 0.03	15.58 ± 17.93	1.44 ± 2.77	0.06 ± 0.07
	Max	15.03 ± 8.72	3.76 ± 0.67	4.03 ± 5.60	1082.26 ± 1211.56	817.24 ± 1573.61	12.22 ± 3.86
	Mean	2.26 ± 2.01	0.48 ± 0.78	1.06 ± 0.46	302.95 ± 97.31	69.03 ± 61.58	2.43 ± 0.53
	Detection frequency(%)	73	25	54	100	58	97
	85th percentile	3.29	0.49	1.32	444.92	54.52	3.76

^a Sum of concentrations of 23 congeners.

^b Sum of concentrations of a-HCH, b-HCH and g-HCH.

^c Sum of concentrations of *ortho* and *para* forms of parent and metabolites.

^d Sum of concentrations of 16 compounds.

^e Sum of concentrations of 7 PCDDs and 10 PCDFs congeners.

Table 3-28 shows the mean (\pm SD) concentrations, detection frequencies and the 85th percentile concentrations POPs and related compounds in bivalves (mussels or oysters), to evaluate the spatial distribution among sites. These results were from nationwide monitoring program performed in the NFRDI. The results for OCPs are only presented for HCHs and DDTs, because detectable concentrations of HCB, heptachlor, heptachlor epoxide, aldrin, endrin, and dieldrin were not found in all samples analyzed. The mean detectable frequencies of four organic contaminants indicated that PCBs, PAHs, BTs, and PCDD/Fs were ubiquitous contaminants along the Korean coast. Among those chemicals, in particular, PAHs and PCDD/Fs should be considered as major environmental problems due to the presence of two contaminant sources up to now. PAHs can originate from a variety of anthropogenic sources that include thermal combustion processes, vehicular emissions, and biomass burning (Oros and Ross 2005). A waste incinerator is known to be one of the main sources of PCDD/Fs. In Korea, 32 municipal solid waste incinerators and about 1,000 various incinerators (small < 200 kg/h and medium scale > 200 kg/h) in service until now (Park et al. 2009). PCBs and BTs, however, were already regulated in 1979 and 2003, respectively. The low detection frequencies of HCHs might be due to differences in the physicochemical and biochemical properties (Simonich and Hites 1995). HCHs have higher biodegradability and lower lipophilicity compared to the other contaminants.

The concentrations of PCBs, HCHs, DDTs, PAHs, BTs, and PCDD/Fs in mussels were in the range of 0.85 to 24.6 ng/g dry weight, nd to 3.01 ng/g dry weight, 0.55 to 16.3 ng/g dry weight, 83.08 to 387 ng/g dry weight, 49.6 to 1,360 ng Sn/g dry weight, and 0.07 to 0.48 pg TEQ/g wet weight, respectively. These results can be compared with previous studies (Kim et al. 2002; Ramu et al. 2007).

Concentrations of PCBs, HCHs, and DDTs found from nationwide monitoring program were similar to the studies by Kim et al. (2002) and Ramu et al. (2007). Ranges reported for shellfish in the literature are usually broad because of differences in the data calculation methods, sampling periods, and influence of shellfish sexual maturity. The levels of PCBs, HCHs, and DDTs determined were apparently lower than those from the east coast of China (Fung et al. 2004) and surprisingly low in comparison with data from Hong Kong mariculture zones (So et al. 2005). The levels of PCBs, DDTs, and PAHs in our study were within the broad range reported in the US mussel watch program (O'Connor and Lauenstein 2006). In the Asia-Pacific mussel watch program, Korean mussels revealed moderate or low levels of OCPs and PCBs compared with levels for 12 countries (Monirith et al. 2003). TBT levels were higher than that in the US mussel watch program. PCDD/Fs levels were comparable with that in mussels from the German market (Karl et al. 2002). Filter-feeding organisms may constitute a problem for human health by their capacity to bioconcentrate compounds from the water column. For the same contaminants, different standards have been adopted by different countries and organizations. The US Food and Drug Administration (US FDA) and Canadian Food Inspection Agency established action levels of 2 μ g/g wet weight for PCBs and 5 μ g/g wet weight for DDTs in edible seafood (Wu et al. 2008).

From mussel watch program, the mean detectable frequencies of PAHs and PCDD/Fs in mussels and oysters were similar to those in sediment (Choi et al., 2011a). However, the mean detectable frequencies of PCBs, HCHs, DDTs and BTs showed higher in sediments than in mussels. These results are likely to ascribe to the difference of characteristics between sediments and mussels on accumulation rate and degradation

rate. Contaminated sediments may constitute a particular threat for benthic organisms and even for fish through the marine food web. The easiest way to assess potential risks to aquatic life from the sediment is simply to compare the concentrations of chemicals with applicable sediment quality guidelines (SQGs) for the protection of aquatic life as a screening tool. The assessment was done using the effects-range low (ERL) and effects-range median (ERM) of the National Oceanic and Atmospheric Administration (NOAA) for PCBs, DDTs and PAHs (Long et al., 1995), and the threshold effect level (TEL) and the probable effect level (PEL) of the Canadian Sediment Quality Guidelines (CCME, 2002) for PCDD/Fs. The ERM and PEL represent the concentrations above which adverse effects are expected to occur frequently, and the ERL and TEL represent the concentration below which adverse biological effects are expected to occur rarely. The concentrations of POPs were below the ERM and PEL at all sites during the seven years, even though the concentrations of DDTs and PCDD/Fs exceeded the ERL at 2–6 sites (8–24%) and the TEL at 9–18 sites (26–72%) during the seven years from 2001 to 2007, respectively. From these results, ecological risks from sediments in Korean coastal waters are estimated to be at safe levels. On the other hand, the mussel watch program also revealed that concentration of organic substances in mussels and oysters were below the action or maximum levels for humans established by the US FDA and EU (Choi et al., 2010a). However, the excess of the TEL for PCDD/Fs at a few sites could be posed potentials risk in benthic organism of Korean coast due to the presence of ongoing sources. Therefore, continuous monitoring is required to watch overall contamination status and to assess ecological risks by the exposure to POPs and related compounds in the marine environment of Korea.

Table 3-28. Concentrations of POPs and related compounds in bivalves (mussels or oysters) from Korean coastal waters during 2001-2007 (Choi et al., 2010a)

Site code	Sampling site	PCBs ^a	HCHs ^b	DDTs ^c	PAHs ^d	BTs ^e	PCDD/Fs ^f
		(ng/g dry wt)				(ng Sn/g dry wt)	(pg-TEQ/g wet wt)
1	Sokcho coast	2.23 ± 1.33	0.33 ± 0.75	1.28 ± 1.47	119.65 ± 55.14	182.01 ± 165.89	0.078 ± 0.085
2	Jumunjin coast	1.14 ± 0.95	0.22 ± 0.39	1.06 ± 1.29	133.16 ± 114.58	312.47 ± 700.87	0.065 ± 0.021
3	Jukbyeon coast	2.09 ± 1.81	1.36 ± 2.35	2.86 ± 4.46	83.08 ± 45.39	143.68 ± 159.11	0.083 ± 0.071
4	Hupo coast	1.88 ± 2.18	0.73 ± 1.20	2.01 ± 2.19	99.88 ± 56.32	67.22 ± 51.60	0.112 ± 0.120
5	Guryongpo coast	2.76 ± 2.43	0.27 ± 0.42	1.61 ± 2.23	85.22 ± 47.17	63.26 ± 40.46	0.077 ± 0.058
6	Ulsan coast	24.59 ± 15.47	0.74 ± 1.27	8.53 ± 11.79	239.83 ± 124.40	1,360.82 ± 674.58	0.222 ± 0.077
7	Onsan coast	23.13 ± 14.77	0.50 ± 0.65	4.38 ± 2.63	261.01 ± 172.91	807.12 ± 1,137	0.208 ± 0.165
8	Busan North Harbor	24.62 ± 14.29	0.36 ± 0.96	8.37 ± 11.76	286.58 ± 151.14	855.05 ± 420.54	0.305 ± 0.155
9	Busan South Harbor	24.15 ± 24.82	0.16 ± 0.40	16.34 ± 16.57	161.29 ± 77.18	650.89 ± 998.28	0.138 ± 0.073
10	Jindong Bay	2.98 ± 2.20	0.55 ± 1.03	0.55 ± 0.89	101.46 ± 45.39	91.54 ± 63.54	0.168 ± 0.193
11	Wonmun Bay	4.51 ± 3.29	Nd ± 0	1.23 ± 1.57	235.44 ± 209.87	176.15 ± 139.19	0.111 ± 0.025
12	Gohyeonseong Bay	4.62 ± 1.95	0.32 ± 0.59	6.59 ± 4.46	162.69 ± 86.25	506.17 ± 343.42	0.478 ± 0.593
13	Haengam Bay	6.58 ± 5.54	0.88 ± 2.25	5.94 ± 5.39	386.93 ± 563.95	217.25 ± 118.00	0.114 ± 0.032
14	Eastern part of Geojedo	11.40 ± 6.71	0.18 ± 0.25	1.81 ± 1.85	379.79 ± 428.21	972.81 ± 785.53	0.090 ± 0.058
15	Masan Bay	22.43 ± 18.10	0.78 ± 1.18	4.99 ± 5.63	182.42 ± 276.69	126.64 ± 66.27	0.227 ± 0.121
16	Gwangyang Bay	2.63 ± 1.99	0.18 ± 0.21	1.05 ± 1.18	94.68 ± 57.24	93.08 ± 62.01	0.104 ± 0.093
17	Gamak Bay	3.35 ± 3.09	0.43 ± 0.77	2.17 ± 3.36	112.72 ± 47.90	149.36 ± 77.94	0.095 ± 0.080
18	Mokpo coast	3.44 ± 4.26	0.40 ± 0.65	3.24 ± 1.03	139.54 ± 113.68	299.47 ± 262.23	0.066 ± 0.045
19	Gochang coast	0.85 ± 0.58	1.17 ± 1.53	2.17 ± 1.14	157.06 ± 99.28	62.71 ± 70.50	0.145 ± 0.068
20	Jeonjupo coast	0.99 ± 0.75	3.01 ± 5.00	6.88 ± 8.72	158.82 ± 192.41	49.62 ± 25.61	0.138 ± 0.098
21	Gunsan coast	1.38 ± 1.13	0.63 ± 0.72	5.37 ± 4.58	121.68 ± 155.24	85.26 ± 75.04	0.180 ± 0.143
22	Cheonsu Bay	1.59 ± 1.28	1.37 ± 1.90	1.61 ± 1.63	121.82 ± 62.67	104.28 ± 87.71	0.182 ± 0.090
23	Garorym Bay	3.40 ± 2.90	1.06 ± 1.12	5.12 ± 2.24	163.81 ± 133.38	98.75 ± 63.17	0.234 ± 0.157
24	Asan Bay	5.42 ± 4.13	1.26 ± 1.37	4.58 ± 6.48	147.03 ± 73.58	149.30 ± 26.94	0.275 ± 0.188
25	Incheon coast	4.23 ± 3.42	0.52 ± 0.66	5.73 ± 4.99	188.52 ± 115.34	108.85 ± 50.20	0.218 ± 0.111
	Min	0.85 ± 0.58	Nd ± 0	0.55 ± 0.89	83.08 ± 45.39	49.62 ± 25.61	0.066 ± 0.045
	Max	24.62 ± 14.29	3.01 ± 5.00	16.34 ± 16.57	386.93 ± 563.95	1,360.82 ± 674.58	0.478 ± 0.593
	Mean	7.46 ± 5.57	0.70 ± 1.10	4.22 ± 4.38	176.96 ± 140.21	309.35 ± 266.63	0.165 ± 0.117
	Detection frequency (%)	96	46	78	100	97	99
	85th percentile	12.13	1.39	7.01	260.35	429.47	0.261

^aSum of concentrations of 23 congeners

^bSum of concentrations of *ortho* and *para* forms of parent and metabolites

^cSum of concentrations of α -HCH, β -HCH, and γ -HCH

^dSum of concentrations of 16 compounds

^eSum of concentrations of parent compounds and metabolites

^fSum of concentrations of seven PCDDs and ten PCDFs congeners

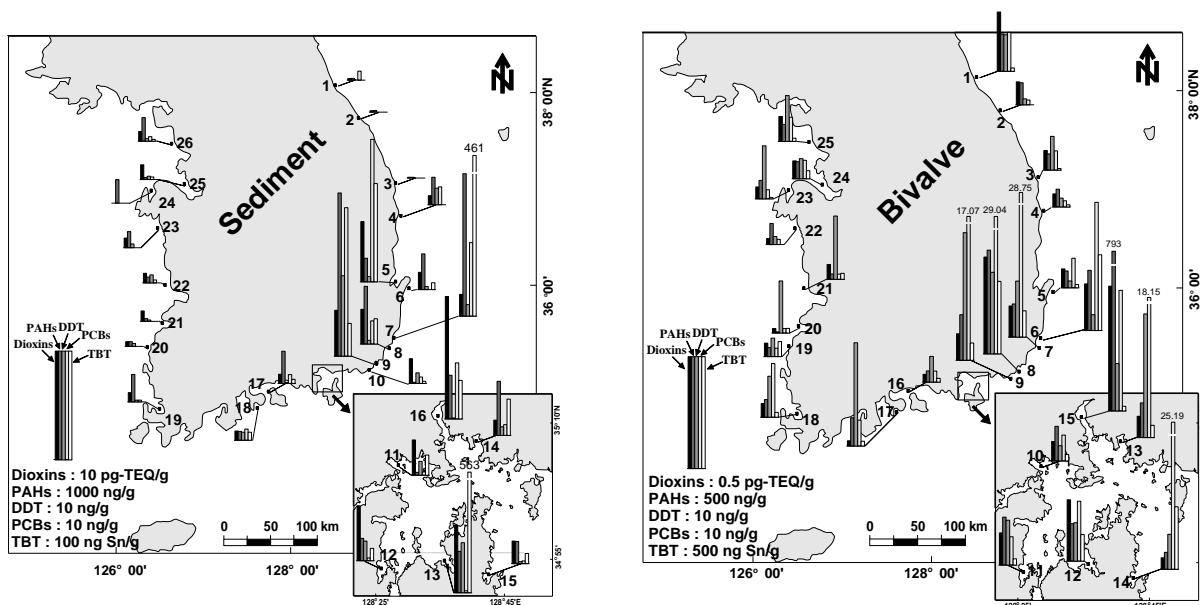


Figure 3-30. Example of monitoring results (spatial distribution) for POPs and related contaminants in marine sediment and bivalves (mussels or oysters) from Korean coastal waters. The present contamination status was the results performed in 2007 from the National Fisheries Research and Development Institute (NFRDI), Korea.

Marine mammals have a high trophic level in the marine food-web. Because marine mammals possess relatively low metabolic activities, they accumulate high levels of POPs. In Korea, traditionally, cetaceans were hunted by fishermen for substance before the ban on commercial whaling was imposed by the Moratorium of the International Whaling Commission (IWC) in 1986 (Moon et al., 2010a, b, c; Park et al., 2010). However, many cetaceans are by-caught in fishing nets and/or stranded. The major species are minke whales, common dolphins and finless porpoises, which accounted for 85% of the total number of individuals in Korea. The National Fisheries Research and Development Institute (NFRDI) with the aid of Cetacean Research Institute (CRI) started the POP monitoring in Korean cetaceans, to investigate the current status and ecotoxicological concerns associated with POPs accumulation. The concentrations of POPs in three kinds of cetaceans collected from Korean coastal waters are presented in Figure 5. Among the POPs in Korean cetaceans, DDTs and PCBs had the highest levels. Although the production of DDTs and PCBs were already banned in 1980s in Korea, these contaminants had the higher residue levels in Korean coastal waters. This results are due to both chemical groups have biomagnification effect in marine food-web. Interestingly, PBDEs had relatively higher levels compared to other POPs chemical groups, although PBDEs have short-term history contamination in Korean environment. This result indicates that PBDEs can be concerns of emerging contaminants in Korean coastal waters.

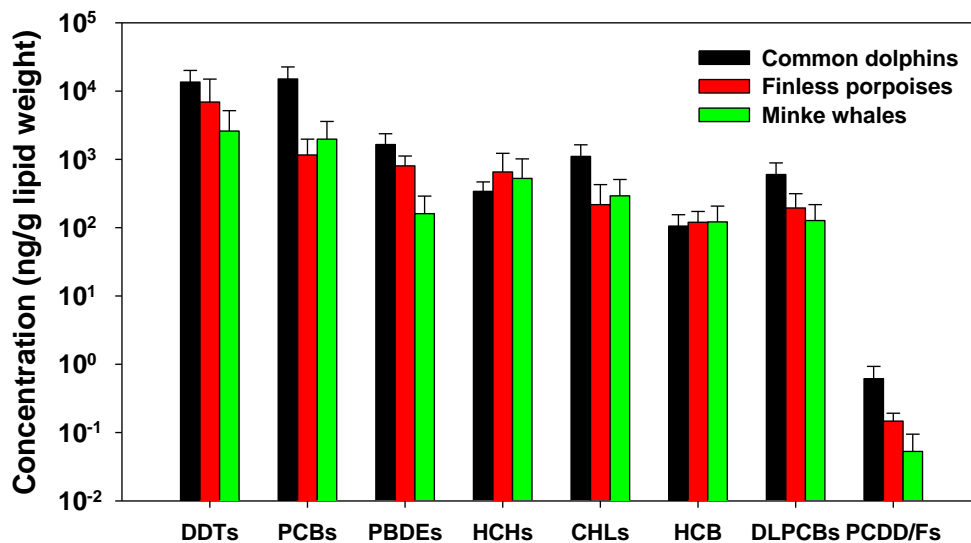


Figure 3-31. Concentrations of POPs in cetaceans from Korean coastal waters. Data were cited from Moon et al. (2010a, b, c, d) and Park et al. (2010).

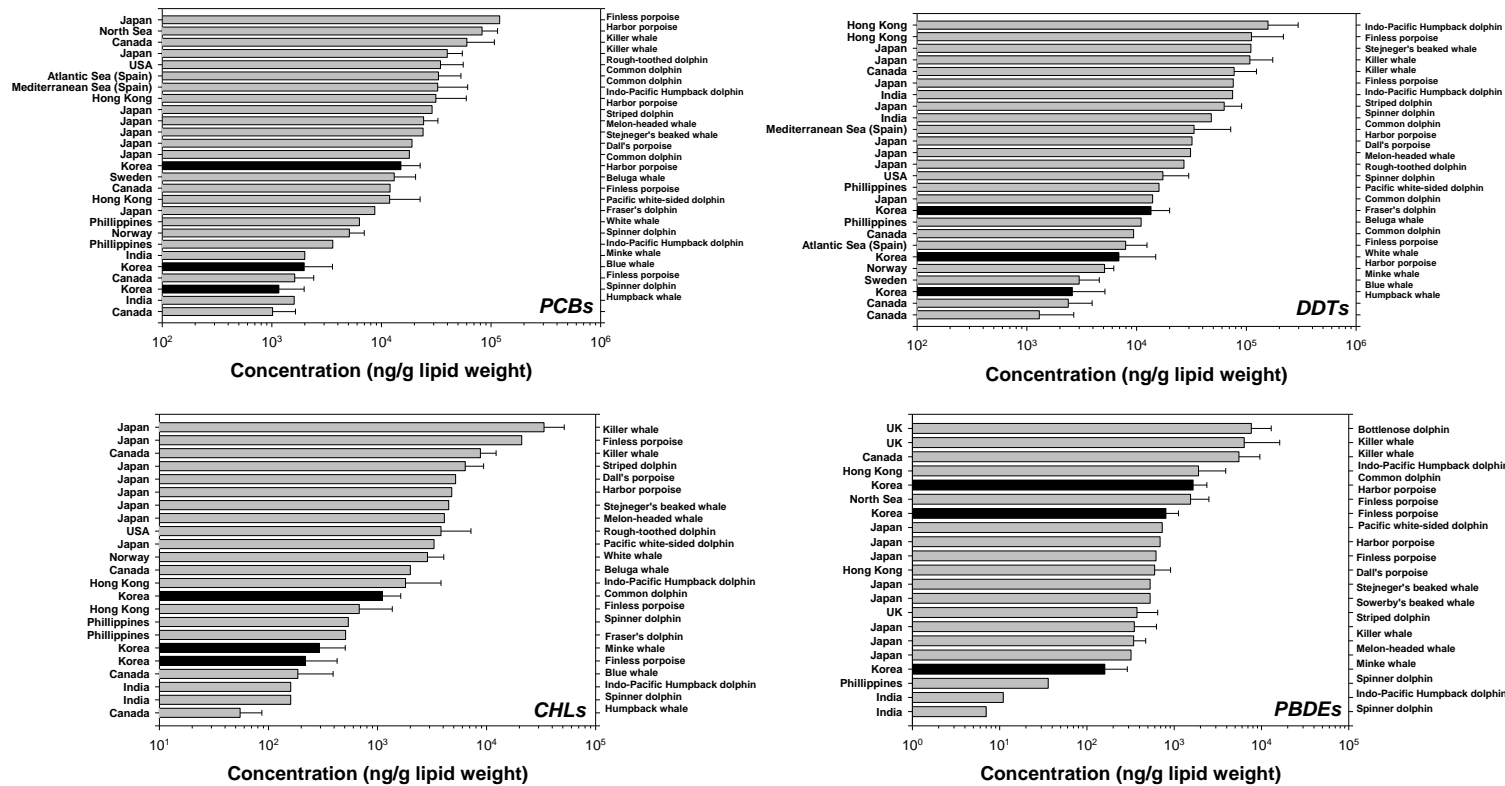
For minke whales, common dolphins and finless porpoises, the residue levels in blubber were in the order of *mono-ortho* PCBs > *non-ortho* PCBs > PCDFs > PCDDs, similar to those observed in cetaceans and pinnipeds from other countries (Kajiwara et al., 2008; Yang et al., 2008; Imaeda et al., 2009). The concentrations of PCDDs, PCDFs, *non-ortho* PCBs and *mono-ortho* PCBs ranged from <0.8–2.5 pg/g, 10–177 pg/g, 0.4–2.7 ng/g and 24–352 ng/g in minke whales and <0.8–11 pg/g, 47–1405 pg/g, 0.9–8.8 ng/g and 54–1192 ng/g in common dolphins, respectively. For finless porpoises, the concentrations (on a lipid weight basis) of PCDDs, PCDFs, *non-ortho* PCBs and *mono-ortho* PCBs in the blubber of finless porpoises were in the ranges of 5.4–31 pg/g, 14–54 pg/g, 0.4–3.6 ng/g and 27–519 ng/g, respectively.

Studies on PCDD/Fs and DL-PCBs have been performed mainly with seals, and data on levels of dioxin-like contaminants in cetaceans are scarce. The total TEQ concentrations in the blubber of finless porpoises (6.5 to 31 pg/g lipid weight) and minke whales (8.2–106 pg/g lipid weight) from Korean coastal waters are similar to those reported for Ganges River dolphins from India (20–120 pg/g lipid wt; Senthilkumar et al., 2001), killer whales from the Indian Ocean (76 ± 5 pg/g lipid wt; Noël et al., 2009), and finless porpoise from China (7–238 pg/g lipid wt; Yang et al., 2008). The total TEQ concentrations in the blubber of common dolphins (31–465 pg/g lipid wt) from Korea were similar to those reported for Caspian seals (10–340 pg/g lipid wt; Kajiwara et al., 2008) and harbor seals from Canada (175 ± 38 pg/g lipid wt; Addison et al., 2005), but lower than those reported for Baikal seals from Russia (82–950 pg/g lipid wt; Imaeda et al., 2009).

The concentration ranges for PCBs, DDTs, CHLs, HCHs, HCB and PBDEs in minke whale blubber samples were 390–6200 ng/g, 270–11000 ng/g, 30–800 ng/g, 40–2100 ng/g, 30–480 ng/g and 30–430 ng/g, respectively, and in common dolphins were

1100–27000 ng/g, 730–23000 ng/g, 60–1900 ng/g, 100–600 ng/g, 20–230 ng/g and 140–3100 ng/g, respectively. The concentrations of DDTs (6900 ± 8000 ng/g lipid weight) and PCBs (1100 ± 800 ng/g lipid weight) were the highest in finless porpoise tissues. The concentrations of HCHs (650 ± 570 ng/g lipid weight), CHLs (220 ± 210 ng/g lipid weight) and HCB (120 ± 50 ng/g lipid weight) were one or two orders of magnitude lower than those of DDTs and PCBs. The concentrations of PBDEs (800 ± 310 ng/g lipid weight) in finless porpoises were higher than those of HCHs, CHLs and HCB.

The overall OC contamination status in cetaceans (minke whales, common dolphins and finless porpoises) from Korea was lower than that reported elsewhere (Figure 6), and this pattern is consistent with the contamination status of fish and shellfish from around the Korean coast. In particular, the concentrations of PCBs (3300 ± 1800 ng/g lipid wt), DDTs (1400 ± 900 ng/g lipid wt), CHLs (500 ± 180 ng/g lipid wt), HCHs (80 ± 30 ng/g lipid wt) and HCB (140 ± 90 ng/g lipid wt) in minke whales from north Atlantic Ocean are similar to the concentrations in Korean cetaceans measured in our study. The overall PBDE levels in the blubbers of minke whales, common dolphins and finless porpoises from Korean coastal waters are similar to the ranges found in cetaceans from several countries. The PBDE contamination status of Indo-Pacific humpback dolphins (1900 ± 2000 ng/g lipid wt) from Hong Kong and harbor porpoises (1540 ± 960 ng/g lipid wt) from the North Sea is comparable to that of common dolphins from Korean coastal waters. Bottlenose dolphins (7700 ± 5300 ng/g lipid wt) and killer whales (6300 ± 9900 ng/g lipid wt) from waters of the UK and killer whales (5500 ± 4100 ng/g lipid wt) from Canada showed higher levels of PBDEs than those found in this study. Spinner dolphins (11 ng/g lipid wt) from India and Spinner dolphins (6.8 ng/g lipid wt) and Fraser's dolphins (40 ng/g lipid wt) from the Philippines contained the lowest levels of PBDEs, probably because of the relatively small use of PBDEs in these countries.

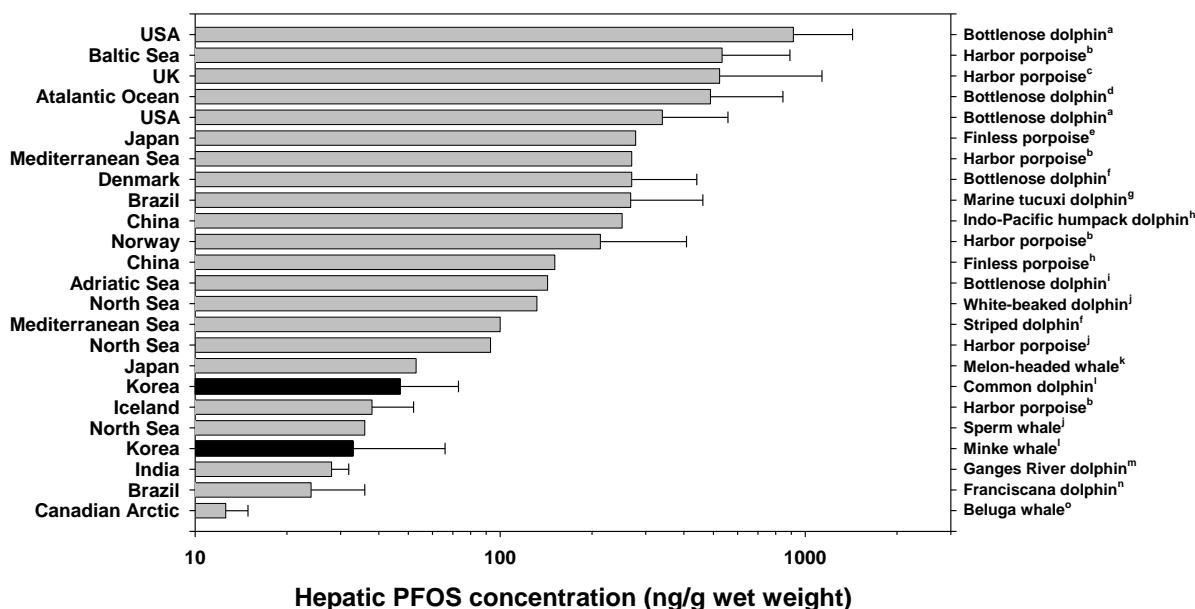


Data were obtained from Karlson et al., 2000; Minh et al., 2000; Andersen et al., 2001; Borrel et al., 2001; Hobbs et al., 2003; Metcalfe et al., 2004; Struntz et al., 2004; Law et al., 2005; Ramu et al., 2005; Kajiwara et al., 2006a, 2006b; Krahn et al., 2007;; Isobe et al., 2009; Weijs et al., 2009.

Figure 3-32. Global comparison of POPs in cetaceans from Korean coastal waters compared with those reported for other countries (Moon et al., 2010a, b, c; Park et al., 2010).

PFOS and PFUnDA were detected in all the liver samples from minke whales and common dolphins from Korean coastal waters. The concentrations of PFOS in the livers of minke whales and common dolphins ranged from 2.8 to 162 ng/g wet wt and from 18 to 152 ng/g wet wt, respectively. The concentrations of PFUnDA ranged from 2.6 to 129 ng/g wet wt in minke whales and 17 to 193 ng/g wet wt in common dolphins. The overall concentration of PFOS and PFUnDA was 3–20 times higher than the concentrations of other PFCs measured in liver samples.

The concentrations of PFOS measured in the livers of minke whales (2.8–162 ng/g wet wt) and common dolphins (18–152 ng/g wet wt) from Korean coastal waters were compared with values reported for cetaceans from other locations worldwide (Figure 3-33). PFOS has been found in all cetaceans, including those from the Arctic Ocean (Tomy et al., 2004). Most studies have shown higher levels of PFOS in cetaceans than those found in the cetaceans from Korea. The highest concentration of PFOS was found in bottlenose dolphins from South Carolina in the USA (914 ± 515 ng/g wet wt, Houde et al., 2006). Harbor porpoises from the Baltic Sea (534 ± 357 ng/g wet wt, Van de Vijver et al., 2004) and the UK (524 ± 611 ng/g wet wt, Law et al., 2008) showed higher concentrations of PFOS compared with cetaceans from other locations. The concentration of PFOS in melon-headed whales from Japan (Hart et al., 2008a), harbor porpoises from Iceland (Van de Vijver et al., 2004), and sperm whales from the North Sea (Kannan et al., 2002a) showed similar values to those measured in this study. Some cetaceans collected from India (Yeung et al., 2009a), Brazil (Leonel et al., 2008), and the Canadian Arctic (Tomy et al., 2004) showed lower PFOS levels than those found in our study.



a: Houde et al., 2006; b: Van de Vijver et al., 2004; c: Law et al., 2008; d: Kannan et al., 2001a; e: Nakata et al., 2006; f: Giesy and Kannan, 2001; g: Dorneles et al., 2008; h: Yeung et al., 2009a; i: Kannan et al., 2002b; j: Van de Vijver et al., 2003; k: Hart et al., 2008; l: Present study; m: Yeung et al., 2009b; n: Leonel et al., 2008; o: Tomy et al., 2004

Figure 3-33. Global comparison of hepatic PFOS in cetaceans collected from Korean coastal waters (Moon et al., 2010d).

Based on the nationwide monitoring results, the temporal trends of PCDD/Fs and PAHs were investigated. As shown in Figures 3-34 and 3-35, PCDD/Fs and PAHs did not show any temporal trends between 2001 and 2007. Although the concentrations of PCDD/Fs in atmosphere gradually decreased due to strong regulation on emission source of PCDD/Fs, sediments and bivalves did not show decreasing trends in Korean coastal waters. In principal, ocean has dilution effects for all the organic contaminants, and sediment and bivalves have longer half-lives of PCDD/Fs compared with atmosphere. However, the decreasing trends of PCDD/Fs in sediments and bivalves would be expected after 2010. In the case of PAHs, they have both contamination sources such as combustion and oil contamination.

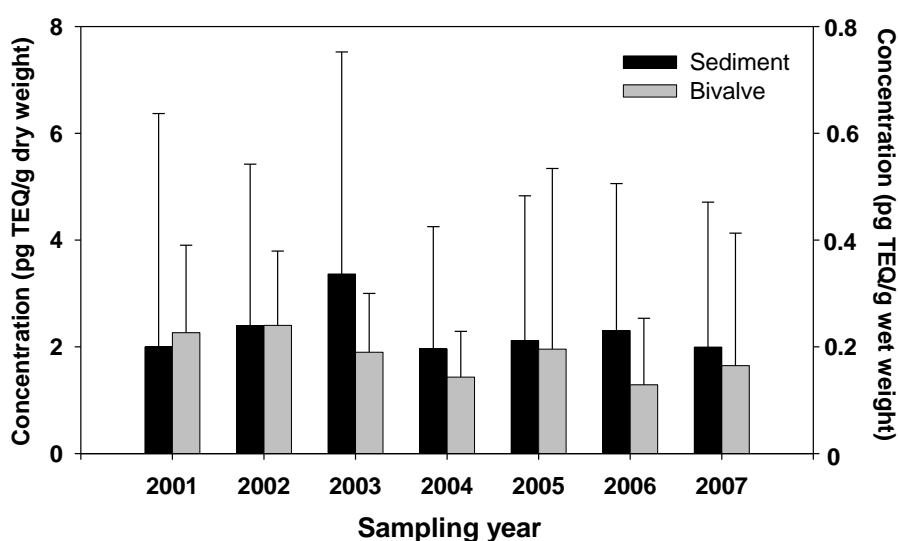


Figure 3-34. Temporal trends of PCDD/F concentrations (pg TEQ/g dry or wet weight) in marine sediment and bivalves (mussels or oysters) from Korean coastal waters.

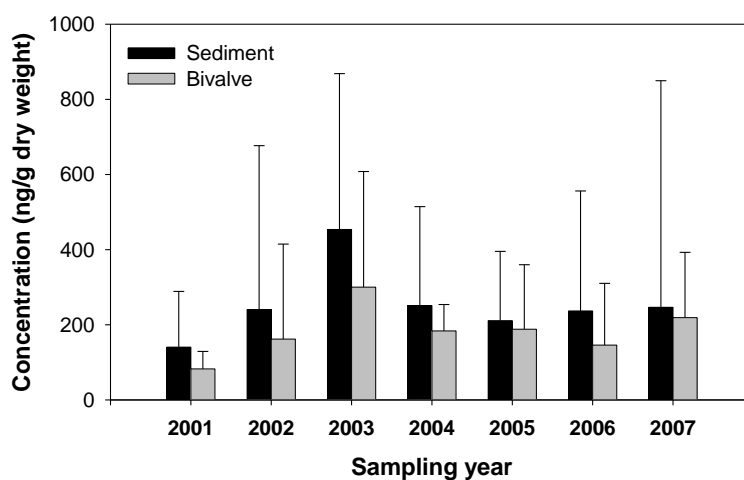


Figure 3-35. Temporal trends of PAH concentrations (n/g dry weight) in marine sediment and bivalves (mussels or oysters) from Korean coastal waters.

Based on the nationwide monitoring survey during 2001-2007, the TBT concentrations varied from <2.0 to 67 ng Sn/L in seawater, from <3.0 to 3918 ng Sn/g dry weight in sediment and from <3.0 to 2576 ng Sn/g dry weight in bivalves, respectively. In seawater samples, annual mean concentrations of TBT were from <2.0 to 11 ng Sn/L, showing that they were around 10 ng Sn/L from 2001 to 2003, and around the detection limit in 2004 (Figure 3-36). TBT concentration in seawater decreased dramatically and the seawater samples did not contain TBT since 2005. In sediment samples, annual mean concentrations ranged from 28 to 226 ng Sn/g dry weight. Unlike seawater samples, sediment did not show any temporal trends of TBT. This obscure temporal variation of TBT levels in sediment may be attributed to TBT properties in matrices such as half-lives of TBT and reflection of contamination in matrices. In bivalve samples, annual mean concentrations of TBT ranged from 38 to 455 ng Sn/g dry wt. Similar to seawater samples, TBT levels in bivalves decreased annually, because mussels and oysters are filter-feeding species living in water-column. Therefore, bio-monitoring such as the mussel watch program is useful in assessing the national status and trend of TBT contamination in the marine environment. Consequently, these results indicate the importance of multimedia monitoring and legislative action on toxic organic contaminants in marine environment.

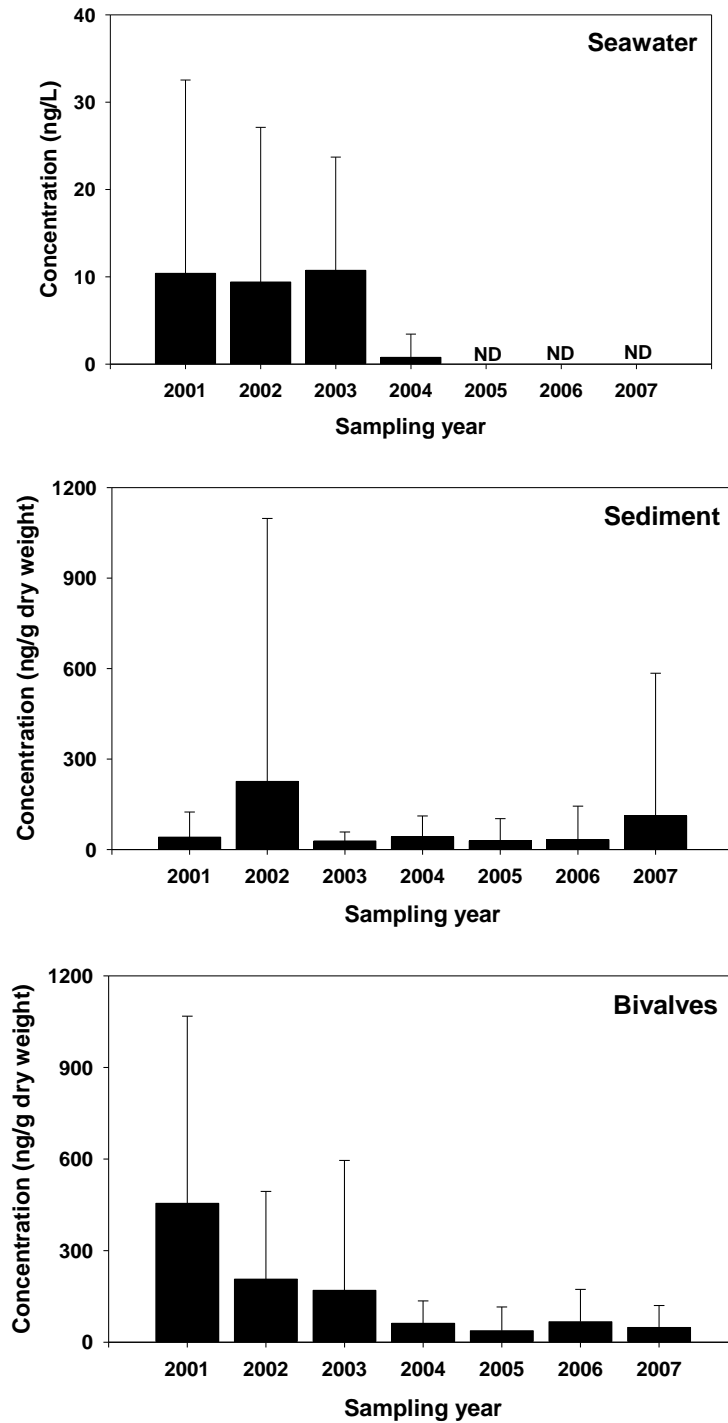


Figure 3-36. Temporal trends of TBT in seawater, sediment and bivalves (mussels or oysters) collected from Korean coastal waters (Choi et al., 2010; 2011).

To investigate current status and temporal trends of BTs in marine mammals, finless porpoises were collected from Korean coastal waters between 2003 and 2010. The concentrations of MBT, DBT, TBT, and total BTs in finless porpoises were significantly different ($p < 0.001$) between the two sampling years of 2003 and 2010

(Figure 3-37). The total concentrations of BTs in finless porpoises collected from the South Sea (S03; 682 ± 291 ng/g wet weight) and Yellow Sea (Y03; 701 ± 371 ng/g wet weight) in 2003 were significantly higher than those measured in the Yellow Sea (Y10; 155 ± 58.4 ng/g wet weight) in 2010, indicating a clear decrease in BTs in marine mammals associated with TBT regulation in Korea. Earlier studies confirmed a clear decreasing trend in the concentrations of TBT in seawater and bivalves from Korean coastal waters (Choi et al., 2009a; 2010a). Therefore, TBT regulation has been effective at decreasing TBT concentrations in marine mammals as well as lower-trophic-level species such as mussels and oysters in the coastal environment of Korea. This result emphasizes the importance of legislative action against chemical contamination in coastal environment.

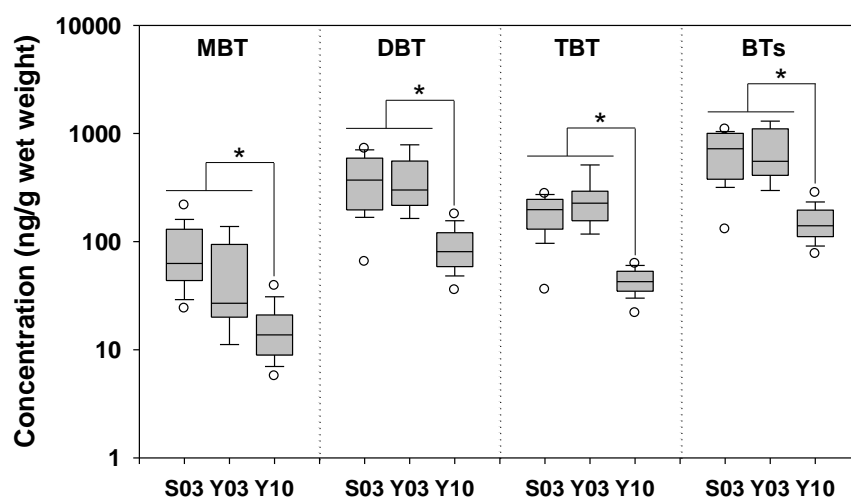


Figure 3-37. Comparison of concentrations of butyltin compounds in finless porpoises collected from the South Sea (S03) and Yellow Sea (Y03) in 2003, and the Yellow Sea in 2010 (Y10). * indicates significant differences at $p < 0.05$ (Choi et al., 2013b).

<Japan>

In Japan, continuous environmental monitoring has been conducted for more than three decades by the government. Ministry of the Environment has been conducting several environmental monitoring programmes, including long term environmental monitoring under “Chemicals in the Environment” programme, and marine environment monitoring. “Chemicals in the Environment” programme is composed of three major activities, i.e., primary environmental survey of chemicals, detailed environmental survey of chemicals, and long term environmental monitoring of POPs and other selected PBTs. Basic design of the long term monitoring is to reveal temporal trends of POPs levels in major environmental media in Japan, i.e., air (37), water (48; rivers, lakes and coastal environment), sediments (64; rivers, lakes and coastal environment) and biota (28; fishes (19), bivalves (6), birds (2) and bird eggs (1)) (numbers in parentheses show sampling locations in each media as of FY2013). The sampling sites are located on land or coastal region; air sampling is conducted about a

few tens to a hundred km interval, and water and sediment sampling is conducted mainly near river mouth region together with several coastal regions nearby densely populated areas, such as Tokyo Bay and Osaka Bay. Marine environmental monitoring, on the other hand, has been monitoring some of POPs, organotins and heavy elements levels along seven transects from coastal environment to offshore areas in order to conserve economic zones in Japan to protect the areas from marine pollution, with particular emphasis on land-based marine pollution and pollution by ocean dumping. Other governmental activities include ocean pollution survey implemented by Japan Coast Guard. The results of these activities will be summarized in the following sections. Major focus will be put on the information of recent spatial distribution of PTS, although information on their temporal trends, if available, will be summarized, too.

A. Dioxins

According to Law Concerning Special Measures against Dioxins, environmental monitoring and human biomonitoring of dioxins have been conducted every year. Currently the most recent data on dioxins monitoring in the environment is in 2011. Air sampling was conducted at 756 sampling locations by either 1,000 m³ sampling for 7 days or three times 1,000 m³ sampling for 24 hrs. Among them, the sampling was conducted twice in summer and winter at 689 locations, including general environment (522 locations), nearby emission sources (142 locations) and roadsides (25 locations), and the average dioxins levels in these locations were calculated and reported in the following tables and figures. Water sampling in public water bodies were conducted at 1,574 locations, including rivers (1,229 locations), ponds or lakes (79 locations) and coastal areas (286 locations). Sediment samples were collected at 1,320 locations in public water bodies, including rivers (1,009 locations), ponds or lakes (68 locations) and coastal areas (243 locations). Ground water was sampled at 538 locations and soil samples were collected at 969 locations, including general environment survey (674 locations) and survey around emission sources (295 locations). The overall data are summarized in Table 3-29, while the temporal trend of the average air dioxin levels among the continuous sampling sites (not all sites but those continuously sampled during 1997 – 2011) is shown in Figure 3-38. As shown in Table 1, all the air sampling data in Japan in FY2011 were below environmental criteria (0.6 pg/m³). The situation was clearly shown in the histograms of air sampling data in Figure 2. Note that all the TEQ data in any environmental media were reported based on different TEF values according to the development of toxicological researches; i.e., TEQ was based on I-TEF (1996) during 1997~2007, and WHO-TEF (2006) after 2008 until present.

Table 3-29. Dioxin levels in Japanese environment in FY2011 (Dioxins control office (2013))

Media	Category	Locations	Total Samples	Max	Min	Average	Environ. Criteria	Locations exceeding criteria
Air (pg-TEQ/m ³)	Total	689 (756)	2,236 (2,337)	0.45 (0.45)	0.0051 (0.0051)	0.028 (0.028)	0.6	0
	General	522 (559)	1,685 (1,740)	0.19 (0.19)	0.0051 (0.0051)	0.028 (0.027)		0
	Nearby sources	142 (172)	461 (507)	0.45 (0.45)	0.0052 (0.0052)	0.032 (0.031)		0
	Roadsides	25 (25)	90 (90)	0.072 (0.072)	0.0096 (0.0096)	0.025 (0.025)		0
Water (pg-TEQ/L)	Total	1,594	2,123	3.4	0.012	0.19	1	28
	Rivers	1,229	1,722	3.4	0.012	0.22		27
	Ponds/Lakes	79	89	1.1	0.022	0.18		1
	Coastal areas	286	312	0.57	0.016	0.065		0
Sediments (pg-TEQ/g)	Total	1,320	1,374	640	0.05	7	150	3
	Rivers	1,009	1,061	640	0.05	6.3		3
	Ponds/Lakes	68	68	34	0.28	9		0
	Coastal areas	243	245	97	0.077	9.5		0
Ground water (pg-TEQ/L)		538	539	0.62	0.0084	0.047	1	0
Soils (pg-TEQ/g)	Total	969	969	140	0	3.4	1,000	0
	General	674	674	96	0	2		0
	Nearby sources	295	295	140	0	6.7		0

* TEQ calculated based on WHO-TEF (2006)

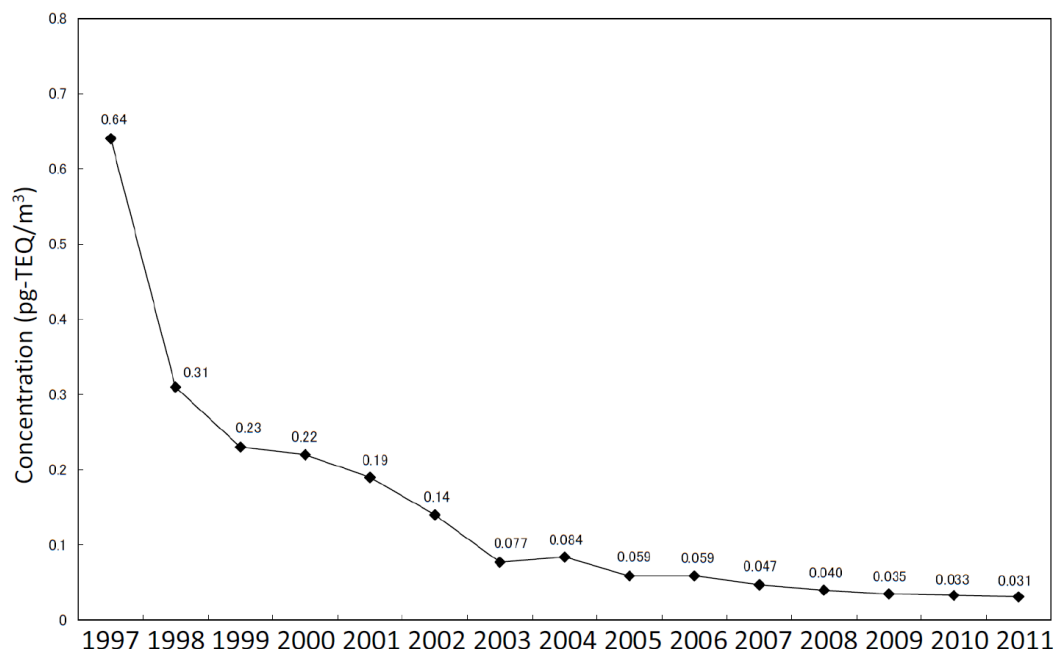


Figure 3-38. Temporal trend of the average of Air Dioxins levels in continuous sampling sites during FY1997 – 2011. TEQ calculation based on I-TEF (1998) (1997~2007) or WHO-TEF (2006) (2008~) (Dioxins control office (2013))

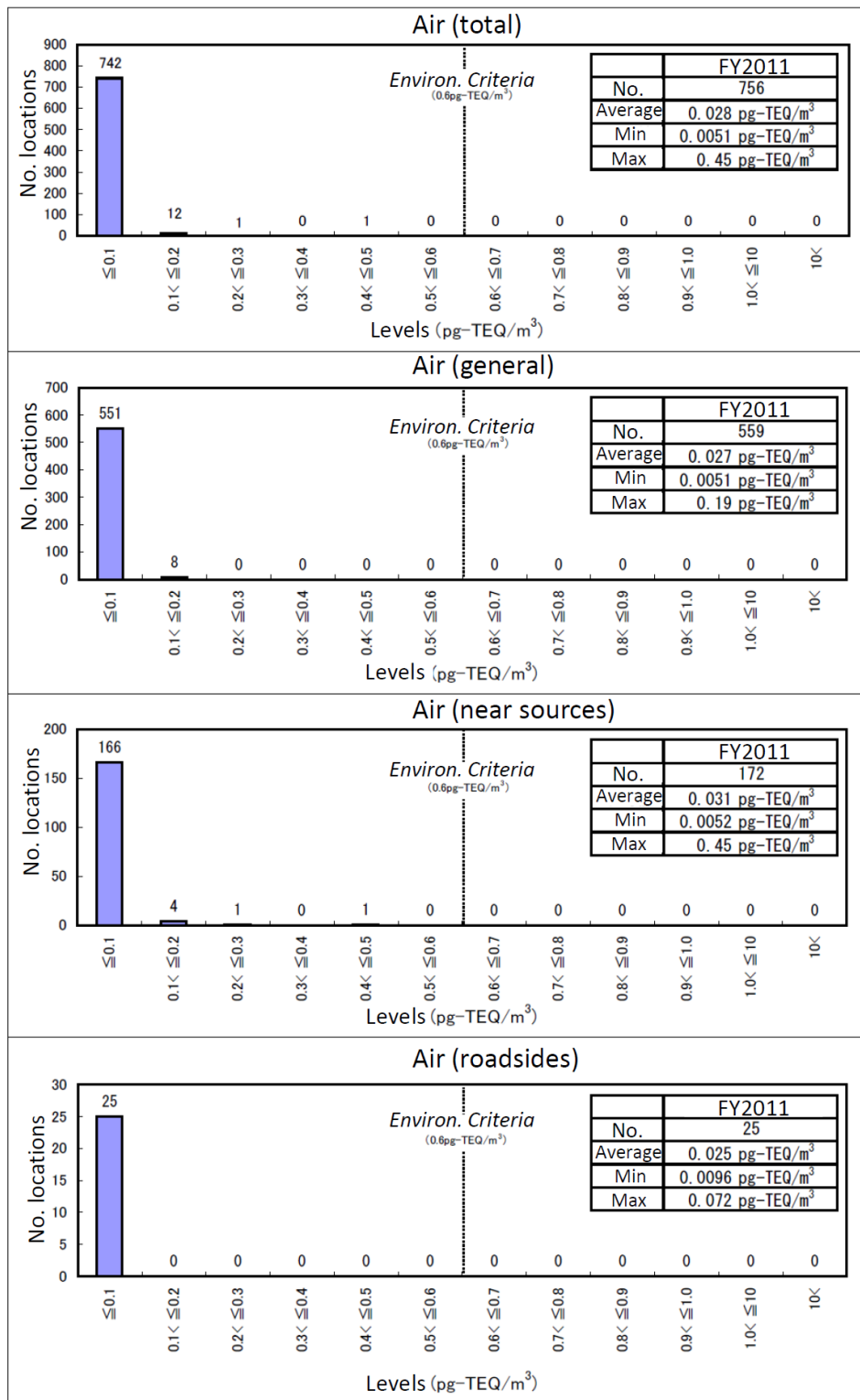


Figure 3-39. Histograms of Air Dioxins monitoring data in FY2011 (Dioxins control office (2013))

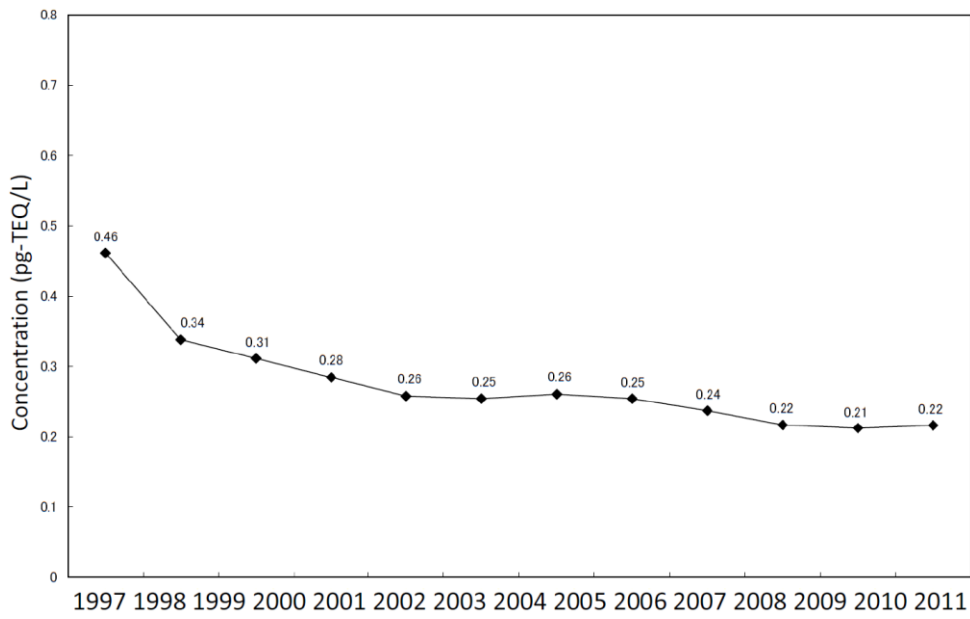


Figure 3-40 Temporal trend of average water dioxins levels in continuous sampling sites during FY1997 – 2011 (Dioxins control office (2013))

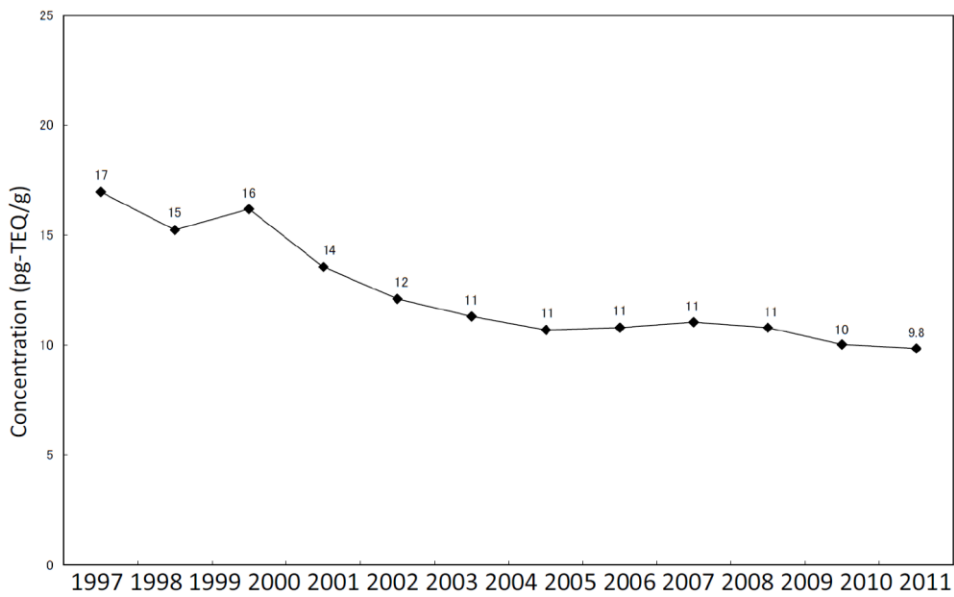


Figure 3-41 Temporal trend of average sediment dioxins levels in continuous sampling sites during FY1997 – 2011 (Dioxins control office (2013))

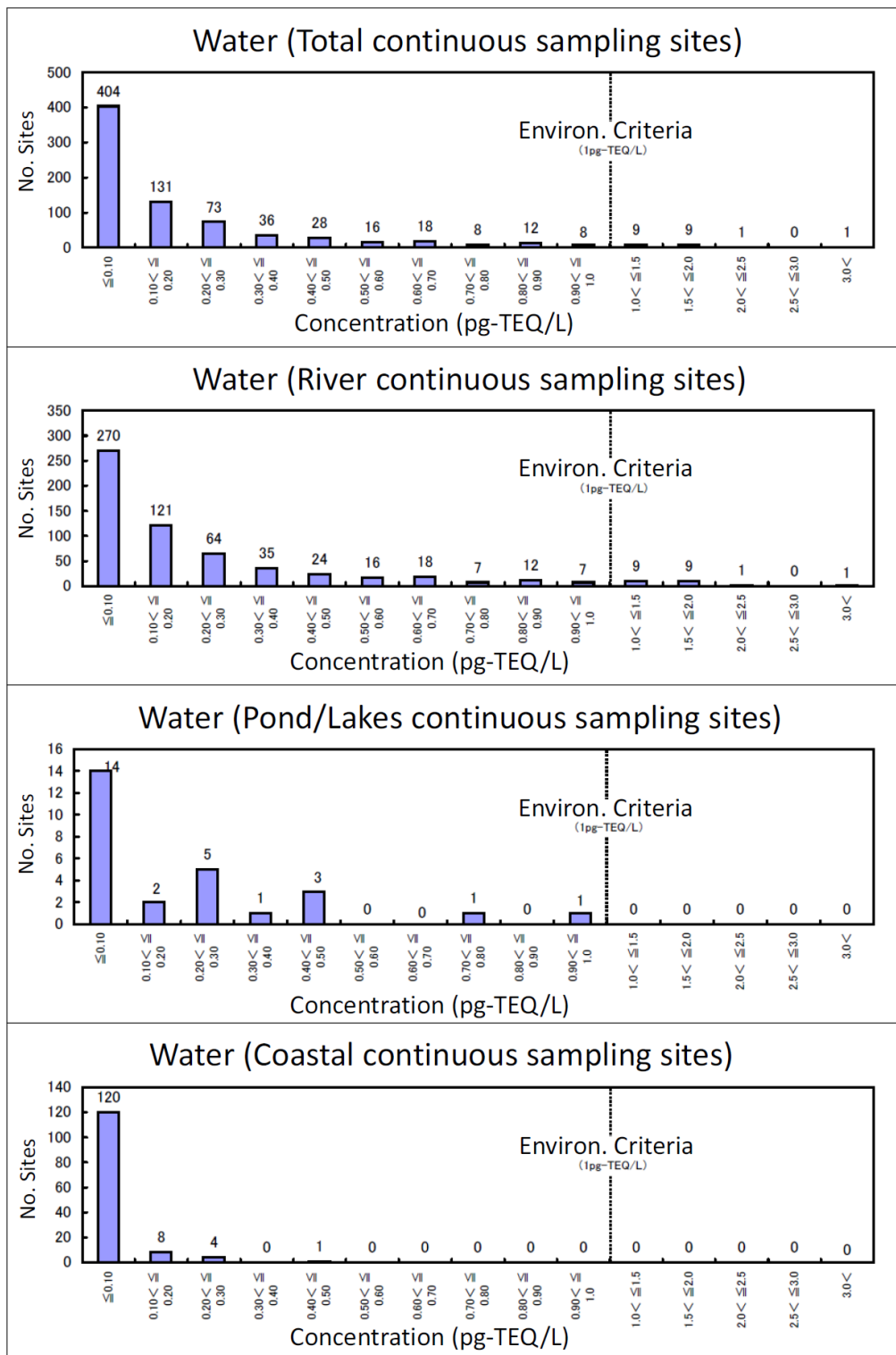


Figure 3-42 Histograms of water dioxins levels in continuous sampling sites during 1997 – 2011 (Dioxins control office (2013))

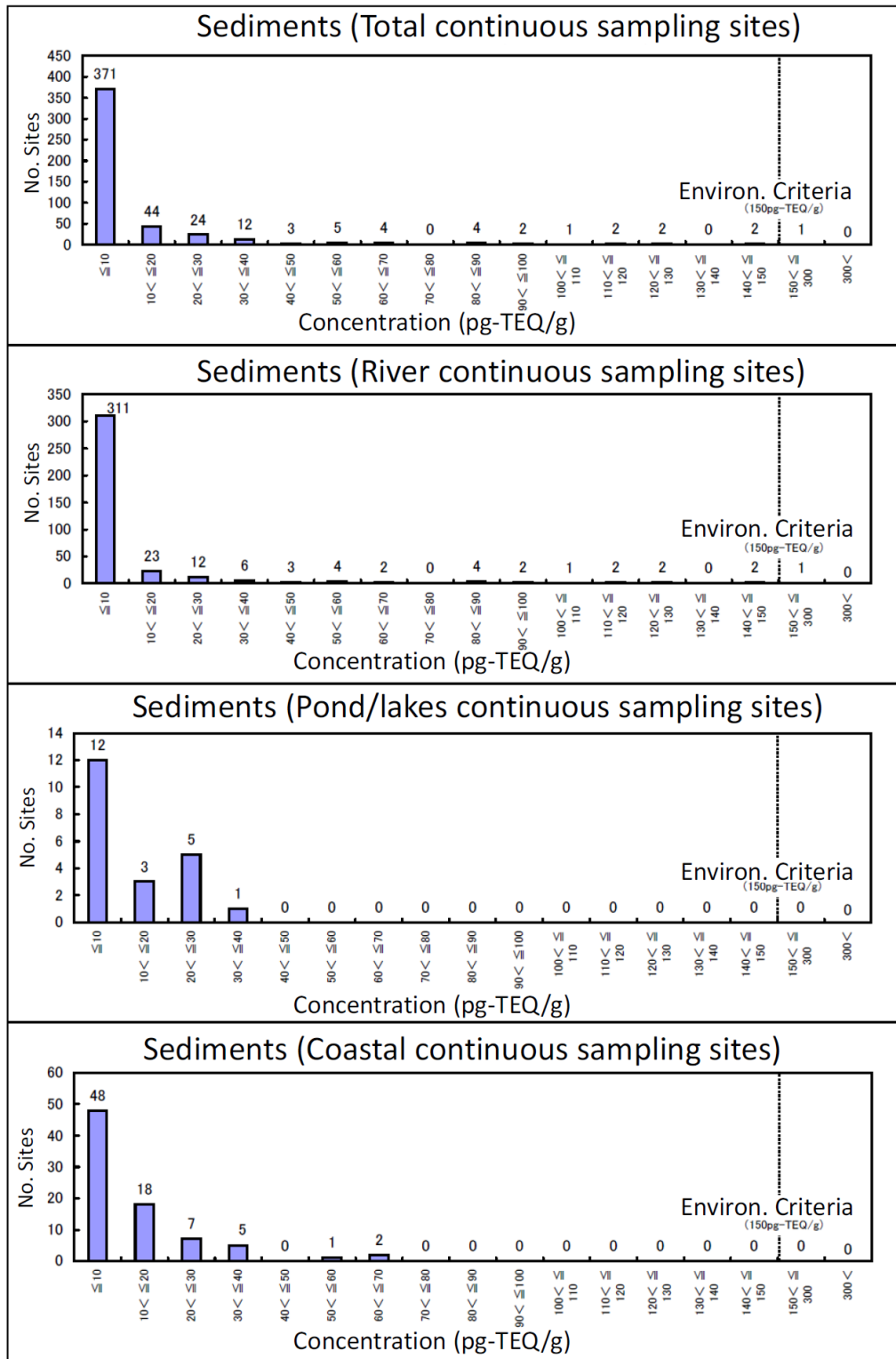


Figure 3-43 Histograms of sediment dioxins levels in FY 2011 in continuous sampling sites during 1997 – 2011 (Dioxins control office (2013))

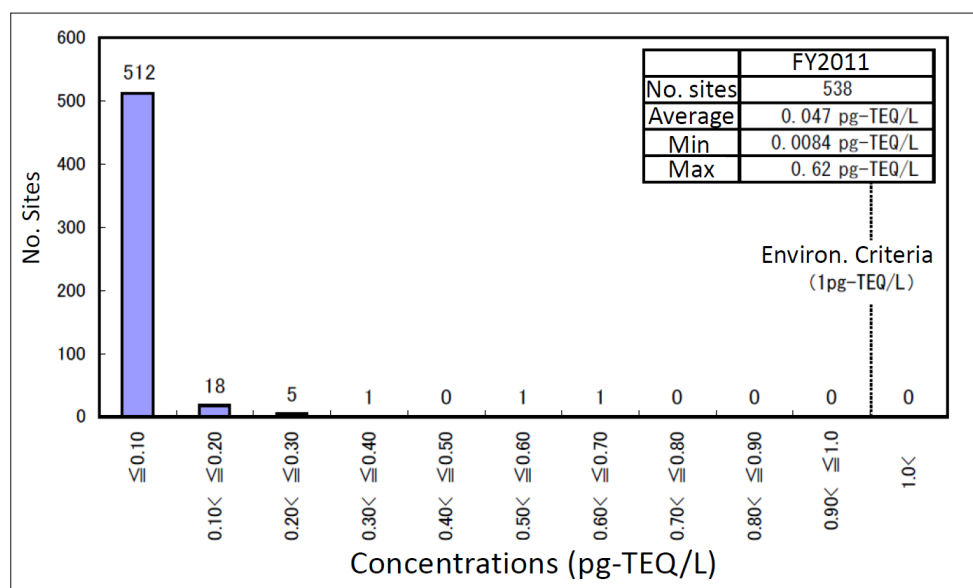


Figure 3-44 Histograms of ground water dioxins levels in FY2011 in continuous sampling sites during 1997 – 2011 (Dioxins control office (2013))

Contrary to the the rapid decrease of air average concentrations, only moderate decreasing trends are observed in the water and the sediment averages as shown in Figures 3-40 and 3-41, respectively. These tendencies are reasonably explained as representing the differences in environmental behaviors of dioxins in different environmental media; i.e., air dioxin levels are primarily reflecting their current emission levels from major sources while those in sediments are mainly reflecting integrated load of past dioxins. Water levels are the sum of new emission from primary sources and emissions from secondary sources, including soils and sediments, and thus may not decrease so rapidly due to long lasting secondary emission loads. Histograms of water and sediments as well as ground water data are shown in Figures 3-42, 3-43 and 3-44, respectively. There still remain several sites in rivers where dioxins levels exceed environmental criteria.

In addition to chlorinated dioxins, furans and dl-PCBs, both emissions and environmental levels of brominated dioxins and furans have been analyzed and reported by the Ministry of the Environment, Japan. This survey has been conducted based on “Law Concerning Special Measures against Dioxins”, too, and major brominated flame retardants, i.e., polybromo-diphenyl ethers (PBDEs), tetrabromo-bisphenol A (TBBPA), tribromo-phenols (TrBPhs), and hexabromocyclododecanes (HBCDs), together with brominated dioxins were analyzed. In the latest report on the monitoring in FY2012, emissions in air and water from 6 different sources, including two municipal waste incinerators and four industrial waste incinerators, were analyzed together with air and public water environmental levels nearby the facilities. Emission levels of PBDDs and PBDFs in the flue gas was reported to be 0.028 ng/m³ (0.0009 – 0.13) with estimated TEQ values of 0.0004 ng-TEQ/m³ in average (based on TEF of corresponding chlorinated isomers of PCDD/Fs). PBDD/Fs in effluent water was reported to be 20 pg/L with estimated TEQ = 0.067 pg-TEQ/L. TeBDDs, TeBDFs and PeBDFs compositions were relatively higher in flue gas while TeBDDs, TeBDFs, HxBDFs and

OBDF compositions were higher in effluent water samples. PBDD/Fs levels in ambient air nearby the facilities was reported to be 2.6 pg/m³ (0.38 – 12) with TEQ = 0.0096 pg-TEQ/m³ in average. PBDD/Fs levels in public water bodies were 24 (up stream) and 37 (down stream) pg/L of a facility along a river, or 0.12 (nearby) and 0.05 (distant) pg/L of a facility along coastline. Among isomers, 1,2,3,4,5,7,8-HpBDF was highest in flue gas while the isomer and OBDF were dominant in effluent water. The two isomers were also dominant in ambient air and water around the facilities. PBDD/Fs were analyzed in general environmental samples during 1998-2000 under “Chemicals in the environment” monitoring program, but were not detected in almost all samples except for a few samples with trace levels of TeBDFs (Note: hepta- and octa-isomers were not analyzed in those environmental data).

In FY 2011 survey, emissions of brominated dioxins and furans from 10 recycling facilities on home appliance, such as TV, refrigerator, air conditioner and washing machine, were analyzed. PBDD/Fs levels in effluent air through dust filters from TV decomposition facilities were reported to be 1.2 ng/m³ (ND - 7.7) (TV crushing machine), 0.023 ng/m³ (TV manual decomposition place), 0.0045 ng/m³ (TV decomposition facility) or 0.083 ng/m³ (overall facility), respectively. PBDD/Fs levels in waste water were reported to be 33,000 and 30,000 pg/L for TV decomposition process and overall facility, respectively. Although the levels in waste water are much higher than those from incinerators, total flow of water is 1 to 4 orders of magnitude lower than other facilities. PBDD/Fs levels in ambient air nearby the facilities were reported to be 20 pg/m³ in average, which is higher than those around incinerators, while those in public water bodies were 20 pg/L (up stream) or 57 pg/L (down stream), respectively.

Chlorinated dioxins levels along seven transects from coastal area to offshore region have been monitored in Marine Environment Monitoring Survey. Decadal changes between 1998 - 2007 along the transects were compiled and reported by the ministry of the Environment. Figure 8 shows geographical distribution of dioxins levels in surface sediments. During ten years, sampling and analysis in each location was conducted twice or three times. Therefore duplicate or triplicate data for each sampling sites are shown in the figure. Sampling method changed from box corer to multiple corer from 2003 in order to get surface sediment with less disturbance, and this change might affect the data to some extent. Higher levels of dioxins (more than 10 pg/g dry) were detected in coastal areas of Tokyo (transect B) and Osaka (transect C) bays. In both transects, dioxins levels show general declining trend in accordance with the distance from the coast, except for C-5 where unknown PCB source seem to be present (report on 2003). Levels of chemicals in sediments depend on not only chemical levels in water but also other factors, such as sedimentation rates and types of sediments. Biomonitoring is an alternative way to know the levels of chemicals in water. Dioxins levels in several organisms commonly present in marine environment have been analyzed and reported. Figure 3-46 shows dioxins levels in squid livers in offshore regions. Squids accumulate both lipid soluble organic chemicals and heavy metals in their livers. Their longevity is usually one year. Environmental monitoring by using squid livers, particularly those in the family Ommastrephidae which are widely distributing in the world ocean, was proposed as a suitable biomonitoring method to

monitor yearly changes in open ocean environment (Yamada et al., 1997; Hashimoto et al., 1999). As shown in Figure 3-46, dioxins levels in squid livers collected in Kuroshio and Oyashio current areas in north Pacific ocean show declining trends in the last 10 years. On the other hand, their levels in squid livers collected in central and western NOWPAP areas generally show higher levels than those in Pacific ocean with no clear decreasing trends. In fact, ratios of dioxins levels in squid livers between NOWPAP and north Pacific had been around 1 – 2 in 1998, but became around 10 in 2007.

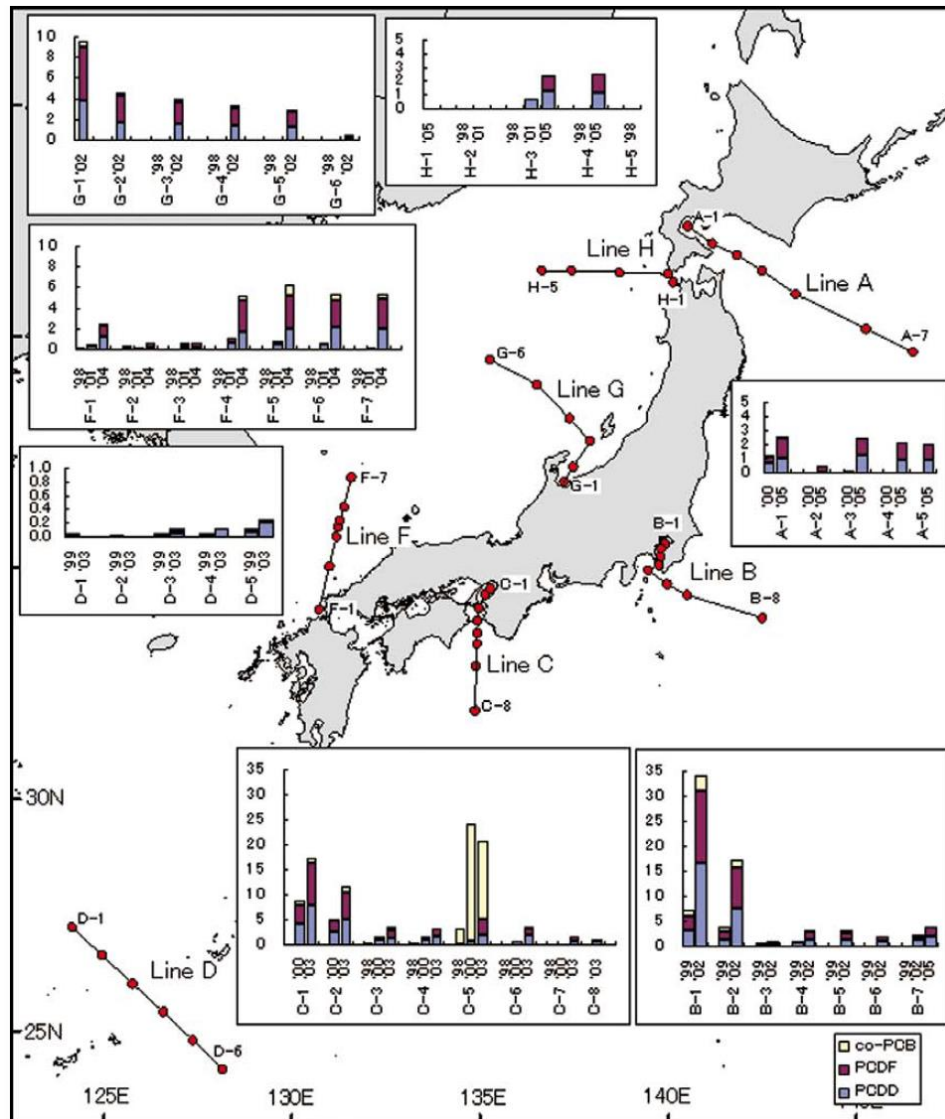


Figure 3-45 Geographical distribution of dioxins in surface sediments along seven transects (1998 – 2007) (Global Environmental Issues Division (2009)).

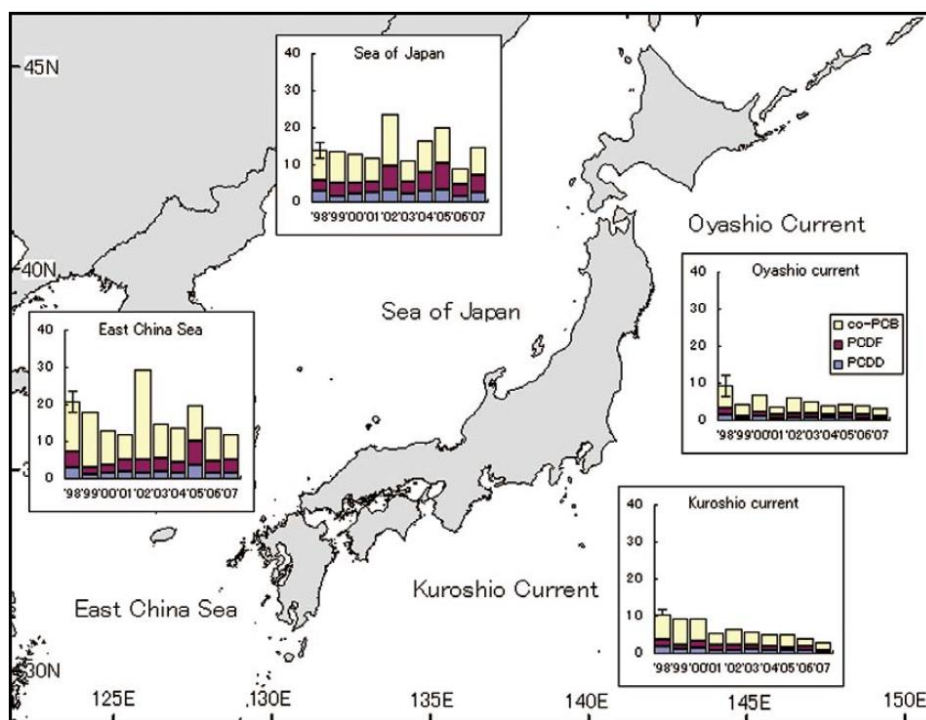


Figure 3-46 Dioxins levels in squid livers collected in four different open oceans around Japan (Global Environmental Issues Division (2009))

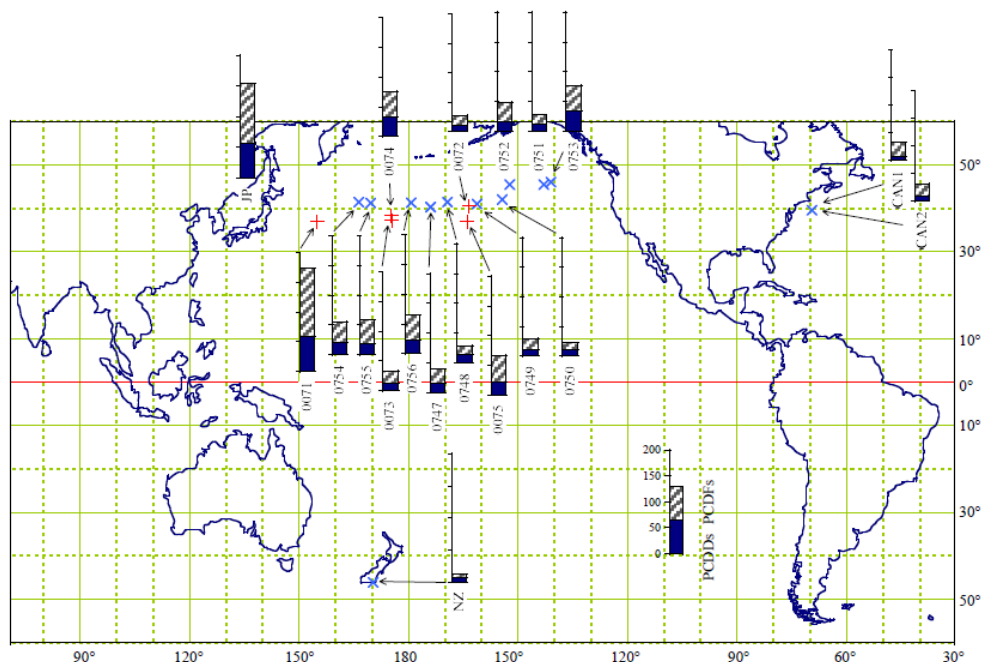


Figure 3-47. Dioxins levels (pg/g wet) in squid livers collected in various places along circumpolar front in north Pacific and central NOWPAP area (Hashimoto 1999).

Hashimoto et al reported PCDD/Fs levels in squid livers in wide areas of north Pacific including NOWPAP region (Figure 3-47). The sampling period was in late 1990's. The levels of PCDD/Fs in figure 10 were shown as concentrations rather than TEQ and also dl PCB were not analyzed; therefore, the data are not comparable with

Figure 9. It is shown in the Figure 10, however, that there were clear declining trend of PCDD/Fs levels from west, the central NOWPAP area, to the east, central north Pacific ocean, in late 1990's, suggesting the occurrence of land-based marine pollution by dioxins.

B. PCBs, HCB and organochlorine pesticides.

Intentionally produced legacy POPs, including PCB, HCB and organochlorine pesticides, have been monitored extensively for long-term in "Chemicals in the environment" program. The long-term monitoring part of the program was re-organized in FY2002 to utilize highly sensitive and precise analytical method, capillary GC-high resolution mass spectrometry, for the analysis of all legacy POPs in order to reveal present POPs levels in the environment, which will serve as baselines for future effectiveness evaluation procedure in Article 16 of the Stockholm Convention. In this program, air (35 sites; sampling twice a year (late summer and early winter) in each location), water (49 sites), sediments (64 sites) and biological samples (fish: 16 sites, bivalves: 4 sites, birds: 1 site) (data in FY 2011) were sampled in fixed long-term sampling sites in Japan, and legacy POPs in the samples were analyzed and reported. As many of the legacy POPs had banned their production, import and use decades of ago in Japan, their decreasing trends in recent years have been slowing down and becomes nearly flat. Also some of the legacy POPs were found to be generally very low and frequently non-detectable even by the newest analytical technique. Therefore some POPs are analyzed not every year but once in two or three years. The following data are compilation of the results in recent few years. Each table shows compound name, environmental media, sampled year, median and geometrical means, ranges, detection frequencies, and method quantification and detection limits (MQL (MDL)). Tr (trace) means the compound was detected (above MDL) but less than quantification limits (MQL), and the number in parenthesis is a reference value (quantified but not reliable enough) (following data from Environmental Health and Safety Division (2013)).

B-1. PCB (FY2011)

PCB was designated as Class 1 Specified Chemical Substance under Chemical Substances Control Law in 1974. PCB is a major POPs in Japan and has been monitored every year. PCB is detected in every environmental sample. Air levels of PCB show clear seasonal variation, possibly reflecting temperature dependence of its air-other media (water, soils etc. as a major secondary PCB emission source) partition. By the statistical analysis of a decadal data between FY2002-2011, PCB levels in water, both in total and in each category (river including river mouth region, coastal water), were found to decrease in a statistically significant manner.

Table 3-30. PCB in air (pg/m³)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
35(Summer)	150	160	660	32	18 (5.9)	35/35
36(Winter)	76	66	320	Tr(17)		37/37

Table 3-31. PCB in water (pg/L)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
49	150	130	2,100	16	4.5 (1.7)	49/49

Table 3-32. PCB in sediments (pg/g dry)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
64	6,300	7,400	950,000	24	12 (4.5)	64/64

Table 3-33. PCB in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
4 (bivalves)	8,900	17,000	65,000	820	220 (74)	4/4
18 (fishes)	14,000	12,000	250,000	900	220 (74)	18/18
1 (bird)	-	5,400	-	-	220 (74)	1/1

B-2. HCB (FY2011)

HCB was designated as Class 1 Specified Chemical Substance under Chemical Substances Control Law in 1979. Atmospheric levels of HCB do not show large variations both in season and location. It is among the most potent POPs chemicals to be transported for long-range in global scale, and their levels in air may reflect not only local or regional sources but also global emission status. By the statistical analysis of decadal data (FY2002-2011), statistically significant decreasing trend was found in water environment as a total, as well as river category including river mouth region.

Table 3-34. HCB in air (pg/m³)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
35(Summer)	120	110	180	87	2.3 (0.75)	35/35
36(Winter)	96	96	160	75	-	37/37

Table 3-35. HCB in water (pg/L)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
49	13	12	140	Tr(3)	5 (2)	49/49

Table 3-36. HCB in sediments (pg/g dry)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
64	150	110	35,000	11	7 (3)	64/64

Table 3-37. HCB in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
4 (bivalves)	45	34	920	4	4 (1)	4/4
18 (fishes)	260	320	1,500	34	4 (1)	18/18
1 (bird)	-	460	-	-	4 (1)	1/1

B-3. Drins (aldrin, dieldrin, endrin)

The three pesticides with common hexachlorocyclopentadienyl structure, i.e., aldrin, dieldrin and endrin (so-called “drins”), were removed from the registered chemicals list under Agricultural Chemicals Regulation Law in 1975, and designated as Class 1 Specified Chemical Substance under Chemical Substances Control Law in 1981. All of the drins have been monitored continuously until 2009, and then dieldrin and endrin was monitored in 2011. Among the data, statistically significant declining trend was observed in endrin levels in ponds/lakes and coastal water during decadal monitoring between 2002 and 2011.

Table 3-38. Drins in air (pg/m³) (S; summer, W: winter)
(Aldrin: FY2009, Dieldrin & Endrin; FY2011)

Compounds No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
25 (Aldrin;S)	0.07	nd	10	Nd	0.04 (0.02)	10/25
24 (Aldrin; W)	Tr (0.03)	nd	1.8	Nd	-	8/24
25 (Dieldrin;S)	12	15	230	0.8	0.42 (0.14)	35/35
24 (Dieldrin; W)	4.3	4.9	96	0.52	-	37/37
25 (Endrin;S)	0.46	0.62	5.1	Nd	0.09 (0.04)	34/35
24 (Endrin; W)	0.16	0.16	1.8	Nd	-	33/37

Table 3-39. Drins in water (pg/L)
(Aldrin: FY2009, Dieldrin & Endrin; FY2011)

Compounds No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
49 (Aldrin)	0.7	0.9	22	Nd	0.7 (0.3)	32/49
49 (Dieldrin)	33	38	300	2.1	1.6 (0.6)	49/49
49 (Endrin)	3.8	4.6	71	Nd	1.6 (0.6)	47/49

Table 3-40. Drins in sediments (pg/g dry)
(Aldrin: FY2009, Dieldrin & Endrin; FY2011)

Compounds No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
64 (Aldrin)	8.9	7.8	540	Nd	0.5 (0.2)	(180/192)*
64 (Dieldrin)	47	44	2,200	Tr (2)	5 (2)	64/64
64 (Endrin)	8.8	14	1,100	Nd	1.1 (0.4)	59/64

*: Three samples collected in each site were analyzed separately until 2009.

Table 3-41. Drins in biological samples (pg/g wet)

Compounds No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Aldrin	FY2009					
7 (bivalves)	Tr (1.6)	Tr (0.8)	89	Nd	2.1 (0.8)	6/7
18 (fishes)	Nd	nd	3.1	Nd	2.1 (0.8)	7/18
2 (bird)	Nd	nd	nd	Nd	2.1 (0.8)	0/2
Dieldrin	FY2011					
4 (bivalves)	390	690	3,800	16	3 (1)	4/4
18 (fishes)	270	340	1,100	17	3 (1)	18/18
1 (bird)	-	770	-	-	4 (1)	1/1
Endrin	FY2011					
4 (bivalves)	33	62	110	Tr (3)	4 (2)	4/4
18 (fishes)	18	19	160	Nd	4 (2)	16/18
1 (bird)	-	Tr (3)	-	-	4 (2)	1/1

B-4. DDTs (FY2010)

DDT, chlordanes and HCHs are among the most heavily used organochlorine pesticides in Japan. DDT was once used to control lice and other pest control, too. DDT was removed from the list of agricultural chemicals in 1971, and designated as Class 1 Chemical Substance in 1981. DDT monitoring has been continued every year until 2010. Due to lack of monitoring data in FY 2011, the statistical analysis has not been conducted on DDT monitoring data yet.

Table 3-42. DDT in air (pg/m³) (FY2010)

Isomers No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
p,p'-DDT						
37(Summer)	3.5	3.1	56	0.28	0.1 (0.03)	37/37
37(Winter)	1.3	0.89	16	0.30	-	37/37
p,p'-DDE						
37(Summer)	4.9	4.1	200	Tr (0.41)	0.62 (0.21)	37/37
37(Winter)	2.2	1.8	28	Tr (0.47)	-	37/37
p,p'-DDD						
37(Summer)	0.20	0.17	1.7	0.04	0.02 (0.01)	37/37
37(Winter)	0.10	0.09	0.41	0.02	-	37/37
o,p'-DDT						
37(Summer)	2.2	1.9	26	0.19	0.14 (0.05)	37/37
37(Winter)	0.81	0.69	5.5	0.22	-	37/37
o,p'-DDE						
37(Summer)	0.49	0.41	9.0	0.09	0.04 (0.01)	37/37
37(Winter)	0.27	0.23	2.3	0.08	-	37/37
o,p'-DDD						
37(Summer)	0.21	0.19	1.8	0.04	0.03 (0.01)	37/37
37(Winter)	0.10	0.09	0.48	Tr (0.02)	-	37/37

Table 3-43. DDT in water (pg/L) (FY2010)

Isomers	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
p,p'-DDT	8.5	7.6	7,500	Tr(1)	2.4 (0.8)	49/49
p,p'-DDE	14	12	1,600	2.4	2.3 (0.8)	49/49
p,p'-DDD	12	10	970	1.6	0.2 (0.08)	49/49
o,p'-DDT	1.5	Tr (1.2)	700	Nd	1.5 (0.5)	43/49
o,p'-DDE	0.97	0.65	180	Tr(0.13)	0.24 (0.09)	49/49
o,p'-DDD	4.6	3.8	170	Tr(0.5)	0.6 (0.2)	49/49

Table 3-44. DDT in sediments (pg/g dry) (FY2010)

Isomers	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
p,p'-DDT	230	200	22,000	9.3	2.8 (0.9)	64/64
p,p'-DDE	680	790	40,000	11	5 (2)	64/64
p,p'-DDD	510	510	78,000	4.4	1.4 (0.5)	64/64
o,p'-DDT	40	33	13,000	1.4	1.1 (0.4)	64/64
o,p'-DDE	37	32	25,000	Tr(0.7)	1.2 (0.5)	64/64
o,p'-DDD	130	130	6,900	Tr(0.8)	0.9 (0.4)	64/64

Table 3-45. DDT in biological samples (pg/g wet) (FY2010)

Organisms No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
p,p'-DDT	180	280	470	43	3 (1)	6/6
p,p'-DDE	1,100	1,300	6,300	230	3 (1)	6/6
p,p'-DDD	180	330	960	11	1.3 (0.5)	6/6
o,p'-DDT	51	67	160	15	3 (1)	6/6
o,p'-DDE	46	58	160	7.8	1.5 (0.6)	6/6
o,p'-DDD	57	50	400	5.8	0.6 (0.2)	6/6
Fishes						
p,p'-DDT	240	280	2,100	7	3 (1)	18/18
p,p'-DDE	2,300	2,100	13,000	260	3 (1)	18/18
p,p'-DDD	560	610	2,900	57	1.3 (0.5)	18/18
o,p'-DDT	58	71	550	5	3 (1)	18/18
o,p'-DDE	47	37	2,800	Tr(1.2)	1.5 (0.6)	18/18
o,p'-DDD	75	99	700	2.6	0.6 (0.2)	18/18
Birds						
p,p'-DDT	3	-	15	Nd	3 (1)	1/2
p,p'-DDE	32,000	-	160,000	6,300	3 (1)	2/2
p,p'-DDD	440	-	1,600	120	1.3 (0.5)	2/2
o,p'-DDT	nd	nd	nd	Nd	3 (1)	0/2
o,p'-DDE	Tr (1.1)	-	3.7	Nd	1.5 (0.6)	1/2
o,p'-DDD	6.3	-	11	3.6	0.6 (0.2)	2/2

B-5. Chlordane and heptachlor

In addition to the use as pesticides, chlordane has been used extensively for termite control in wood materials and houses. Chlordane was removed from the list of agricultural chemicals in 1968, but was continuously used for termite control until 1986 when it was designated as Class 1 Specified Chemical Substance. Technical chlordane is a mixture of various isomers, including major isomers of heptachlor. Heptachlor itself was also used as agrochemical in Japan, particularly in northern part including Hokkaido. Heptachlor was removed from the list of agricultural chemicals in 1975, and was designated as Class 1 Specified Chemical Substance in 1986. Total heptachlor (sum of heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide) vs. total chlordane (sum of trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor and oxichlordane) ratio in environmental samples has been shown to be a good indicator of the past usage of heptachlor as agrochemical. Both of them have been monitored continuously, and the data in FY2011 are summarized below. Based on the statistical analysis of the data, statistically significant declining trends are shown in cis-chlordane levels in water (total as well as river and coastal marine environment), sediments (total as well as river mouth, ponds/lakes, and coastal area) and air (summer season), trans-chlordane in sediments (total and marine area) and air (summer season), cis-nonachlor in sediments (coastal) and air (summer), trans-nonachlor in water (river), sediments

(total as well as river mouth and coastal area) and air (summer), oxychlordanes in air (summer), and cis-heptachlor epoxide in sediments (river mouth).

Table 3-46. Chlordane and heptachlor in air (pg/m³)

Isomers Seasons	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Cis-chlordane						
Summer	66	95	700	1.5	1.3 (0.42)	35/35
Winter	20	31	240	Tr (0.88)	-	37/37
Trans-chlordane						
Summer	76	110	810	Tr (1.4)	1.6 (0.53)	35/35
Winter	24	37	290	Tr (0.7)	-	37/37
Cis-nonachlor						
Summer	7.4	8.8	89	0.24	0.15 (0.05)	35/35
Winter	1.9	2.9	28	nd	-	36/37
Trans-nonachlor						
Summer	53	72	550	1.2	1.1 (0.35)	35/35
Winter	16	24	210	Tr (0.7)	-	37/37
Oxychlordanes						
Summer	1.5	1.5	5.2	0.28	0.07 (0.03)	35/35
Winter	0.61	0.57	2.6	0.21	-	37/37
Heptachlor						
Summer	16	25	110	0.73	0.3 (0.099)	35/35
Winter	6.1	10	56	Tr (0.13)	-	37/37
Cis-hept. epoxide						
Summer	2.0	2.3	6.0	0.29	0.04 (0.01)	35/35
Winter	0.10	0.09	0.48	Tr (0.02)	-	37/37
Trans-hept. epoxide						
Summer	nd	nd	0.13	nd	0.13 (0.05)	5/35
Winter	nd	nd	Nd	nd	-	0/37

Table 3-47. Chlordane and heptachlor in water (pg/L)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Cis-chlordane	20	16	500	3.8	1.4 (0.6)	49/49
Trans-chlordane	16	13	470	3.2	1.0 (0.4)	49/49
Cis-nonachlor	5.0	4.3	130	0.8	0.6 (0.2)	49/49
Trans-nonachlor	15	12	480	2.6	1.3 (0.5)	49/49
Oxychlordanes	1.9	1.8	34	nd	1.3 (0.5)	44/49
Heptachlor	nd	nd	22	nd	1.3 (0.5)	6/49
Cis-hept. epoxide	5.8	5.8	160	0.7	0.7 (0.3)	49/49
Trans-hept. epoxide	nd	nd	2.8	nd	0.8 (0.3)	3/49

Table 3-48. Chlordane and heptachlor in sediments (pg/g dry)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Cis-chlordne	70	58	4,500	1.7	1.1 (0.4)	64/64
Trans-chlordane	73	64	4,300	3.2	1.3 (0.5)	49/49
Cis-nonachlor	41	38	2,900	nd	1.1 (0.4)	63/64
Trans-nonachlor	68	52	4,500	1.7	0.8 (0.3)	64/64
Oxychlordane	Tr (1.6)	Tr (1.2)	83	nd	2.2 (0.9)	36/64
Heptachlor	Tr (1.3)	Tr (1.2)	48	nd	1.8 (0.7)	40/64
Cis-hept. epoxide	2.8	2.5	160	nd	0.6 (0.2)	63/64
Trans-hept. epoxide	nd	nd	2.4	nd	2.3 (0.9)	2/64

Table 3-49. Chlordane and heptachlor in biological samples (pg/g wet)

Organisms Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
Cis-chlordne	790	880	3,400	160	3 (1)	4/4
Trans-chlordane	490	470	2,900	150	4 (1)	4/4
Cis-nonachlor	250	280	1,300	77	1.8 (0.7)	4/4
Trans-nonachlor	640	680	3,000	200	3 (1)	4/4
Oxychlordane	68	100	260	8	3 (1)	4/4
Heptachlor	4	4	51	nd	3 (1)	3/4
Cis-hept. epoxide	55	110	320	3.9	2.0 (0.8)	4/4
Trans-hept. epoxide	nd	nd	Tr (6)	nd	7 (3)	1/4
Fishes						
Cis-chlordne	580	660	3,800	79	3 (1)	18/18
Trans-chlordane	180	240	1,300	20	4 (1)	18/18
Cis-nonachlor	440	450	2,900	45	1.8 (0.7)	18/18
Trans-nonachlor	1,100	1,000	5,000	190	3 (1)	18/18
Oxychlordane	140	130	2,300	33	3 (1)	18/18
Heptachlor	Tr (1)	Tr (1)	7	nd	3 (1)	13/18
Cis-hept. epoxide	50	62	540	3.2	2.0 (0.8)	18/18
Trans-hept. epoxide	nd	nd	Nd	nd	7 (3)	0/18
Birds						
Cis-chlordne		6			3 (1)	1/1
Trans-chlordane		5			4 (1)	1/1
Cis-nonachlor		76			1.8 (0.7)	1/1
Trans-nonachlor		400			3 (1)	1/1
Oxychlordane		590			3 (1)	1/1
Heptachlor	-	nd	-	-	3 (1)	0/1
Cis-hept. epoxide		410			2.0 (0.8)	1/1
Trans-hept. epoxide		nd			7 (3)	0/1

B-6. Mirex and Toxaphene (FY2009)

Toxaphene and mirex are both organochlorine pesticides, but are never registered in Japan as agrochemicals. They are designated as Class 1 Specified Chemical Substance in 2002. Their environmental monitoring started in FY2002 and continued until FY2009 when their monitoring frequency was reduced; i.e, mirex will be analyzed every two years while toxaphene once in 6 years (interval of effectiveness evaluation), due to their lower levels as well as lower frequencies of detection in Japanese environment. There may be some purpose of importing small amount of mirex to Japan other than agrochemicals, for a low level of mirex was detected in sediments of several ports and river mouths near densely populated areas. Toxaphene in organisms, on the other hand, showed a unique distribution profile; i.e., the levels of toxaphene expressed in lipid-base in a pelagic fish, Pacific saury, caught in north Pacific were similar to the levels in sea bass collected in Tokyo bay. This suggests that local, land-based marine pollution of toxaphene around Japan is negligible compared with global pollution levels of the chemical.

The following data was obtained in FY 2011 for mirex and FY2009 for toxaphene.

Table 3-50. Mirex and toxaphene in air (pg/m³)

Chemicals/Isomers Seasons	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Mirex						
Summer	66	95	700	1.5	1.3 (0.42)	35/35
Winter	20	31	240	Tr (0.88)	-	37/37
Toxaphene						
* Parlar-26						
Summer	Tr (0.18)	Tr (0.19)	0.26	Tr (0.11)	0.23 (0.09)	37/37
Winter	Tr (0.12)	Tr (0.13)	0.27	nd	-	33/37
* Parlar-50						
Summer	nd	nd	Tr (0.1)	nd	0.3 (0.1)	11/37
Winter	nd	nd	Tr (0.1)	nd	-	1/37
* Parlar-62						
Summer	nd	nd	Nd	nd	1.6 (0.6)	0/37
Winter	nd	nd	Nd	nd	-	0/37

Table 3-51. Mirex and toxaphene in water (pg/L)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Mirex	nd	nd	0.8	nd	0.5 (0.2)	3/49
Toxaphene						
* Parlar-26	nd	nd	Nd	nd	5 (2)	0/49
* parlar-50	nd	nd	Nd	nd	7 (3)	0/49
* Parlar-62	nd	nd	Nd	nd	40 (20)	0/49

Table 3-52. Mirex and toxaphene in sediments (pg/g dry)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Mirex	1.2	0.9	1,900	nd	0.9 (0.4)	42/64
Toxaphene						
* Parlar-26	nd	nd	Nd	nd	10 (4)	0/64
* parlar-50	nd	nd	Nd	nd	12 (5)	0/64
* Parlar-62	nd	nd	Nd	nd	80 (30)	0/64

Table 3-53. Mirex and toxaphene in biological samples (pg/g wet)

Organisms Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
Mirex	10	7.1	44	5.2	1.9 (0.8)	4/4
Toxaphene						
Parlar-26	9	9	23	nd	7 (3)	(27/31)*
parlar-50	9	9	31	nd	8 (3)	(27/31)*
Parlar-62	nd	nd	Nd	nd	70 (20)	(0/31)*
Fishes						
Mirex	12	15	41	Tr (1.3)	1.9 (0.8)	18/18
Toxaphene						
Parlar-26	25	20	690	nd	7 (3)	(82/90)*
parlar-50	30	23	910	nd	8 (3)	(85/90)*
Parlar-62	Tr(20)	nd	660	nd	70 (20)	(24/90)*
Birds**						
Mirex		58			1.9 (0.8)	1/1
Toxaphene						
Parlar-26	26	200	500	nd	7 (3)	(6/10)*
parlar-50	29	250	620	nd	8 (3)	(5/10)*
Parlar-62	Tr (40)	80	210	nd	70 (20)	(5/10)*

* Biological samples in each site were separated into five groups and analyzed separately until FY 2009 to know variations as well as averaged concentrations.

** Bird species included a terrestrial bird (gray stirling) and a marine one (black-tailed gull) in FY2009 while terrestrial one only in FY2011.

B-7. PCB levels in marine environment.

PCB monitoring in water, sediments and several marine organisms have been conducted under Marine Environmental Monitoring Survey. Geographical distribution of PCB in surface sediments is shown in Figure 3-48. PCB in sediments show a higher concentration in inner bays / coastal areas with a metropolitan area located in the background, and lower concentrations in offshore areas, indicating that loadings from

terrestrial origins are apt to accumulate in coastal areas. As pointed out in the previous dioxins monitoring data, a strong PCB source rich with KC-300, possibly PCB used for stabilizer of fluorescent lamp, paper condenser, heating medium or rubricant, seems to be present nearby the site C-5.

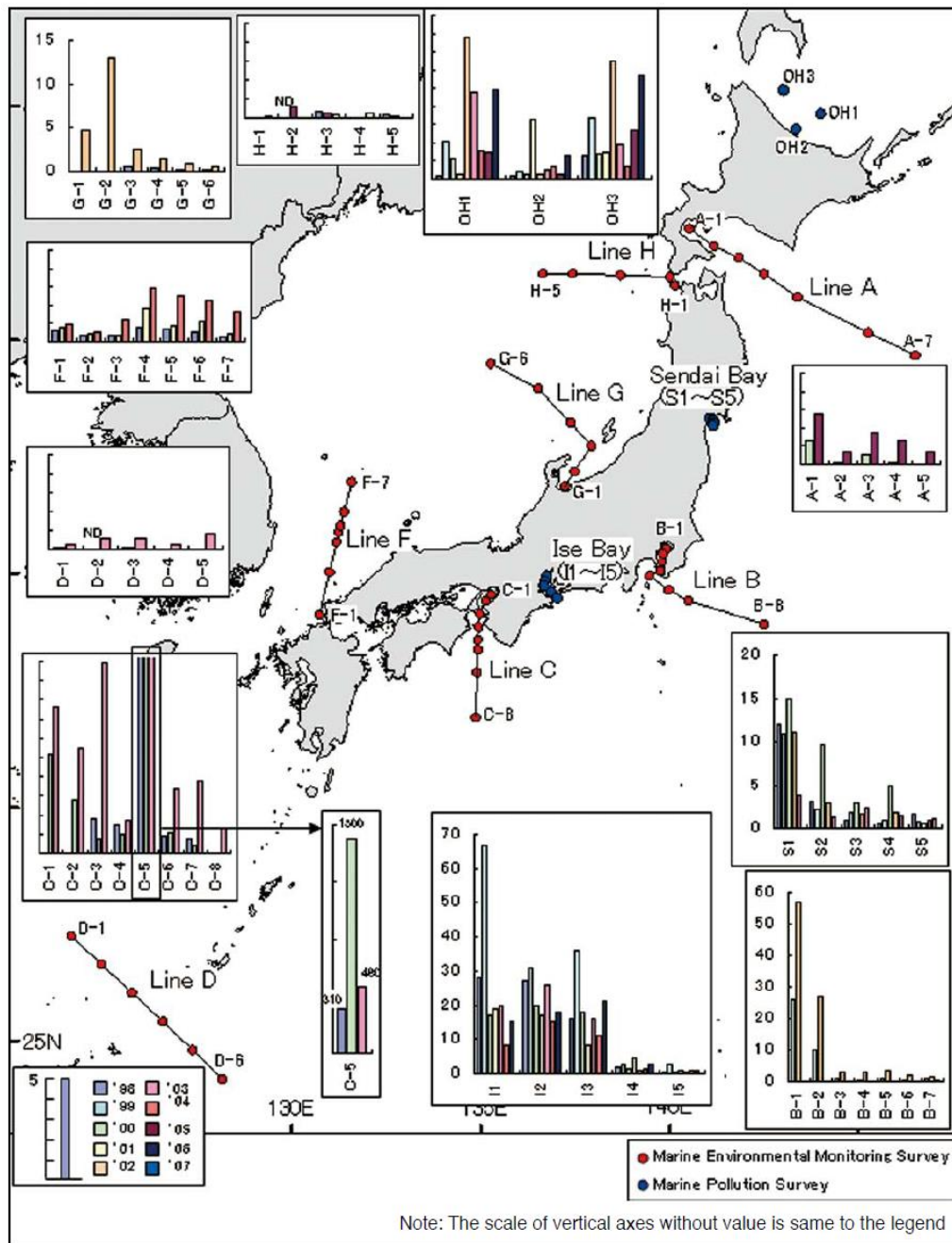


Figure 3-48 Geographical distribution of PCB in surface sediments along the transects (Global Environmental Issues Division (2009)).

Chronological changes of PCBs in livers of benthic sharks in several bays or inner seas are shown in Figure 3-49. No statistically significant downward trend has been observed in the PCB levels in marine organisms ($P > 0.05$).

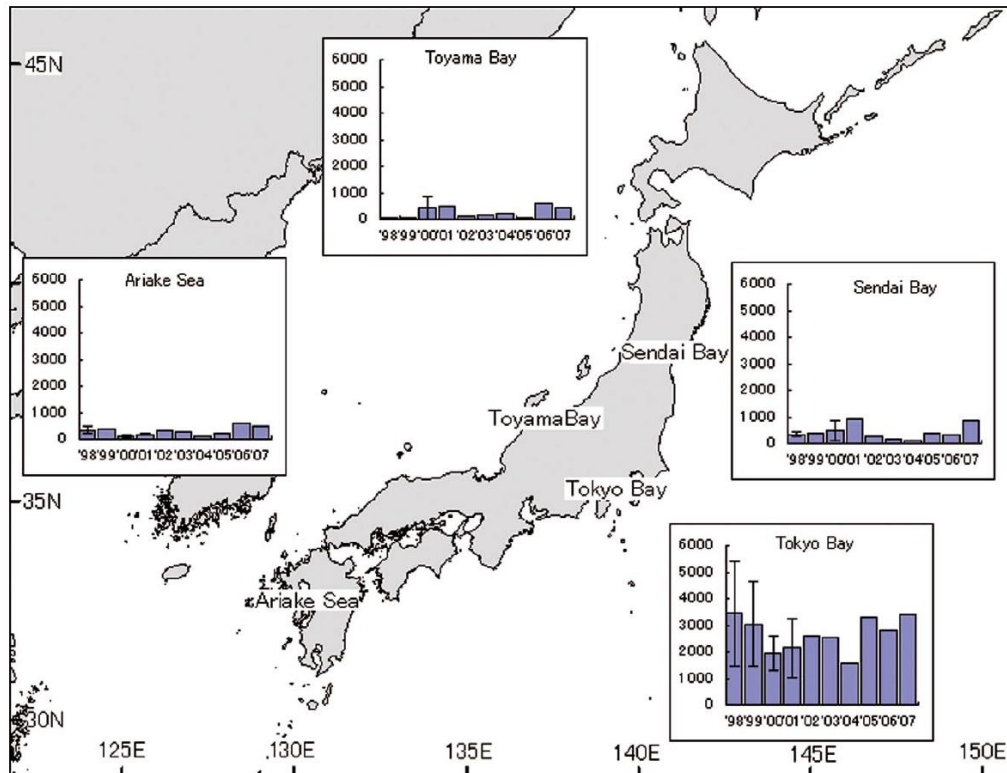


Figure 3-50 Chronological changes in PCB levels in liver of benthic shark (ng/g wet) (Global Environmental Issues Division (2009))

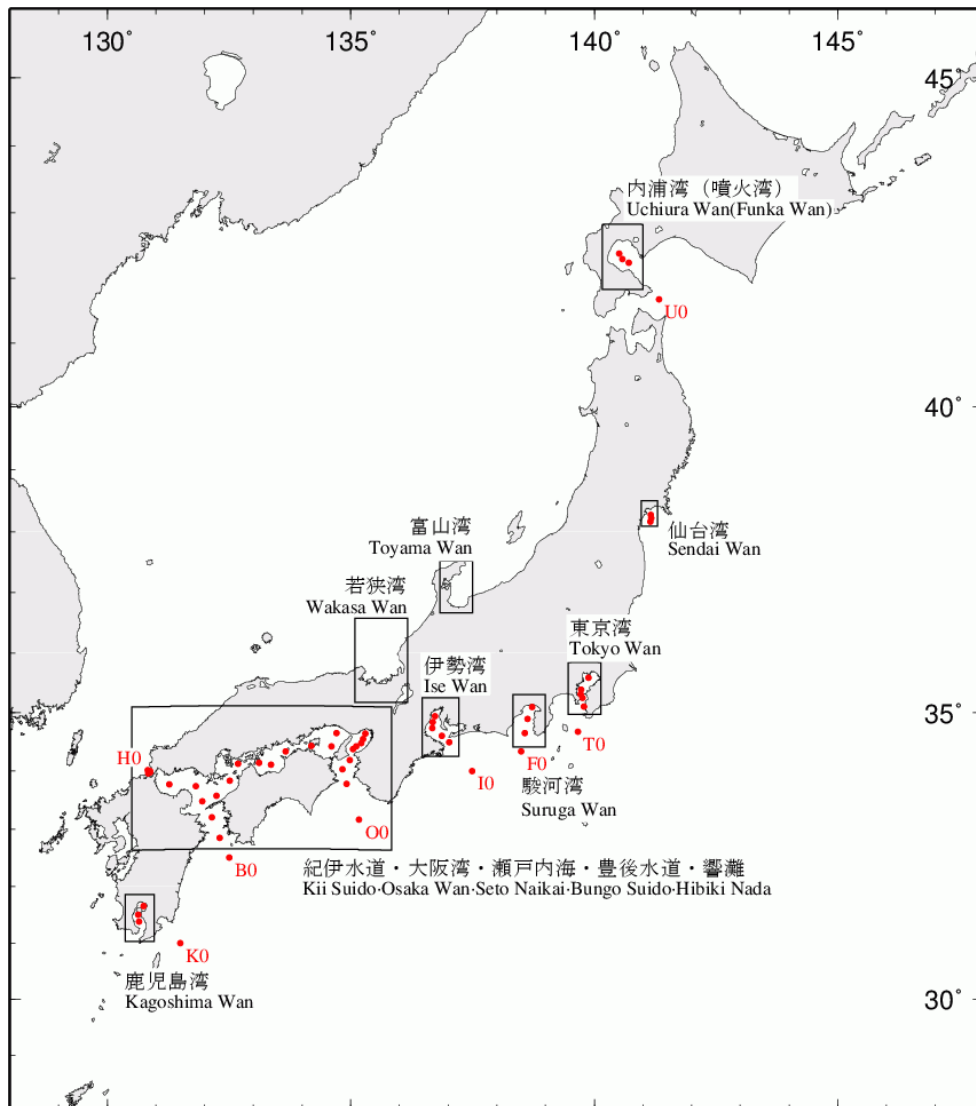


Figure 3-51 Sampling locations of Marine Pollution Surveys by Japan Coast Guard (2013)



Figure 3-52 PCB levels in surface sediments (Japan Coast Guard (2013))

Hydrographic and oceanographic department of Japan Coast Guard has been conducting marine environmental monitoring from 1982. In addition to oils and heavy metals (Cd, Hg, Cu, Zn, Cr, Pb), PCB concentrations in sediments were monitored and reported every year.

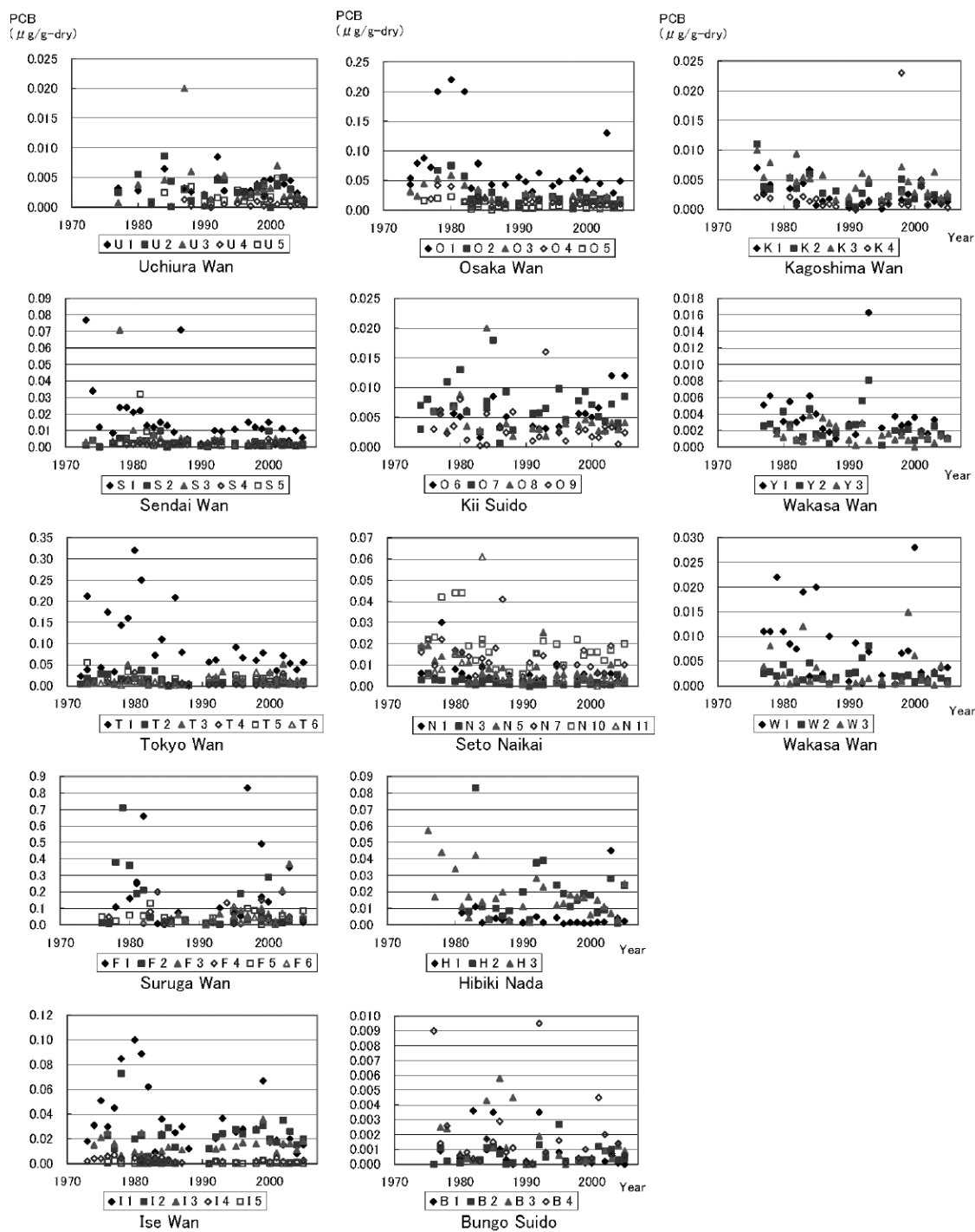


Figure 3-53 Temporal trends of PCB levels in the past three decades as revealed by the Marine Pollution Surveys (Shimizu et al., 2008)

Sampling locations and PCB levels in sediments are shown in Figures 3-51 and 3-52, respectively. In this program, PCB has been analyzed by a traditional GC-ECD method, a different method from that currently used by the Ministry of the Environment. As shown in Figure 3-52, clear decreasing trends of PCB levels are found along many

transects from coastal to offshore direction. Higher PCB levels were detected in Suruga Bay, where severe marine pollution by effluents and sludges from paper mill companies had occurred in 1960's - early 70's. In addition to the data in Figure 3-52, sediment PCB levels are also analyzed in three locations along Sea of Okhotsk.

A trend analysis of the results of Marine Pollution Surveys for three decades was reported by Shimizu et al (2008) (Figure 3-53). Although considerable variations are observed, general declining trends seem to be present in several locations, particularly those located nearby densely populated areas, such as Tokyo Bay and Osaka Bay ("Wan" in Figure 3-53 means "Bay" in English). The authors reported statistically significant increasing trend of PCB at F-3 location (most distant location from the coast in Suruga Bay (Figure 3-52)), and suggested possible spread of PCB from hotspots near coastline to more offshore location.

C. Newly added POPs and other PTSs, including fluorosurfactants, brominated flame retardants and organotins

Environmental monitoring of newly added POPs to the Convention, i.e., α -HCH(hexachlorocyclohexane), β -HCH, γ -HCH, PeCBz (pentachlorobenzene), tetra-/penta-BDEs (brominated diphenyl ethers), hexa-/hepta-BDEs, hexabromobiphenyl (HxBB), chlordecone, PFOS, endsulfan and HBCD (hexabromocyclododecane), were started under the long-term environmental monitoring in "Chemicals in the Environment" program (Environmental Health and Safety Division (2013)).

HCHs were produced and used in large amount in Japan for agrochemical and other purposes. They were removed from the list of registered agrochemicals in 1971, but continuously used for wood protection and termite control for years. They were registered as Class 1 Specified Chemical Substance in 2010. During the decade between 2002 and 2011, β -HCH levels in ponds/lakes water and γ -HCH levels in water (total, rivers, river mouths and coastal areas) showed statistically significant decreasing trend. Similarly α -HCH and γ -HCH in fishes showed statistically significant decreasing trends in the same period.

Table 3-54. HCHs in air (pg/m³)

Chemicals/Isomers Seasons	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -HCH						
Summer	43	44	410	9.5	2.5 (0.83)	35/35
Winter	18	15	680	6.5	-	37/37
β -HCH						
Summer	5.0	5.2	49	0.84	0.39 (0.13)	35/35
Winter	1.7	1.7	91	Tr (0.31)	-	37/37
γ -HCH						
Summer	14	17	98	2.7	1.6 (0.52)	35/35
Winter	5.1	4.8	67	Ttr (1.1)	-	37/37
δ -HCH						
Summer	1.1	1.1	33	0.11	0.063 (0.021)	35/35
Winter	0.35	0.34	26	Tr (0.05)	-	37/37

Table 3-55. HCHs in water (pg/L)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -HCH	67	60	1,000	11	7 (3)	49/49
β -HCH	130	120	840	28	2.0 (0.8)	49/49
γ -HCH	23	20	170	3	3 (1)	49/49
δ -HCH	8.6	8.9	300	0.7	0.4 (0.2)	49/49

Table 3-56. HCHs in sediments (pg/g dry)

Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -HCH	120	140	5,100	1.6	1.5 (0.6)	64/64
β -HCH	180	210	14,000	3	3 (1)	64/64
γ -HCH	35	42	3,500	nd	3 (1)	62/64
δ -HCH	37	47	5,000	nd	1.4 (0.5)	63/64

Table 3-57. HCHs in biological samples (pg/g wet)

Organisms Isomers	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
α -HCH	64	33	1,200	13	3 (1)	4/4
β -HCH	130	68	2,000	39	3 (1)	4/4
γ -HCH	26	17	320	5	3 (1)	4/4
δ -HCH	9	Tr (2)	1,400	Tr (1)	3 (1)	4/4
Fishes						
α -HCH	37	54	690	Tr (2)	3 (1)	18/18
β -HCH	100	140	710	4	3 (1)	18/18
γ -HCH	12	15	160	Tr (1)	3 (1)	18/18
δ -HCH	3	4	19	nd	3 (1)	14/18
Birds						
α -HCH		48			3 (1)	1/1
β -HCH		4,500			3 (1)	1/1
γ -HCH		26			3 (1)	1/1
δ -HCH		5			3 (1)	1/1

Chlordecone was never registered as agrochemicals in Japan. Environmental monitoring of chlordecone started in FY 2008 (except air), and continued in FY 2010 and 2011 including air samples. It was detected in only small number of the samples in low levels.

Table 3-58. Chlordecone in air (pg/m³)

Season	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Summer	nd	nd	nd	nd	0.04 (0.02)	0/35
Winter	nd	nd	nd	nd		0/37

Table 3-59. Chlordecone in water (pg/L)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
49	nd	nd	0.7	nd	0.20 (0.05)	15/49

Table 3-60. Chlordecone in sediments (pg/g dry)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
64	nd	nd	1.5	nd	0.4 (0.2)	9/64

Table 3-61. Chlordecone in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
4 (bivalves)	nd	nd	nd	nd	0.5 (0.2)	0/4
18 (fishes)	nd	nd	nd	nd	0.5 (0.2)	0/18
1 (bird)	-	nd	-	-	0.5 (0.2)	0/1

Hexabromobiphenyl (HxBB) was designated in Class 1 Specified Chemical Substance in 2010. It is seldom detected in the Japanese environmental samples.

Table 3-62. HxBB in air (pg/m³)

Season	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Summer	nd	nd	nd	nd	0.3 (0.1)	0/35
Winter	nd	nd	nd	nd		0/37

Table 3-63. HxBB in water (pg/L)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
	nd	nd	nd	nd	2.2 (0.9)	0/49

Table 3-64. HxBB in sediments (pg/g dry)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
64	nd	nd	6.3	nd	3.6 (1.4)	8/64

Table 3-65. HxBB in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
4 (bivalves)	nd	nd	nd	nd	3 (1)	0/4
18 (fishes)	Nd	nd	3	nd	3 (1)	5/18
1 (bird)	-	3	-	-	3 (1)	1/1

Three different commercial products of **polybromobiphenyls (PBDEs)** have been used in Japan; i.e., tetra- or penta-BDEs (until 1990), octa-BDEs (until 1999), and decaBDE (until present). In Japan, PBDE congeners with 4 to 10 bromine atoms have been monitored simultaneously and reported.

Table 3-66. PBDEs in air (pg/m³)

Season	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Summer						
Tetra-	0.80	0.72	9.3	Tr (0.11)	0.18 (0.07)	35/35
Penta-	0.19	0.17	8.8	nd	0.16 (0.06)	31/35
Hexa-	Tr (0.11)	Tr (0.10)	1.2	nd	0.14 (0.05)	28/35
Hepta-	Tr (0.1)	Tr (0.1)	1.1	nd	0.3 (0.1)	20/35
Octa-	0.24	0.31	1.9	nd	0.2 (0.08)	27/35
Nona-	Tr (0.8)	0.9	3.9	nd	0.9 (0.4)	29/35
Deca-	Tr (8.2)	Tr (9.0)	30	nd	12 (4)	31/35
Winter						
Tetra-	0.36	0.34	7.0	nd	0.18 (0.07)	35/37
Penta-	0.16	Tr (0.14)	2.6	nd	0.16 (0.06)	31/37
Hexa-	0.16	0.18	1.7	nd	0.14 (0.05)	30/37
Hepta-	Tr (0.2)	Tr (0.2)	2.3	nd	0.3 (0.1)	25/37
Octa-	0.35	0.44	7.0	nd	0.2 (0.08)	30/37
Nona-	1.1	1.1	14	nd	0.9 (0.4)	30/37
Deca-	Tr (8.4)	Tr (9.0)	44	nd	12 (4)	29/37

Table 3-67. PBDEs in water (pg/L)

Congeners	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Tetra-	11	10	180	nd	4 (2)	48/49
Penta-	5	4	180	nd	3 (1)	48/49
Hexa-	Tr (1)	nd	39	nd	3 (1)	21/49
Hepta-	nd	nd	14	nd	6 (2)	14/49
Octa-	4	3	98	nd	2 (1)	44/49
Nona-	33	24	920	nd	10 (4)	47/49
Deca-	200	140	58,000	nd	60 (20)	45/49

Table 3-68. PBDEs in sediments (pg/g dry)

Congeners	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Tetra-	30	30	2,600	nd	9 (4)	55/64
Penta-	26	19	4,700	nd	6 (4)	55/64
Hexa-	31	42	2,000	nd	9 (3)	52/64
Hepta-	29	32	2,400	nd	7 (3)	55/64
Octa-	57	4	36,000	nd	10 (4)	55/64
Nona-	710	630	70,000	nd	23 (9)	62/64
Deca-	4,200	4,700	700,000	nd	40 (20)	62/64

Table 3-69. PBDEs in biological samples (pg/g wet)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
4 (bivalves)						
Tetra-	96	120	490	26	16 (6)	4/4
Penta-	51	60	160	Tr (12)	15 (6)	4/4
Hexa-	38	41	81	20	10 (4)	4/4
Hepta-	14	26	44	nd	11 (4)	4/4
Octa-	7	9	29	nd	7 (3)	3/4
Nona-	Tr (12)	Tr (11)	40	nd	22 (9)	3/4
Deca-	nd	nd	240	nd	230 (80)	1/4
18 (fishes)						
Tetra-	110	110	860	Tr (9)	16 (6)	18/18
Penta-	39	39	300	nd	15 (6)	17/18
Hexa-	53	50	430	nd	10 (4)	17/18
Hepta-	13	21	130	nd	11 (4)	13/18
Octa-	Tr (6)	Tr (7)	150	Nd	7 (3)	10/18
Nona-	nd	nd	Tr (15)	Nd	22 (9)	5/18
Deca-	nd	nd	Tr (90)	Nd	230 (80)	2/18
1 (bird)						
Tetra-		67			16 (6)	1/1
Penta-		110			15 (6)	1/1
Hexa-		96			10 (4)	1/1
Hepta-		44			11 (4)	1/1
Octa-		66			7 (3)	1/1
Nona-		62			22 (9)	1/1
Deca-		Tr (170)			230 (80)	1/1

Among the congeners, deca-BDE was dominant in air, water and sediment samples while its proportion was rather small in organisms, possibly reflecting its lower bio-concentration factors.

PFOS and PFOA are among the most popular perfluorosurfactants. These chemicals have been used for nearly half a century for variety of purposes. PFOS was designated as Class 1 Specified Chemical Substance in 2010. PFOA was listed in Type 2 Monitored Chemical Substance. After amendment of Chemical Substance Control Law in April 2013, perfluoroalkyl carboxylates with carbon chain length of 12 to 16 are now listed in Monitored Chemical Substance.

Table 3-70. PFOS and PFOA in air (pg/m³)

Chemicals Season	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
PFOS						
Summer	4.4	4.2	10	0.9	0.5 (0.2)	35/35
Winter	3.7	3.8	9.5	1.3	-	37/37
PFOA						
Summer	20	18	240	Tr(3.5)	5.4 (1.8)	35/35
Winter	12	11	97	nd	-	36/37

Table 3-71. PFOS and PFOA in water (pg/L)

Chemicals	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
PFOS	480	360	10,000	Tr (20)	50 (20)	49/49
PFOA	2,000	1,700	50,000	380	50 (20)	49/49

Table 3-72. PFOS and PFOA in sediments (pg/g dry)

Chemicals	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
PFOS	92	110	1,100	nd	5 (2)	63/64
PFOA	100	93	1,100	22	5 (2)	64/64

Table 3-73 PFOS and PFOA in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
PFOS	38	44	100	16	10 (4)	4/4
PFOA	Tr (19)	Tr (22)	Tr (40)	nd	41 (14)	3/4
Fishes						
PFOS	82	95	3,200	nd	10 (4)	16/18
PFOA	nd	nd	51	nd	41 (14)	7/18
Bird						
PFOS		110			10 (4)	1/1
PFOA		nd			41 (14)	0/1

Monitoring of pentachlorobenzene started in 2007. It was continuously monitored in 2010 and 2011. Like HCB, LRTP of PeCB is quite large. The air levels of PeCB are rather similar each other irrespective of the sampling location and sampling season.

Table 3-74. PeCB in air (pg/m³)

Season	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Summer	61	60	140	30	2.1 (0.7)	35/35
Winter	59	57	180	26	2.1 (0.7)	37/37

Table 3-75. PeCB in water (pg/L)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
	11	11	170	2.6	2.4 (0.9)	49/49

Table 3-76. PeCB in sediments (pg/g dry)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
	95	76	4,500	3	5 (2)	64/64

Table 3-77. PeCB in biological samples (pg/g wet)

No. Sites	Geo.Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves	28	16	260	10	4 (1)	4/4
Fishes	36	37	220	5	4 (1)	18/18
Bird		52			4 (1)	1/1

Two isomers of **endosulfan**, **α-endosulfan** and **β-endosulfan**, were analyzed in various environmental media in FY 2011.

Table 3-78. Endosulfan in air (pg/m³)

Season	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α-endosulfan						
Summer	26	24	190	Tr (7.8)	12 (4)	35/35
Winter	Tr (9.6)	Tr (9.8)	45	nd	12 (4)	35/37
β-endosulfan						
Summer	2.1	1.8	11	nd	1.2 (0.39)	34/35
Winter	Tr (0.8)	Tr (0.8)	8.3	nd	1.2 (0.39)	31/37

Table 3-79. Endosulfan in water (pg/L)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -endosulfan	Nd	nd	180	nd	120 (50)	2/49
β -endosulfan	Nd	nd	270	nd	22 (9)	8/49

Table 3-80. Endosulfan in sediments (pg/g dry)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -endosulfan	Tr (13)	Tr (11)	480	nd	30 (10)	35/64
β -endosulfan	Tr (5)	Tr (4)	240	nd	9 (4)	38/64

Table 3-81. Endosulfan in biological samples (pg/g wet)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
α -endosulfan	62	120	330	nd	50 (20)	3/4
β -endosulfan	16	26	52	Tr (4)	11 (4)	4/4
Fishes						
α -endosulfan	Tr (20)	Tr (20)	140	nd	50 (20)	10/18
β -endosulfan	Nd	nd	37	nd	11 (4)	9/18
Bird						
α -endosulfan		nd			50 (20)	0/1
β -endosulfan		nd			11 (4)	0/1

Five isomers of HBCD, i.e., α -HBCD, β -HBCD, γ -HBCD, δ -HBCD and ε -HBCD, were analyzed in water, sediments and biota for the first time in FY 2011.

Table 3-82. HBCD in water (pg/L)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -HBCD	nd	nd	6,300	nd	1,500 (600)	4/47
β -HBCD	nd	nd	1,300	nd	1,300 (500)	4/47
γ -HBCD	nd	nd	65,000	nd	1,200 (500)	5/47
δ -HBCD	nd	nd	nd	nd	790 (300)	0/47
ε -HBCD	nd	nd	nd	nd	740 (300)	0/47

Table 3-83. HBCD in sediments (pg/g dry)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
α -HBCD	430	nd	24,000	nd	420 (280)	35/62
β -HBCD	nd	nd	14,000	nd	250 (170)	21/62
γ -HBCD	670	nd	570,000	nd	400 (260)	36/62
δ -HBCD	nd	nd	800	nd	350 (250)	6/62
ε -HBCD	nd	nd	Tr (260)	nd	280 (210)	1/62

Table 3-84. HBCD in biological samples (pg/g wet)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
α -HBCD	1,100	1,200	13,000	Tr (86)	170 (70)	4/4
β -HBCD	Tr (70)	Tr (85)	240	nd	98 (40)	3/4
γ -HBCD	440	470	3,300	nd	210 (80)	4/4
δ -HBCD	nd	nd	nd	nd	140 (60)	0/4
ε -HBCD	nd	nd	nd	nd	140 (60)	0/4
Fishes						
α -HBCD	770	850	69,000	nd	170 (70)	16/17
β -HBCD	nd	nd	760	nd	98 (40)	5/17
γ -HBCD	210	Tr (90)	50,000	nd	210 (80)	10/17
δ -HBCD	nd	nd	nd	nd	140 (60)	0/17
ε -HBCD	nd	nd	nd	nd	140 (60)	0/17
Bird						
α -HBCD	200	nd	530	nd	170 (70)	1/1
β -HBCD	nd	nd	nd	nd	98 (40)	0/1
γ -HBCD	Tr (180)	nd	460	nd	210 (80)	1/1
δ -HBCD	nd	nd	nd	nd	140 (60)	0/1
ε -HBCD	nd	nd	nd	nd	140 (60)	0/1

Organotins were monitored in the long-term monitoring program in FY 2010. The data are summarized in the following tables. Compared with the previous data obtained in Fy2002, 2003 and 2005, both TBTs and TPTs in fishes showed dramatical decrease during the period.

Table 3-85. Organotins in water (pg/L)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
TBTs	nd	nd	1,600	nd	200 (100)	12/49
TPTs	nd	nd	250	nd	120 (50)	4/49

Table 3-86. Organotins in sediments (pg/g dry)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
TBTs	2,500	3,400	1,300,000	nd	160 (80)	53/64
TPTs	290	190	210,000	nd	70 (30)	42/64

Table 3-87. Organotins in biological samples (pg/g wet)

No. Sites	Geo. Means	Median	Max	Min	MQL (MDL)	Detection frequency
Bivalves						
TBTs	6,400	6,000	30,000	1,600	420 (160)	6/6
TPTs	1,700	1,500	6,500	490	270 (110)	6/6
Fishes						
TBTs	1,100	760	23,000	nd	420 (160)	17/18
TPTs	2,300	3,100	14,000	Tr (140)	270 (110)	18/18
Bird						
TBTs	nd	nd	nd	nd	420 (160)	0/2
TPTs	nd	nd	Tr (120)	nd	270 (110)	1/2

Organotins have been monitored in surface sediment samples from coastal to offshore regions in Marine Environmental Pollution Surveys. Butyltin compounds in sediments show higher concentrations in inner bays/coastal areas located in metropolitan areas, and lower concentrations in offshore areas as shown in the Figure. Interestingly a higher levels of butyltins were observed in distant places from coastline along the transect F (F-4 ~ F-6) in FY2004 survey. A similar phenomenon was observed in the case of dioxins and PCB (F-4 ~ F-7 in both cases). The specific pattern in dioxins and PCB had been observed in the past monitoring surveys, too, and were attributed to higher sedimentation rates in the area due to characteristic depth profile of the sea (Figure). On the other hand, specific pattern of butyltins had not been observed before. It was reported that phenyltins did not show such a distinct pattern in 2004 survey. A characteristic monobutyltin-rich pattern was commonly observed in F-4 ~ F-7 in FY2004 monitoring data, suggesting old or weathered nature of the sources.

Butyltin compounds within marine organisms showed a statistically significant downward trend ($P < 0.05$) in some sea areas and some marine organisms (mussel (soft

parts) in Sendai Bay and Toyama Bay, and in benthic sharks (liver) in Tokyo Bay and the Sea of Ariake) but not in a general and definite manner (Figure).

Organotins in marine sediments were also monitored in Marine Pollution Surveys conducted by Japan Coast Guard. The data obtained in FY2011 Survey is shown in Figure.

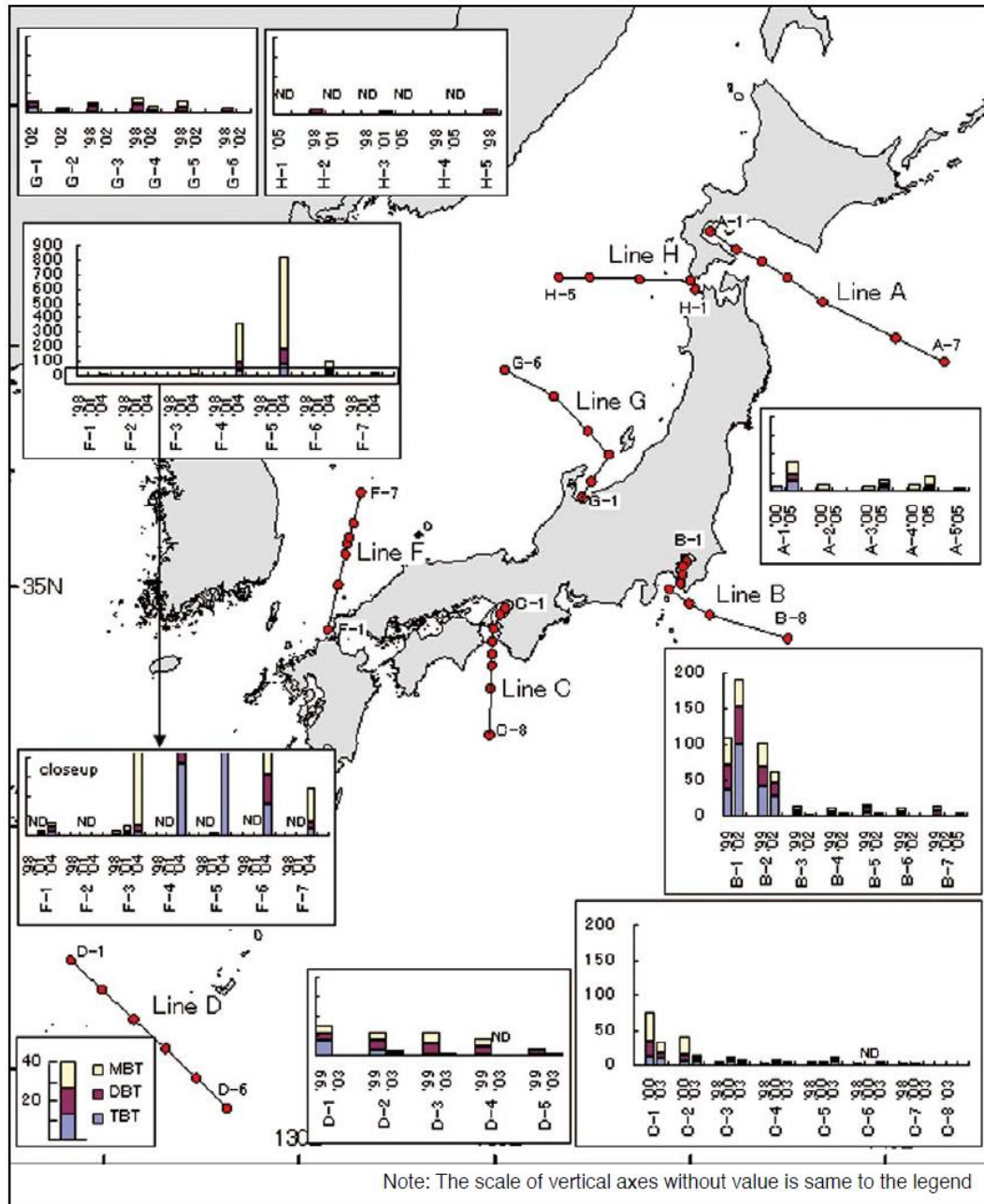


Figure 3-54 Geographical distribution of BTs in surface sediments (Global Environmental Issues Division (2009))

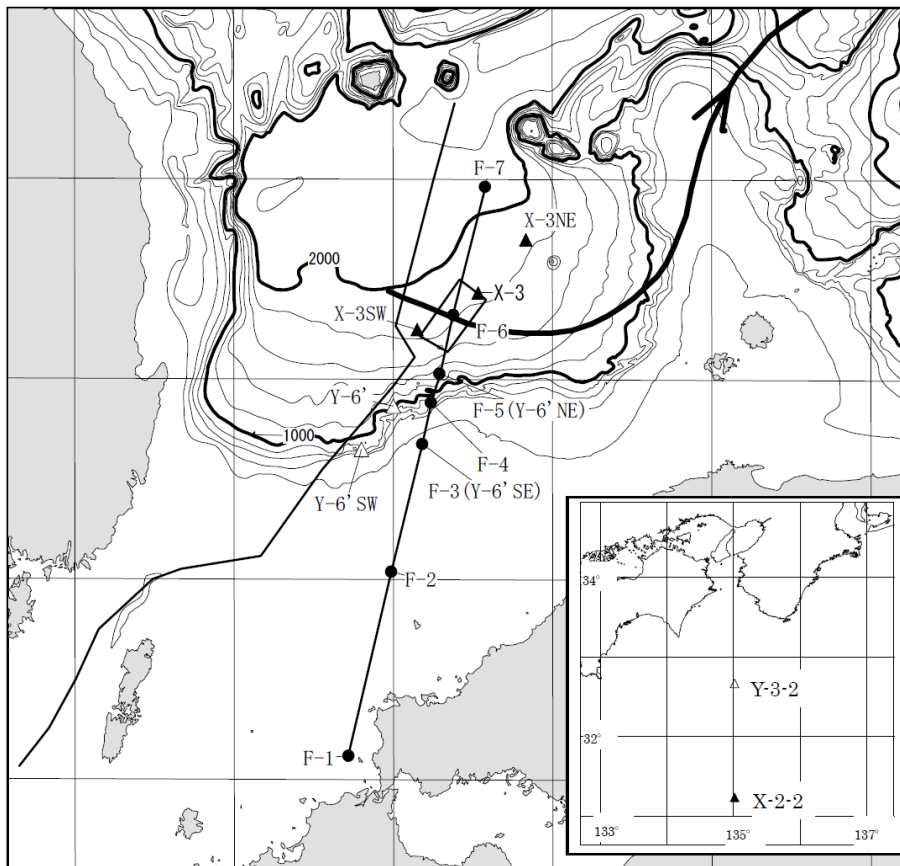


Figure 3-55 Detailed map of sampling sites in FY2004 survey (MOE (2006))

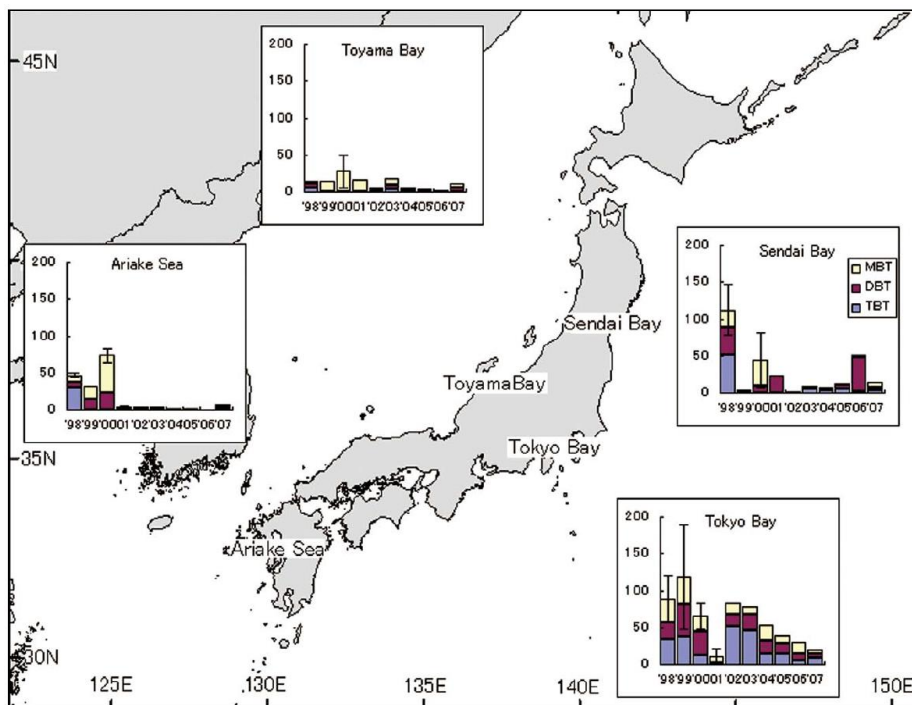


Figure 3-56 Chronological changes of BTs in livers of benthic sharks (Global Environmental Issues Division (2009))

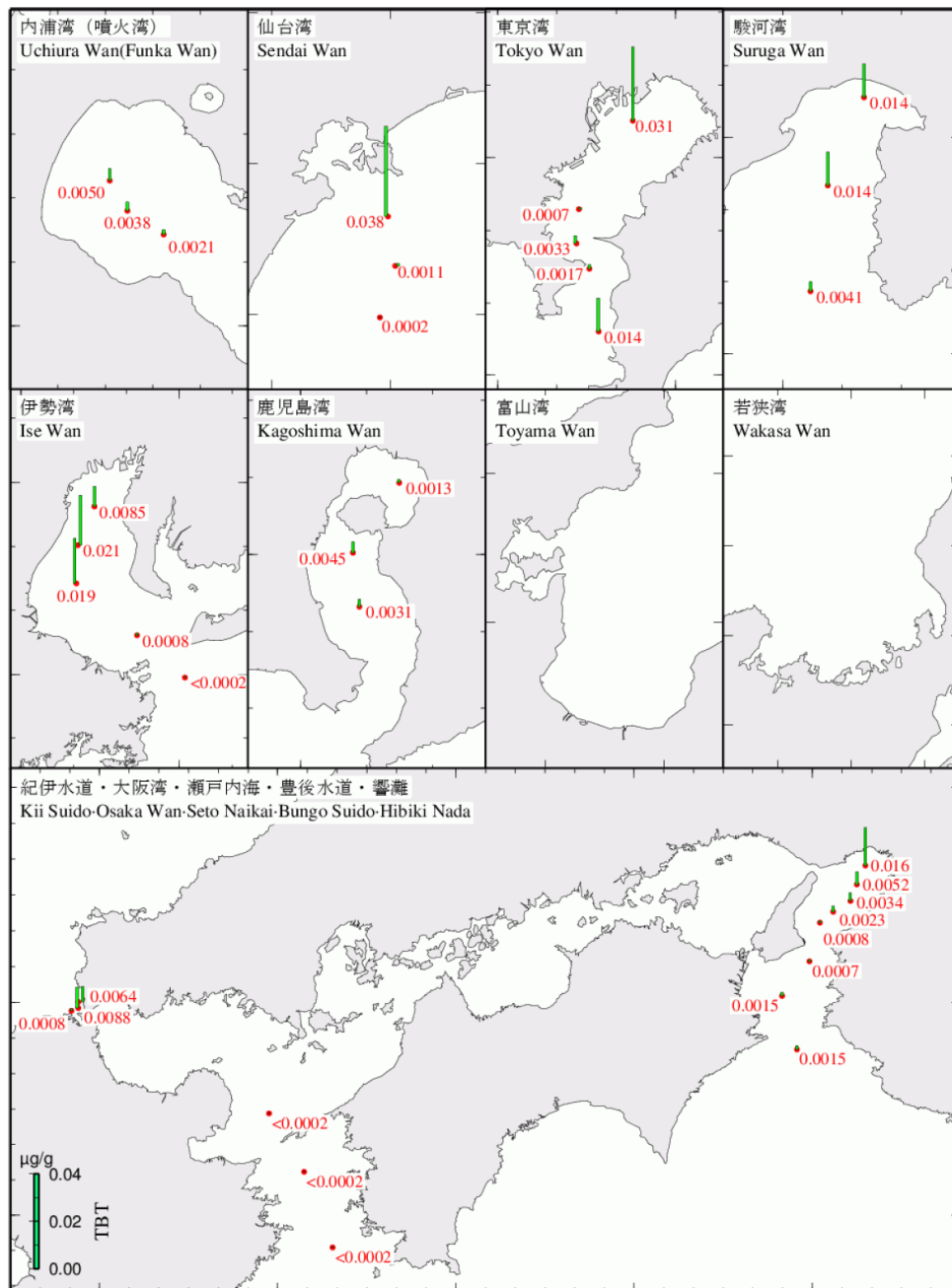


Figure 3-57 TBT levels in sediments in Marine Pollution Surveys conducted in FY2011 (Japan Coast Guard 2013)

D. Polycyclic aromatic hydrocarbons (PAHs)

Yang et al (2007) conducted PAHs monitoring in the atmosphere at a remote station in Noto peninsula, Japan, and found elevated levels of PAHs particularly in winter season when coal combustion for heating was extensive in East Asian countries. They concluded that PAHs came from North Eastern part of China based on back trajectory analysis and principal component analysis of the composition of PAHs. Li et al (2012), on the other hand, developed a highly sensitive on-line concentration

followed by HPLC- fluorescence detection system and analyzed PAHs levels in sea water around Noto peninsula. They reported drastic decrease of benzo(a)pyrene in sea water, from 8.1 ng/L to 0.2 ng/L, during a decade after crude oil pollution by the tanker accident. Chizhova et al (2013) reported depth profiles of 13 PAHs in sea water in 13 locations in the central NOWPAP region. The mean concentration of total PAHs in surface water was 8.5 ng/L, with higher levels of dissolved phase (5.6 ng/L) than those in particulate phase (2.7 ng/L). The highest levels in both phases (6.5 and 10.6 ng/L, respectively) were found for a depth of 300m, and their possible sources were attributed to the atmosphere.

3.5. Ecotoxicological effects of PTS within NOWPAP Region

Ecosystem is an extremely complex system, which consists of huge number of different organisms (biological species) with large spatial and temporal variations under different geographical and climatic conditions as well as impact of human activities. It is not a simple and easy task at all to extract the ecotoxicological effects by man-made chemicals in the real environment. In chemical management system, assessment of ecotoxicity of chemicals has been conducted by the combination of exposure assessment and experimental toxicity data. Variety of ecotoxicity test methods have been developed, including assessment of acute toxicities by using whole organisms, test batteries of different species for assessment of sub-acute or chronic toxicities (combination of crustacean, alge, and fish species is frequently used for the purpose), and specific test methods, such as mutagenicity tests to evaluate genotoxicity or carcinogenicity of chemicals, reporter gene assays to detect specific binding to particular receptors and multi-generation assays to assess the effect of chemicals to the next generation (see OECD test guideline for more detailed information (OECD)). Another systematic evaluation method, WET (whole effluent toxicity), has also been developed, particularly for ecotoxicity evaluation of effluent from factories (US EPA (2002)). On the other hand, careful observations of wildlife and/or ecosystem structure as well as environmental monitoring of chemicals have been conducted to evaluate effectiveness of the measures / regulations conducted based on the ecotoxicological risk assessment of the chemicals.

It should be pointed out that many of these test methods do not aim to assess the status of natural ecosystem in general, but rather aim to evaluate toxicity of chemicals themselves, or of effluents from factories or other emission sources, and thus utilize short-lived small organisms, which are not top-predators but rather lower trophic level organisms in foodweb structure. LOEC (lowest observed effect concentration) and NOEC (no observed effect concentration) are important experimental factors; ecotoxicological risk of a chemical is generally judged by the comparison of PNEC (predicted no effect concentration) calculated from NOEC and LOEC of several test organisms with PEC (predicted environmental concentration), which is a predicted highest concentration in the environment. PTS, on the other hand, tends to be accumulated through food web to top-predators, such as mammals and birds, during their long lives. The ecotoxicological risks of PTS may not be properly assessed by current test organisms, and thus proper assessment of toxicity to long-lived, and preferably carnivorous species will be of prime importance for ecotoxicological assessment of PTS chemicals. Although toxicological data on such organisms are limited, there are research activities to evaluate potential ecotoxicological effects of some of PTS on wildlife by the combination of monitoring data and experimental toxicological data. Some of PTS may show particular accumulation properties in the ecosystem. For example, PFOS tends to be bioaccumulated through foodweb, but shows no lipophilicity but binds to proteins strongly. As a result PFOS levels are generally higher in blood and livers in a body of wildlife than in lipid/fat, and their levels through foodweb may not be properly presented by fat basis, which has been the common way to represent levels of other lipophilic PTS in wildlife. Occasionally stable

isotope analysis has been conducted together with pollutant analysis in order to support proper interpretation of analytical results of PTS with respect to the foodweb structure.

It is also clear that toxicity to a single or a few species in the environment may not properly represent the toxicological effect of chemicals to the ecosystem, or environment as a whole. The selection of biological species and the establishment of appropriate endpoints to assess the toxicity are the key issues for the assessment. Various endpoints have been developed for assessing different types of “toxicities” of chemicals against organisms, including mortality, growth rates (weight / length of bodies, organs etc), pathological effects including tumor or other diseases, morphological effects, mobility or other neurobiological effects, number of offsprings and/or hatchability, sex ratios, biochemical effect including activities of particular enzymes, activation / suppression of specific genes, etc. A detailed discussion on the combined use of “bioindicators”, suitable organisms to monitor the environmental levels of POPs, and “biomarkers”, representative biological responses to toxicological effects of POPs to the organisms, to properly assess the effects of POPs to the ecosystem was conducted and reported (GEF/STAP (2004)). Part of the executive summary is reproduced here;

“Bioindicators are defined as the animal(s) or plant(s), which accumulate POPs in their tissues and organs in direct relation to the presence of POPs in their surroundings. ... Bioindicator programmes can therefore be designed to reveal environmental contamination, the transfer of contaminants through the food chain, and can hence identify potential health hazards for other animals and for human beings.”

“Measurable effects on organisms are therefore used as biomarkers. ... Effects at the molecular level tend to occur first, followed by responses at the cellular (biochemical), tissue/organ and whole-body levels. Responses that occur at individual, population and ecosystem level are generally accepted to have ecological relevance ... Biomarkers are especially useful as an early warning signal of emerging environmental problems... .”

Note that the above description was primarily aiming to assess the eco-toxicity of man-made chemicals to the wildlife, and may not fit to the terminology commonly used in the field of ecology / conservation of ecosystem. Composition of biological species, their numbers, sex ratios, age distributions and biomass in a particular environment has been monitored in ecosystem monitoring to assess the environmental quality and human impact. The term “bioindicator” has been used in the field of ecology as a representative biological species to a particular type of environment or its condition; i.e., its presence / absence can be interpreted as a marker representing environmental condition and human impact. A typical example is macroinvertebrates in rivers; they are grouped into several categories, such as disturbance-intolerant taxa and disturbance-adapted taxa, and the presence of either group of species are thought to represent water quality of the river. While these species are sensitive to pH, DO, degree of eutrophication etc, their presence / absence may not represent chemical pollution status sensitively except for some particular monitoring where some specific organisms rather sensitive to the target group of chemicals, such as crustaceans and microalgae for monitoring insecticides and

herbicides, respectively, are selected. Interpretation of traditional ecological researches with respect to chemical exposures are not easy due to complicated nature of ecosystem response to various environmental changes. Competition among different species for a niche further complicates the situation and the interpretation. While recently developing concept of “Ecosystem health” (Rapport et al, 1998, Costanza 2011) may be improved further in future to be able to deal with ecotoxicity of environmental chemicals including PTS explicitly, selected combination of specific biomarkers and bioindicator organisms has been and will be most frequent choices in ecotoxicological monitoring of pollutants. In this section, the term “bioindicators” will be used as biological organisms (wildlife), which are commonly or widely present in natural environment of target area (NOWPAP region) and either are sensitive to particular toxicity of chemicals or accumulate PTS in considerable levels so that the analysis of the species will show us status of environmental pollution and their changes in appropriate manner.

Molluscs, particularly mussels and other bivalves, as well as fish species have been selected as bioindicator organisms for the environmental monitoring of POPs due to their ease of collection and representativeness of local environment and their temporal / spacial changes. Marine mammals and birds, particularly of carnivorous species, are also suitable bioindicators for POPs monitoring due to their long lives as well as their higher trophic level positions, while their data may represent POPs status in wider locations (due to bigger size of their territories or migration behaviors) and longer time interval. Although controlled exposure tests, such as “caged mussels”, have occasionally been reported, majority of biomonitoring have been using naturally inhabiting wildlife in each location. In the design of biomonitoring method using bioindicator organisms, it is important to minimize variations reflecting other factors such as differences in species / sex / age / other physiological conditions in order to reveal PTS levels and their changes in the environment.

As for specific biomarkers, imposex or intersex, i.e, malformation of male sex organs to female molluscs or mixture of male and female organs in a body, has been used extensively to assess the ecotoxicological effects of organotins (Gibbs & Bryan, 1986). Other (suspected) effects of PTS include thinning of egg shell of gulls / raptors by DDT exposure, skull bone lesion (Zakhalov et al, 1990, Bergman et al, 1992, Mortensen et al, 1992) and other organs (Bergman 2007) in Baltic seals possibly by PCB/DDT or other organochlorines, and endocrine disruptive effects in alligators (Guillette et al 2000). Induction of particular biochemical response against the exposure to chemicals, including cytochrome P450 or other xenobiotic-metabolizing enzymes, enzymes and substrates to protect organisms from oxidative stress or other particular pollutants, and DNA hydroxylation / adduct formation etc., have also been extensively analyzed (Huggett et al, 1992). In these cases, their occurrence themselves does not necessarily represent “toxic” status but rather indicate “exposure” status or “early warning of higher risks” to such types of chemicals in the environment.

Although detailed research on the toxicological mechanism of PTS are beyond the scope of this report, a brief description on the induction mechanisms of P450, a so-called “xenobiotic or drug-metabolizing enzymes”, together with the receptors involved in the processes may be useful to understand ecotoxicological effects of POPs and other

PTS chemicals as well as their preferential use as biomarkers. Cytochrome P450s are a group of phase I drug-metabolizing enzymes with a prosthetic heme group for the activities (see, for example, Goto (2012), Pascucci et al (2008)). They are often functionally categorized into catalysts of “endogenous”, “secondary” and “xenobiotic” compounds. Particularly interesting is the finding that many of POPs and other PTS chemicals or their metabolites can induce some of the P450 family enzymes. In mammals, dioxins and PAHs, for example, induce CYP1 family through their binding with Ah receptor. Likewise PFOS and PFOA are known to interact with another receptor, PPAR α , to induce CYP4 family (Takacs & Abott (2007)). PPAR α is among the nuclear receptor superfamily with characteristic domain structure including 1) DNA binding domain composed of two zinc fingers aligned in either parallel or palindromic manner, 2) ligand-binding domain which interacts with particular chemicals, and 3) transactivating domain to promote or suppress gene activity. Ah receptor, on the other hand, has a different motif, i.e., helix-loop-helix structure for DNA binding and a characteristic ligand binding called PAS, which specifically interacts with ARNT (Aryl hydrocarbon Receptor Nuclear Translocator) protein. Other nuclear receptors known to interact with xenobiotics, sometimes called “xenosensors”, include CAR (constitutively activated receptor), PXR (pregnane X-receptor), LXR (liver X-receptor) and FXR (farnesoid receptor), all of which belong to NR1 family and commonly form heterodimer with RXR (retinoid X-receptor) for the interaction with DNA. Other nuclear receptors known to interact with xenobiotics are hormonal receptors, ER (estrogen receptor) and TR (thyroid hormone receptor). Variety of chemicals, including PCDD/Fs, PCB, hydroxylated PCB, PBDE and their hydroxylated metabolites, triclosan, BPA, phthalate esters, polyhalogenated PAHs, and several pesticides are known to disrupt these hormonal activities, particularly of thyroid hormone, by binding with receptors, hormone-transporting proteins or other mechanisms (Janosek et al., 2006). TBT is also reported to interact with RXR (Nishikawa et al. 2004) and PPAR (Pascoal et al 2013), which are suspected signal transduction routes to finally cause imposex in gastropod molluscs. Due to these effects, such chemicals are also called endocrine disruptive chemicals (EDCs) or endocrine disruptors. PTS include a quite wide range of chemicals with different structural motifs. Interestingly, many of them seem to have a common property of interacting with either of the receptors in nuclear receptor superfamily or Ah receptor, which, in turn, affect gene expression through their binding to some specific DNA sequences. Information on the toxicological mechanisms of PTS will be key factors to promote assessment of their ecotoxicological effects further by linking *in vitro* experiments to natural field studies more tightly.

<Russia>

The accumulation of pesticides and other PTS causes disturbances of metabolic pathways in marine organisms. Various tests and indicators have been proposed for integral evaluation of an ecosystem's health. Different biomarkers are used for estimating the state of organisms in a polluted environment. These are biochemical parameters that allow assessing both the presence of a toxicant and the response of the organism to the environmental impact (Lukyanova, 2001).

The impact of adverse factors of various origins, including toxic agents, induces a nonspecific response in cells, upon which free radicals are released. The accumulation of products of free radical processes can cause dysfunction of biological membranes and lead to oxidative modification of macromolecules such as proteins, DNA, and RNA, exerting a complex detrimental effect at the cellular level. To suppress free radicals, cells activate a complicated defense antioxidative system involving low molecular weight scavengers and enzymes. A disbalance between pro - and antioxidative processes, which can arise under the effect of a disturbing factor, causes oxidative stress to develop in cells and tissues. The activities of antioxidant enzymes, such as catalase and superoxide dismutase (SOD), the enzyme of phase II of biotransformation, glutathione -S- transferase (GST), as well as the concentration of glutathione (GSH) and the level of lipid peroxidation (LPO) can serve as molecular biomarkers.

Glutathione-S-transferase is a key enzyme of phase II of the biotransformation of organic pollutants and some endogenous compounds. The enzyme catalyzes the conjugation of the tripeptide glutathione with electrophilic substrates, including, among xenobiotics, above all polycyclic aromatic hydrocarbons and polychlorinated biphenyls, and organochlorine pesticides. GST, along with metallothioneins and cytochrome P450, belongs to biomarkers of the defense response that develops in an organism under the influence of various pollutants, in contrast to, for instance, lipid peroxidation or breaks in DNA chains, which are biomarkers of damage.

The integrated activity of GST in fishes, mollusks, and crustaceans which are considered as regional indicator species and are exposed to chronic pollution in Peter the Great Bay was examined in 2004-2008.

Among pollutants flowing into Amursky and Ussuriisky Bays with wastewaters, there are petroleum products, pesticides, phenols, detergents, and heavy metals (Nigmatullina, 2007). In mollusks and fish from these areas, the accumulation of DDT and hexachlorocyclohexane was recorded (Lukyanova et al., 2007). It has been experimentally shown that GST takes part in the detoxication of such electrophilic compounds as Aroclor, DDT, lindane, and atrazine (Hayes and Pulford, 1996), and other organophosphorous and organochlorine compounds. The presence of these substances in the organs of marine animals activates the intracellular system of biotransformation, including GST. The activity of this enzyme in marine organisms is high and demonstrates a significant correlation with the level of pollution. The advantage of such parameters compared to the traditionally measured levels of the pollutant in animal organs is that biomarkers provide more reliable information not only

on the level of pollution, but also on the health of individuals. In each region, for each climatic zone, studies are performed on a particular set of indicatory species.



Fig.3-58 .Mussels *Crenomytilus grayanus* Mysids *Neomysis mirabilis* Flounder *Liopsetta pinnifasciata*

Mussels, mysid shrimps, and flounders (Figure 3-58) are boreal species, widespread in adjacent seas of the Russian Far East, accessible for capture, and sensitive to the impact of pollution. These species were used as bioindicators in 2001 – 2009.

In Amursky Bay, increased GST activity was recorded in hepatopancreas, gills and gonads of mussels *Crenomytilus grayanus* from the inner, more polluted areas - Perevoznaya bay and Peschany Cape (Figure 3-59).

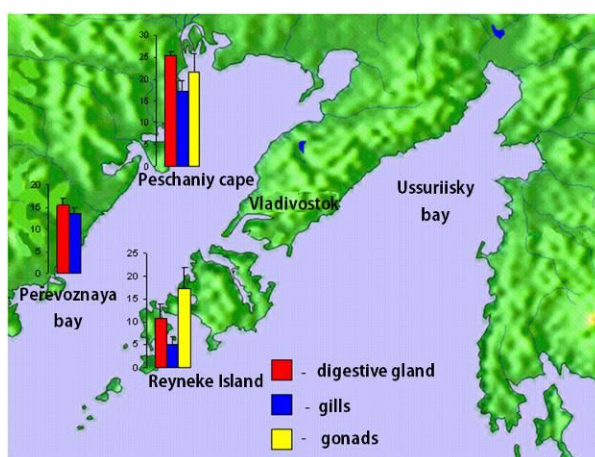


Figure 3-59. GST activity in organs of mussels *Crenomytilus grayanus* from Amursky Bay (Lukyanova,Ireykina,2012)

A similar trend was observed for mussels from Ussuriisky Bay. The activity of GST in the hepatopancreas of mussels from the inner, more polluted areas of the bay (Sukhodol Bay and Lazurnaya Bay) was, on average, 42 and 58 nmol/(min·mg of

protein), respectively, which was two and three times higher than in mussels taken near Reyneke Island (non-impact reference area) (Figure 3-60). Different mean of GST activity in mussels from Reyneke Island at Fig.3-59 and Fig.3-60 reflect the results of GST activity determination in mussels sampling during two field cruise, in 2004 (Amursky Bay) and 2006 (Ussuriisky Bay). Enzymatic activity in mussels in reference site revealed normal inter-annual dynamic; however, in each case there were significant differences between mussels from Reyneke Island and more polluted inner parts of the bays.

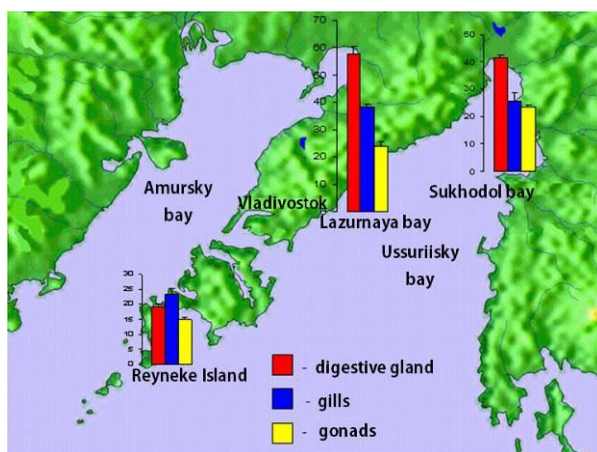


Figure 3-60. GST activity in organs of mussels *Crenomytilus grayanus* from Ussuriisky Bay (Lukyanova,Ireykina,2012)

Correlation analysis of the enzyme's activity in the hepatopancreas of mussels and the concentration of petroleum hydrocarbons in the bottom sediments of the same areas showed a significant correlation between these factors (Pearson's correlation coefficient $r = 0.89$, $p < 0.05$ (Chernyaev et al., 2006).

Enzymatic activity in sessile mussels, inhabiting the polluted sites, corresponds to the anthropogenic pressure in the local areas (bights) in the bays. In contrast to mussels, moving fish are used as bioindicators of pollution at rather large water basins. Differences in enzymatic activity in fish may indicate the different anthropogenic pollution in the Amursky and Ussuriisky bays and different degree of impact on the biota. The activity of GST in the livers of flounders *Liopsetta pinnifasciata* from Amursky bay was 140 nmol/(min·mg of protein), which was approximately 30% higher than in flounders from Ussuriisky bay (105 nmol/(min·mg of protein) (Figure 3-61). These data correlated with the volume of wastewaters and amount of pollutants discharged to Amursky and Ussuriisky bays. Calculations suggest the pollution of Amursky bay (tons of pollutants per 1m³ per year) was much higher than Ussuriisky bay (Nigmatulina, 2007).

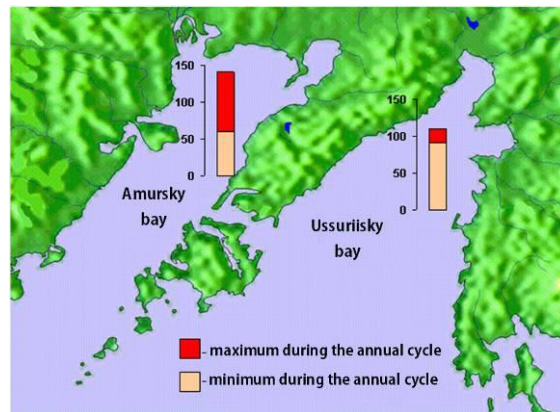


Figure 3-61. GST activity in the liver of flounder *Liopsetta pinnifasciata* from Amursky and Ussuriisky bays (Lukyanova,Ireykina,2012)

Estuaries are usually more contaminated than the border adjacent riverine and marine ecosystems. Concentrations of pollutants, including PTS, in estuaries are the highest. Estuaries organisms are exposed to a high level of contamination.



Figure 3-62. Estuaries fish haarder (*Liza hematochiela*)

Estuaries fish haarder (*Liza hematochiela*) (Figure 3-62) were caught in the estuaries of the Razdol'naya river and the Amba River flowing into Amursky bay. Due to the lack of developed human activity along the Amba River, its drainage basin and estuary zone are considered to be an unpolluted reference area.

Significant differences in the concentration of glutathione and the activity of glutathione- S-transferase and superoxide dismutase in organs of haarder from these areas were estimated (Figure 3-63). Glutathione is a component of the first barrier in the cell's defense system, and, as a rule, its concentration increases under stress impacts. However, the intracellular pool of this low-molecular-weight antioxidant is depleted afterwards, and its concentration falls.

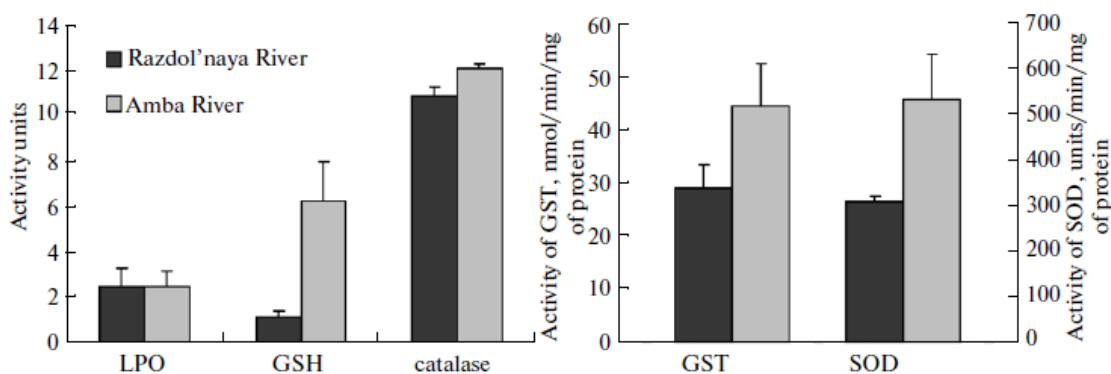


Figure 3-63. Molecular biomarkers of oxidative stress in the liver of the haarder (*Lisa haematocheila*) from estuaries of the Razdol'naya River and the Amba River. Measurement units: *lipid peroxidation* (LPO), nmol of malondialdehyde (MDA) per mg of protein; *glutathione* (GSH), μg of glutathione per mg of protein; *catalase*, activity units per mg of protein ($M \pm m$, $N = 5$). (Lukyanova et al., 2010)

A similar dependence is typical for biotransformation enzymes (GST) and antioxidant enzymes (superoxide dismutase SOD and catalase); their activities are suppressed under the continuous impact of high doses of toxic agents or to the chronic pollution. A significant six fold decline in glutathione concentration and decreased activity of GST (by 35%) were recorded in haarder in the Razdol'naya estuary as compared to fish from the estuary of the Amba River. It means the suppression of the biotransformation system and the antioxidant defense in liver cells of fish from the Razdol'naya River. These changes in the metabolism of estuarine fish species under the continuous impact of complicated pollution including PTS can lead to pathologic alterations and finally decrease the reproductive potential and survival of organisms.

Molecular biomarkers of oxidative stress were studied in some mollusks: mussels, bloody clams and oysters from different areas of Peter the Great Bay. Data show that according the accumulation of the oxidized products in marine organisms the Bay's areas can be ranked as follows: Golden Horn Bay > Desantnaya bay > Sukhoputnaya bay > Starka strait (Chelomin et al., 2007).

Various types of morphological pathology including tumors were observed in organs of mollusks and flounders from Amursky bay and southern-western part of Peter the Great Bay (Syasina, Durkina, 2008).

The high level of histopathological disturbances was revealed in gonads of sea urchins in the inner part of Amursky bay (Vaschenko, Zshadan, 2003).

Ecotoxicological effects of PTS as a component of complex contamination of Peter the Great Bay have been observed as molecular and organisms and community levels. The most significant negative effect of pollution is a decline in the species diversity and numbers of aquatic organisms. Small species and early development of marine organisms, for example mysids (Crustacea) are the most vulnerable to pollution.

11 mysid species have been observed in Peter the Great bay. The abundance, sex ratio, and age composition, as well as the structure of the mysid community in the Bay is subjected to considerable changes; i.e., it is stressed under the current pollution level (Cherkashin and Veideman, 2005; Lukyanova et al., 2012). The decreasing of species number and changes in population structure of mysids in 1982-2010 have been revealed. They are typically absent in the most environmentally polluted areas. Absence of adult individuals of stenobiotic mysid *Paracanthomysis sp.* suggested unfavorable state of sampling areas in 1988-2000. Evidently, pollutants caused avoidance of impact areas by mysids, but also accelerated the abundance of euriobiotic mysid *Neomysis mirabilis*. Ecotoxicological situation in many areas of the Amursky and Ussuriisky Bays, the Nakhodka Bay, internal bights of the Possyet Bay was estimated as unfavorable in 1982 -2000. In recent years the ecological situation in the Bay has improved, and mysids have appeared again in the areas where they disappeared in previous years (Figure 3-64)

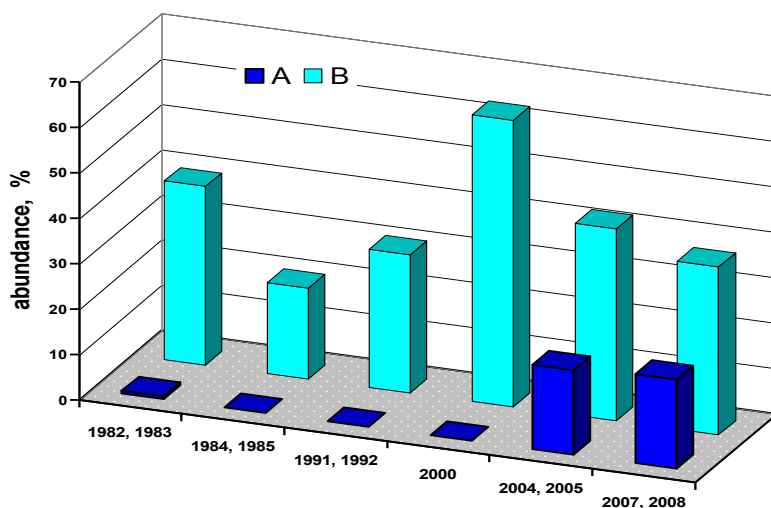


Figure 3-64. Interannual dynamics of abundance of mysids *Paracanthomysis sp.* in polluted (A) and reference (B) sites of Amursky bay (Lukyanova et al., 2012)

Generally, PTS are not dominated contaminants in marine pollution in Russian areas of NOWPAP regions. Biological effects are not specific mainly and are caused by combined interaction of different pollutants in wastewaters discharging to coastal ecosystems.

<China>

At present, a great deal of environmental pollutants pose a threat to our health and harm the ecosystem. The research on environmental risk assessment of PTS has focused on the environmental field. Based on the regional scale, methods of environmental risk assessment of PTS in three marine media (aqueous phase, sediment phase and organism phase) such as PEC/PNEC, Ecological Risk Index and ERI/ERM has been applied (Wang et al, 2011).

Human health risk and ecological risk were assessed in some areas of China. *Philippines clams* were used as the indicator species to assess the health risk of heavy metals around Bohai area (Zhang et al, 2012). Health risk assessment of mercury, chrome, arsenic and lead pollution was made in different areas around Bohai Bay. By using human health risk assessment model, results showed that the health risks of mercury and lead were not posed any threat to human beings. The health risk of arsenic carcinogenic pollutants was at level 3 and can be accepted. While the health risk of chrome carcinogenic pollutants was at level 5 that may be posed threat to human health. But further research should be carried.

A comprehensive study of pesticide levels and bio-accumulation characteristics in human adipose tissues among residents in the three regions of Jiangsu province was reported (Wang et al, 2011). A large number of adipose samples (n=633) were selected for 58 pesticides and were analyzed by high sensitive Gas Chromatography-Tandem Mass Spectrometry (GC-MS/MS). The results showed that POPs pesticides were frequently detected, including 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, α -HCH, β -HCH, γ -HCH, δ -HCH, hexachlorobenzene (HCB), and mirex. Other detected pesticide species were dicofol, methamidophos and chlordimeform, which have rarely been reported. Comparing to different countries, the concentrations of total DDT and HCH in these three Chinese southeastern sites were in the middle range, whereas the HCB and mirex were in the lower end. A significant correlation was observed between region as well as age and POPs pesticide levels. Some pesticide residue levels were also found significantly correlated to occupation. However, there was no significant correlation between gender and pesticides. Meanwhile, it is interesting to find that mortality of malignant tumors tends to associate with the pesticides levels in human adipose tissue. More importantly, the measured data presented in this study provide realistic information which is useful for assessing human exposure to pesticides in the general population of Southeast China.

It is interesting to find that mortality of malignant tumors tends to associate with the pesticides levels in human adipose tissue. The sum of concentration values of all the detected pesticides in human adipose tissue was 4.00 mg kg⁻¹ in Nantong, 2.57 mg kg⁻¹ in Hexian and 1.31 mg kg⁻¹ in Dachang, respectively. Corresponding to the pesticides levels, the incidents of malignant tumors of the three regions also followed the order: Nantong>Hexian>Dachang. More over, the human epidemiological study was the future studying task.

In order to ensure the balance of numbers of farmers and non-farmers, the subjects in Hexian and Dachang of Jiangsu Province were selected as the targets to study the correlation between pesticides levels in the adipose samples and occupation of the donors (Wang et al, 2011). An independent sample *t*-test (confidence interval = 95%) was conducted using SPSS, and the result was listed in Table 3-88. The concentrations of DDT, HCH, HCB, Chlordimeform in human adipose tissue of farmers are significantly higher than those of non-farmers (2-tailed significance at $P < 0.05$). It can be concluded that the potential exposure risks to pesticide applicators or farm workers are greater than to the general population exposed only to the trace levels of pesticides in food and/or water.

In order to ensure the balance of numbers of farmers and non-farmers, the subjects in Hexian and Dachang of Jiangsu Province were selected as the targets to study the correlation between Pesticides levels in the adipose samples and occupation of the donors (Wang, 2011). An independent sample *t*-test (confidence interval = 95%) was conducted using SPSS, and the result was listed in Table 3-88. The concentrations of DDT, HCH, HCB, Chlordimeform in human adipose tissue of farmers are significantly higher than those of non-farmers (2-tailed significance at $P < 0.05$). It can be concluded that the potential exposure risks to pesticide applicators or farm workers are greater than to the general population exposed only to the trace levels of pesticides in food and/or water.

Although the number of donors was too few to obtain a reasonable epidemiological conclusion to correlate the pesticides levels in human adipose tissues to certain health impact, through retrospective study, the death cases among residents in the three regions of Southeast China were investigated and the characteristics and causes of deaths were analyzed. It is found that the mortality of malignant tumors during 2003-2005 in Nantong of Jiangsu Province was 230.77/100000 and standardized mortality was 109.43/100000, which was higher than the result of the Chinese third national retrospective investigation of causes of death (mortality of malignant tumors: 135.88/100000 and standardized mortality: 91.24/100000) (Huang et al., 2010). Nantong city in Jiangsu province was a typical area with high cancer incidence in China (Huang et al., 2010). Meanwhile, a study on the epidemic characteristics and trend for malignant tumor in Jiangsu province by Xue and Zhang (2006) proposed that the mortality of malignant tumors was higher in rural than that in urban area.

Bodies of fish and benthos taken at seven sites were measured to understand the issue of ecological health of Yangtze River at Jiangsu section (Hu, 2009). The highest levels for DDTs, the total 20 PCBs, the total 16 PAHs and HCHs in fish bodies were 0.076 $\mu\text{g}/\text{kg}$, 23.1 $\mu\text{g}/\text{kg}$, 7.44 ng/kg and 0.028 $\mu\text{g}/\text{kg}$, respectively, and those in benthos bodies were 0.082 $\mu\text{g}/\text{kg}$, 14.3 $\mu\text{g}/\text{kg}$, 21.1 ng/kg and 0.026 $\mu\text{g}/\text{kg}$, respectively. The PAHs concentrations in benthos were higher than those in fish, and they had a significant positive correlation ($P < 0.05$). Among the detectable chemicals, DDTs were 100% of *p,p'*-DDE isomers, the main PCBs were tetra- and penta-chlorinated biphenyls in which PCB 105 had the highest detection frequency and the main PAHs were the compounds of 2-4 rings. PCBs were accumulated in fish bodies which enrichment factors were as high as 508-42,414 folds occurred at sampling sites. The results

demonstrated that the accumulation measurements can be used to test the affects of PAHs, DDTs, PCBs and HCHs on aquatic ecological health.

Tab. 3-88 Comparison of detected pesticide levels in different occupation groups in Dachang and Hexian.

Pesticide Species	Mean value (ng g ⁻¹)		t-test for equality for means Sig (2-tailed)
	Farmer (n=155)	Non-farmer (n=145)	
2,4'-DDD	0.631	0.883	0.702
2,4'-DDE	4.41	4.99	0.636
2,4'-DDT	6.43	8.99	0.543
4,4'-DDD	12.7	10.1	0.153
4,4'-DDD	1967	1174	0.002
4,4'-DDD	47.1	46.1	0.886
Total DDT	2038	1245	0.002
α-HCH	3.50	2.68	0.183
β-HCH	419	309	0.043
γ-HCH	0.543	0.251	0.266
Total HCH	423	312	0.041
HCB	42.7	27.4	0.000
Mirex	1.86	2.26	0.279
Dicfol	7.00	9.89	0.659
Chlordime	6.41	3.87	0.001

<Korea>

Trace (sub-ppb) levels of TBT in seawater can cause reduced growth and viability of various larvae, oyster shell anomalies and spat fall failure, and the induction of imposex phenomenon in gastropods. As a consequence, the serious ecotoxicological impacts of TBT on target and non-target marine organisms led to legal restrictions in most developed countries during the 1980s and early 1990s. The International Maritime Organization (IMO) adopted the International Convention on the Control of Harmful Antifouling Systems on Ships that the application of TBT based paint was completely banned in 2003 and the presence of those paints on vessel's hulls were banned in 2008. In Korea, restrictions on the use of TBT-based antifouling paints were introduced in 2000 for small boats, and their use was totally banned in 2003, and their residues in ships were banned in 2008. As a result, BT contamination in coastal waters is expected to decrease gradually, and the affected marine animal populations are expected to recover in the near future.

Imposex has been widely adapted for monitoring TBT contamination and assessing the effectiveness of TBT control measures in many coastal environments. Imposex monitoring is important to establish geographical distribution and temporal trends based on bioavailability of TBT in the marine environment, providing time-integrated information on those portions of the total ambient load that are of direct ecotoxicological relevance. *Thais clavigera* is a neogastropod widely distributed along the coasts of western Pacific, and has been widely used as a biomonitor of TBT pollution in Asia Pacific. However, a few data have been reported on imposex in the coastal environment since 2003 and 2008 when the prohibition on the use and presence of TBT based paints on vessel's hulls was implemented (Figure 3-65). Moreover, no

data are available on recovery of imposex from BT contamination in Korean coastal waters, although there are a few reports on decreases of BT levels in seawater and bivalves from Korean coastal waters (Choi et al., 2010b; 2011b).

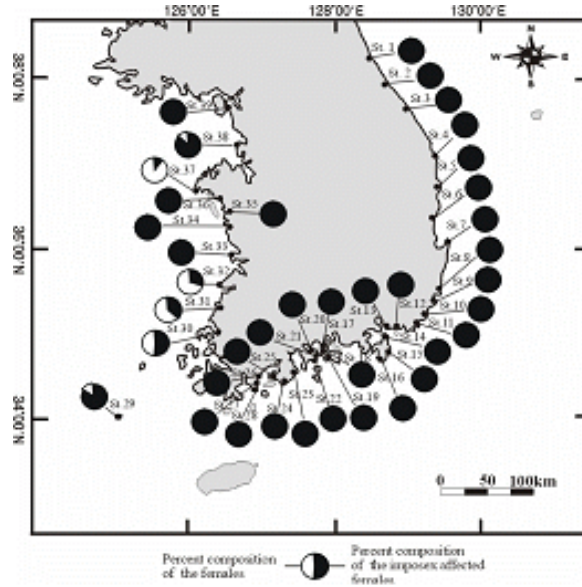


Figure 3-65. Example of imposex survey for gastropods (*Thais clavigera*) collected from Korean coastal waters performed in 2003 (Choi et al., 2013).

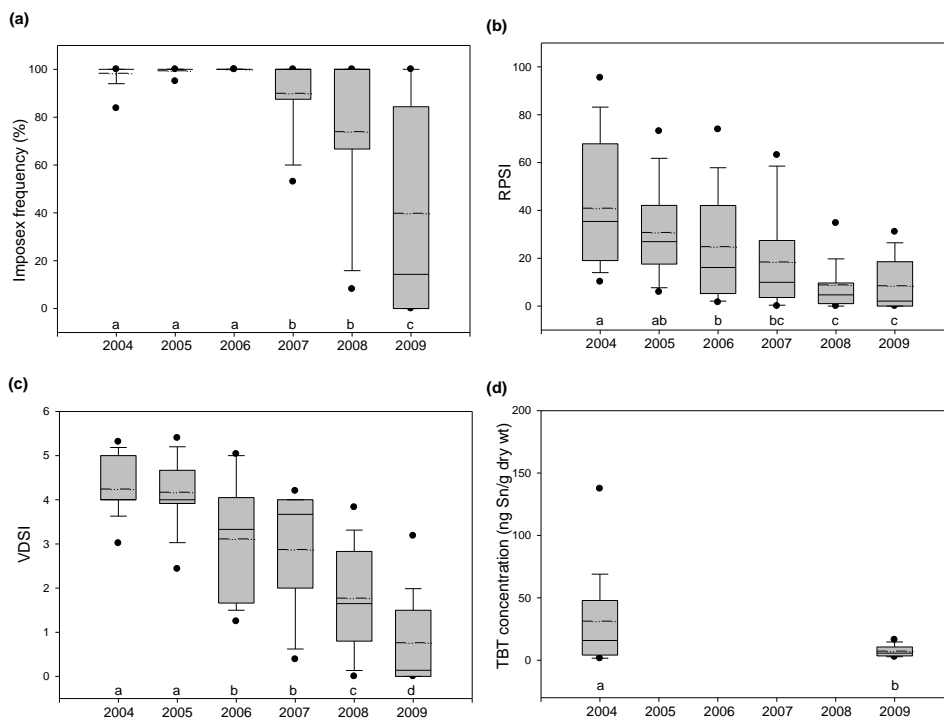


Figure 3-66. Temporal trends of (a) imposex frequency, (b) Relative Penis Size Index (RPSI), (c) Vas Deference Sequence Index (VDSI), and (d) gastropod (*Thais clavigera*)

Temporal trends of imposex frequency, RPLI, VDSI, and TBT levels between 2004 and 2009 are shown in Figure 3-66. All the imposex indices decreased over sampling year and their significant differences in imposex and related indices among sampling year were also found ($p < 0.0001$). This indicates that imposex of *T. clavigera* in Korean coastal waters decreases over time. The mean imposex frequency showed higher values than 95% during 2004–2006, and started to be significantly decreased from 2007. Similar to imposex status, of the RPLI and VDSI were significantly decreased from 2006.

Significant declines of imposex status, based on RPLI and VDSI were observed at sites near large ports, small ports and non-port areas (Figure 3-67). Despite the overall decreasing trend of imposex levels in *T. clavigera* along the Korean coast, all imposex indices including VDSI were still higher in large ports than in small ports and background areas. At sites near background areas, all imposex indices had decreased to zero which can be completely recovery from imposex. Based on these results, improvement and recovery from TBT contamination will occurs in areas with very low marine activities earlier than with high marine activities.

Imposex indices such as VDSI, RPSI, and other imposex indices are not equally sensitive to seasonal changes in the environment. Monthly sampling of *T. clavigera* in Hong Kong showed that VDSI slightly changed among sampled months, but RPSI dramatically varied among sampled months. The high VDSI in the Korean coast indicates that Korea may be categorized in a high BT contamination area worldwide. The tissue levels of TBT in gastropods significantly ($p < 0.001$) decreased from 2004 to 2009, similar to temporal trends of TBT levels in seawater and mussels along the Korean coast. It suggests that the ban restricting the use of TBT in Korea continues to be significantly effective in Korea.

Choi et al. (2013b) reported that the concentrations of BTs in finless porpoises (*Neophocaena asiaorientalis*) caught off the Korean coast in 2003 and 2010. The concentrations of BTs ranged from 65.1 to 1432 (average: 370) ng/g wet weight, within the ranges reported by previous studies. The threshold value of BTs that causes adverse health effects in marine mammals is unknown. Nakata et al. (2002) suggested that 100 ng/g of DBT plus TBT was cytotoxic level based on in vitro experiments using peripheral blood isolated from Dall's porpoise lymphocytes. In this study, all the finless porpoises collected in 2003 (n=33) and 37 of the 49 samples collected in 2010 had levels higher than the cytotoxic level, implying that the porpoises may have experienced potential adverse health effects due to BT exposure.

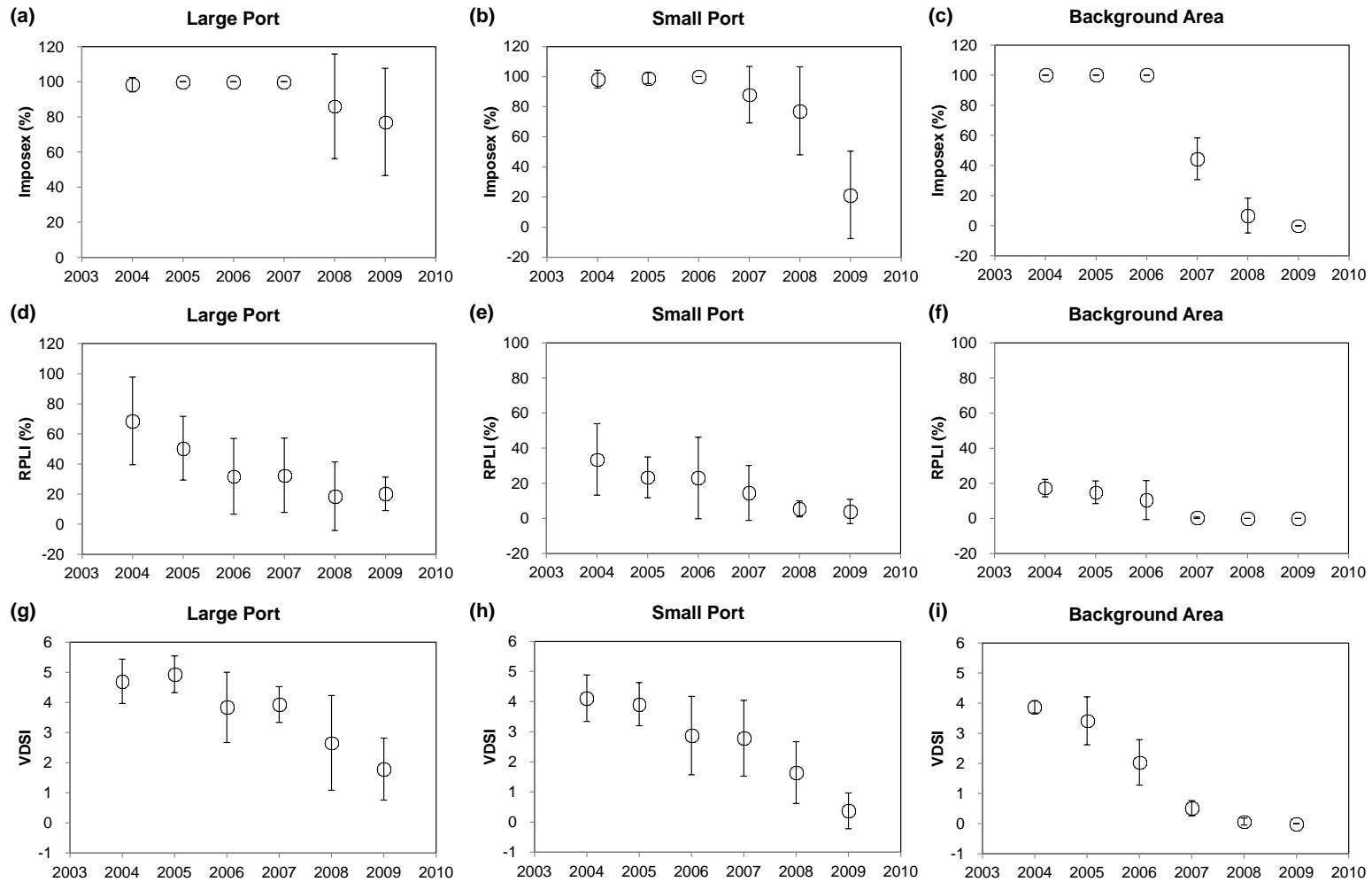


Figure 3-67. Temporal trends of imposex, RPLI and VDSI in large ports, small ports, background area from the Korean coasts. Circles indicate means and bars indicate standard deviations for sampling years.

Several studies have reported that high burdens of POPs in marine mammals result in reproductive impairments and declining populations of species. Only a few studies have suggested that the levels of NOAEL (no observed adverse effect level) and LOAEL (lowest observed adverse effect level) of immunomodulation by dioxin-like contaminants in harbor seals are estimated to be 62 pg TEQ/g lipid wt and 209 pg TEQ/g lipid wt, respectively (Ross et al., 1995; De Swart et al., 1996). In Korea cetaceans, 37% of 27 blubber samples from minke whales exceeded the NOAEL but did not exceed the LOAEL. Almost all blubber samples from common dolphins exceeded the NOAEL (20 of total 22 samples) and LOAEL (19 of total 22 samples), implying an adverse health effect on this species. Kannan et al. (2000) reported a threshold value for TEQs in aquatic mammals to be 520 pg/g lipid weight. The TEQ concentrations in livers and blubbers of cetaceans analyzed were below the suggested threshold values, but within a factor of 2. All blubber samples of finless porpoises did not exceed the NOAEL, LOAEL and a threshold value suggested from other studies.

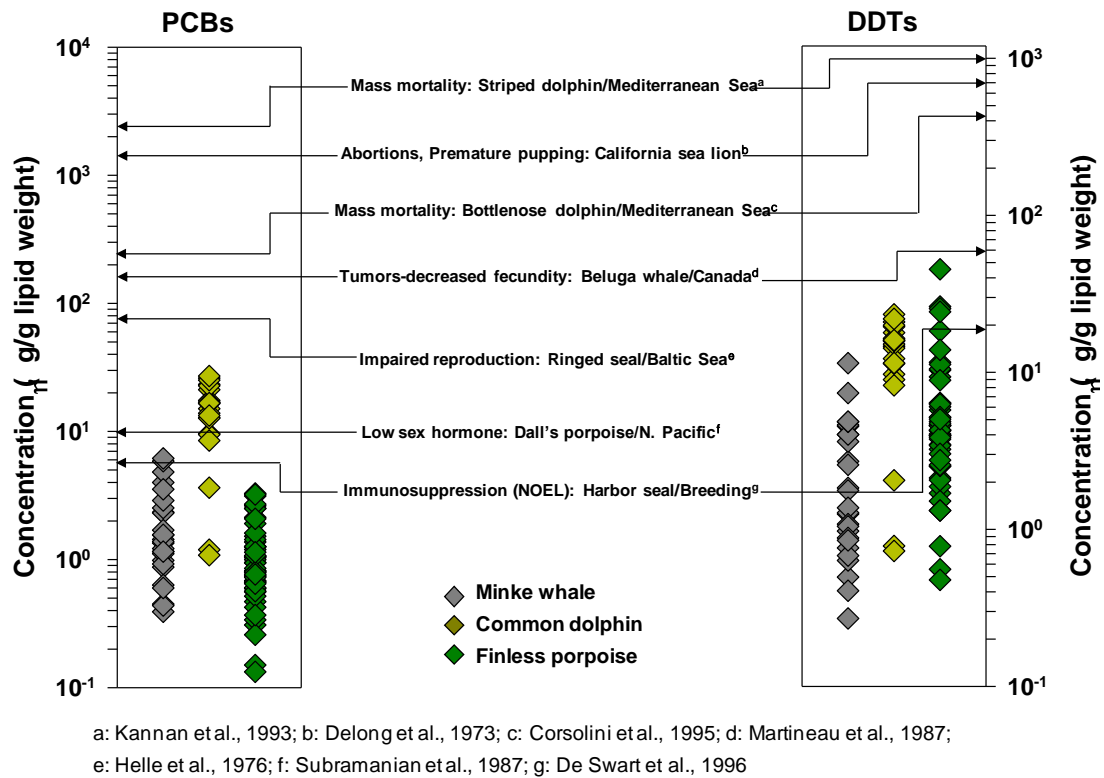


Figure 3-68. Ecotoxicological implications of the concentrations of PCBs and DDTs in blubbers of cetaceans (minke whales, common dolphins and finless porpoises) collected from Korean coastal waters (Moon et al., 2010a; Park et al., 2010).

Many studies have focused on the levels of PCBs and DDTs in marine mammals, which cause adverse health effects including immunosuppression, tumors, decreased

fecundity, mass mortality, abortions and premature parturition (DeLong et al., 1973; Helle et al., 1976; Martineau et al., 1987; Kannan et al., 1993; Corsolini et al., 1995; De Swart et al., 1996; Kannan et al., 2000). In Korean cetaceans, the levels of PCBs and DDTs in finless porpoise tissues did not exceed the threshold values of PCBs and DDTs proposed to cause various toxic effects in other studies (Figure 15). Of 52 finless porpoise samples, 27% exceeded the NOAEL (no observed adverse effect level) of immunosuppression by DDTs of harbor seals (De Swart et al., 1996), implying adverse health effects on this species. Of 22 blubber samples from common dolphins, 86% exceeded the NOAEL for PCBs and 14% exceeded the level for DDTs (20 µg/g lipid wt), implying potential adverse health effects by PCBs and DDTs on this species. Kannan et al. (1993) reported a threshold value for PCBs in cetaceans at 8.7 µg/g lipid wt in blubber. For common dolphins, 80% of 22 blubber samples exceeded a threshold value for PCBs. However, no cetacean samples exceeded the toxic levels proposed in other studies. Although the present levels of PCBs and DDTs are mostly below the levels that cause adverse health effects in other marine mammals, no long-term trend studies on POPs in cetaceans from Korea are available. Therefore, continuous monitoring and ecotoxicological studies are required to understand the contamination status of POPs and emerging contaminants in marine ecosystems and to accurately evaluate the potential

<Japan>

1. General description of ecotoxicological assessment of chemicals in Japan

Ecotoxicological risks of existing chemicals has been being assessed by the combination of PEC and PNEC against aquatic organisms as part of the Initial Environmental Risk Assessment program. In this program, target chemicals to be assessed is nominated every year from chemical management divisions in the Ministry of the Environment. After development of their environmental analytical procedures, initial environmental survey of the proposed chemicals is conducted as part of Chemicals in the Environment program. Ecotoxicological risks are assessed based on the ratio (MOE; margin of exposure), i.e., predicted non effect concentrations (PNEC) based on literature / other test data divided by the predicted environmental concentrations (PEC) estimated from environmental survey data (toxicological risks to human beings are also assessed similarly and simultaneously, but will not refer in the following description). If the MOE is equal or less than 10, the chemical is considered to have potential risks to aquatic organisms and should be assessed further by accumulating more information on the ecotoxicity as well as the exposure levels. Among these chemicals, those having both strong exotoxicity (NOEC is equal or less than 0.1 mg/L) and potential of elevated exposure (either of the followings; detection in several sites in environmental survey, annual production and/or import of more than 100 tons, or more than 10 tons in the case of Class 1 carcinogenic chemicals or agrochemicals (to be sprayed in the open field) or chemicals having ozone layer destruction potential) are designated as Class 1 Specified Chemicals under the Law for PRTR (Pollutant Release and Transfer Register). Together with those having toxicological risks against human beings, so far 462 chemicals have been designated as Class 1 Specified Chemicals under the Law and controlled. On the other hand, 1,231

chemical substances have been analyzed in the environment, and 688 substances have been detected in either of the environmental media from 1974 until present.

Ecotoxicological assessments as well as toxicological assessment (to human beings) of new chemicals for production / import / usage are conducted under Chemical Substances Control Law, and chemicals shown or suspected of their risks are specified and controlled according to their levels of risks, i.e., presence or absence of persistence, bioaccumulative property and ecotoxicity, respectively. The chemicals recognized to have all the three properties are classified as Class I Specified Chemical Substances and are eliminated or strictly restricted their production / import / usage under the CSCL. Persistent and toxic, but not highly bioaccumulative chemical substances are classified as Class II Specified Chemical Substances and administrative action is done to reduce their environmental release. Currently 28 and 23 chemicals are listed as Class I and Class II Chemical Substances, respectively. Those having persistence and suspected toxicity/ecotoxicity are classified as Priority Assessment Chemical Substances (currently 163 substances) and their environmental levels are analyzed by Detailed Environmental Survey in the Chemicals in the Environment Program in order to assess their potential risks against aquatic organisms (as well as human beings). Chemicals with persistence and highly bioaccumulative properties but insufficient information on toxicity / ecotoxicity are classified as (Type I) Monitored Chemical Substances, and their amount of production / import / uses are monitored.

2. Ecotoxicological assessment of dioxins by the Ministry of the Environment, Japan

Among PTS chemicals, dioxins and other POPs levels in wildlife were monitored extensively during a decade from 1998 until 2007 (MOE Japan (2007)). 1,428 specimens in 18 species in Dioxin survey, and 258 specimens in 5 species in Endocrine Disruptive Chemicals Survey are investigated of their dioxin levels. Isomers with TEFs, i.e., 7 PCDDs, 10 PCDFs and 12cdl-PCBs, were analyzed. The list of species and their dioxin levels are compiled in the Table 3-89. Highest levels of dioxins were found in livers of great cormorant and raptors (41,000 and 38,000 pg TEQ/g fat, respectively) followed by their muscles (raptors include Hodgson's hawk eagle, goshawk, peregrine falcon and owls). Contribution from dl-PCBs were more than half in marine mammals and birds eating marine fishes, while they were comparable to PCDDs and PCDFs in terrestrial mammals and amphibians (Table 3-90). There are general tendencies of increasing dioxins levels in accordance with the age of males. On the other hand, statistically significantly lower levels of dioxins was observed in adult females than adult males in finless porpoises, large Japanese field mice and great cormorants. This is considered to be due to elimination of dioxins through birth, lactation and egg-laying in the case of females. Two examples are shown in Figures 3-69 and 3-70, respectively. In the case of finless porpoise, dioxin levels in adult female is even lower than immature ones. On the other hand, adult female is higher than immature cormorants. Statistically significantly higher levels of dioxins were observed in black kites caught in coastal areas than those in inland areas. Also dioxin levels in muscle of jungle crows in urban areas were significantly higher than those in rural areas. Among the tendency of hepatic sequestration (higher levels of dioxins in liver than in whole organism) observed in all the wildlife, marked tendency was observed in large Japanese field mice and racoon dogs (100 and 17 times, respectively).

Table 3-89 Concentrations of dioxins in Japanese wildlife (pg TEQ/g fat)

Taxon	Species	Specimen	N	Average	Standard deviation	Median	Range
Reference	Japanese People	Blood	1,656	20	14	16	0.64 - 120
Fish	Carp	Muscle	48	160	110	130	27 - 630
Amphibians	Frogs	Whole body	101	310	190	250	43 - 950
Birds	Feral pigeon	Mixed (incl. liver)	15	50	50	18	9.0 - 150
	Jungle crow	Muscle	33	21	13	18	4.2 - 66
		Liver	66	79	67	58	6.0 - 360
	Black kite	Adipose tissue	17	540	520	330	41 - 1,600
		Muscle	98	670	1,500	300	31 - 14,000
		Liver	57	760	1,300	420	74 - 9,200
		Mixed (adipose tissue, muscle)	20	560	520	380	78 - 2,300
	Raptors ¹⁾ (excluding black kite)	Muscle	33	3,500	5,300	1,400	130 - 27,000
		Liver	18	3,800	9,000	790	86 - 38,000
		Mixed (adipose tissue, muscle)	4	270	180	250	81 - 510
		Egg	11	2,300	2,100	1,400	230 - 8,100
	Great cormorant	Adipose tissue	6	3,600	3,300	3,000	180 - 8,400
		Muscle	194	2,300	2,900	1,500	23 - 24,000
		Liver	128	2,900	4,300	1,800	39 - 41,000
Egg		90	2,900	1,600	2,600	850 - 12,000	
Terrestrial mammals	Large Japanese field mouse	Body ³⁾	167	61	56	44	3.6 - 490
		Liver	66	2,700	2,800	1,900	110 - 16,000
		Mixed (body, liver)	37	880	720	720	41-2,700
	Japanese monkey	Adipose tissue	16	40	47	19	5.6 - 170
		Muscle	4	54	84	18	0.85 - 180
		Mixed (adipose tissue, muscle)	10	12	13	5.7	1.2 - 43
	Raccoon dog	Mixed (incl. liver)	10	19	22	5.7	1.4 - 56
		Adipose tissue	71	56	87	22	9.8 - 450
		Muscle	10	230	260	97	20 - 650
	Bears	Liver	24	290	160	280	56 - 810
		Mixed (incl. liver)	6	32	27	25	14 - 87
		Adipose tissue	10	0.51	0.61	0.30	0.21 - 2.2
	Sika deer	Mixed (adipose tissue, liver)	6	0.62	0.61	0.35	0.26 - 1.8
		Kidney; Mixed (kidney, adipose tissue)	48	27	46	14	3.1 - 310
	Wild boar	Liver; Mixed (liver, adipose tissue)	30	44	40	34	7.3 - 200
		Muscle	7	6.3	7.3	3.4	2.9 - 23
	Marine mammals	Seals	Adipose tissue	26	11	4.3	11
Finless porpoise		Blubber ⁴⁾	90	56	46	41	7.7 - 280
		Muscle	23	40	31	32	5.1 - 110
Stejneger's beaked whale		Blubber	37	95	48	83	10 - 200
		Muscle	19	110	88	60	38 - 380
Other whales ²⁾		Blubber	16	64	45	59	3.7 - 150

1) Including Hodgson's hawk eagle, goshawk, peregrine falcon and owls.

2) Including dolphins and baleen whales.

3) For this survey, we use the word "body" to refer to large Japanese field mouse specimens after skinning and removal of internal organs, head, tail, and extremities.

4) Blubber is a fat-storing dermal tissue unique to cetaceans.

Table 3-90 Dioxin levels and *dl*-PCB ratios in Japanese wildlife (unit: pg TEQ/g fat)

		Fish	Amphibians	Birds	Terrestrial mammals	Marine mammals
Number of individuals surveyed		48	101	387	287	171
Dioxin concentrations (pgTEQ/g fat)	Average	160	310	1,700	60	62
	Standard deviation	110	190	2,900	85	68
	Median	130	250	640	35	45
	Range	27 - 630	43 - 950	4.2 - 27,000	0.21 - 650	3.7 - 680
Co-PCBs ratio in the concentration (%)	Average	54	34	63	34	84
	Standard deviation	8.5	9.4	21	21	10
	Median	54	34	70	36	85
	Range	28 - 74	9.5 - 53	7.0 - 95	3.7 - 95	6.9 - 99

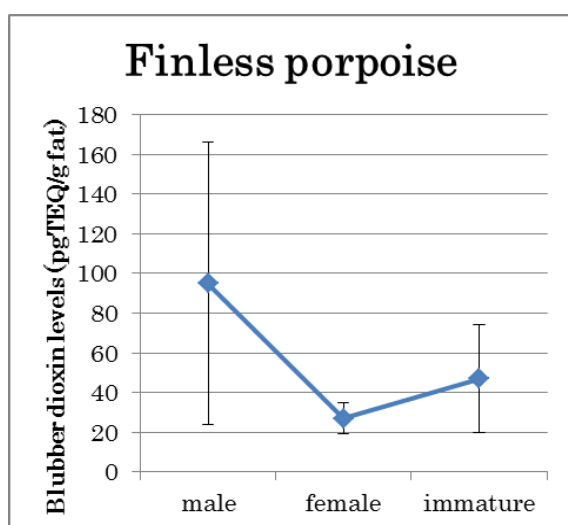


Figure 3-69 Dioxin levels in finless porpoise

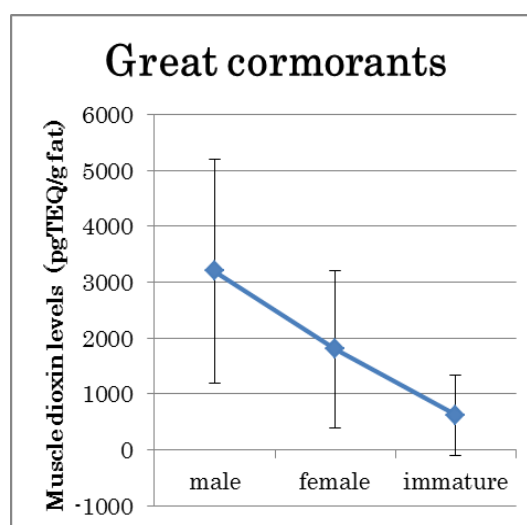


Figure 3-70 Dioxin levels in great cormorants

Histopathological examination revealed abnormalities in thyroid gland and gonadal tissues of some individuals, but a correlation between these abnormalities and dioxin concentrations was not found. In great cormorants and jungle crows, a statistically significant positive correlation was found between liver dioxin concentrations and drug-metabolizing enzyme activity (Figure 3-71), suggesting that dioxins were inducing drug-metabolizing enzyme activity. Measurement of thyroid hormone concentrations in peripheral blood also revealed a statistically significant negative correlation with dioxin accumulation levels in great cormorants and other species (Figure 3-72).

The amount of dioxins being released into the environment is declining in response to measures to curb dioxin emissions, and dioxin concentrations in the air, water and other media are declining as a result (see the results in Section 3.4). However, there are environmental media such as bottom sediments in which declining of dioxin concentrations are not clear, and similarly no clear declining trend of dioxin concentrations in the wildlife was observed (Figure 3-73). These trends generally reflect residence time of dioxins in each environmental media as well as multimedia movement of dioxins in the environment.

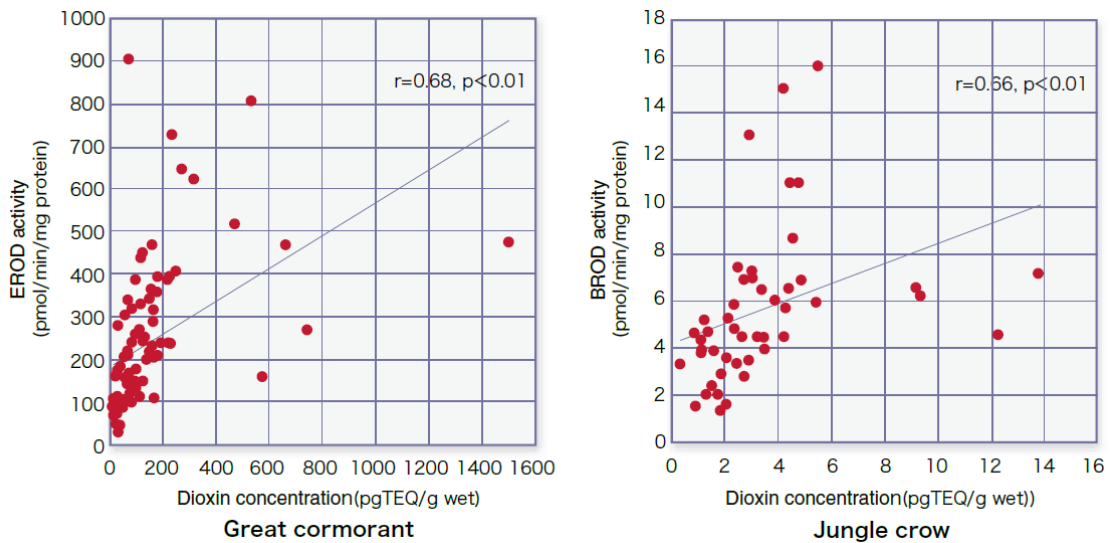


Figure 3-71 Dioxin levels and drug-metabolizing enzyme activities
 EROD: Ethoxyresorufin-O-deethylase (P450 1A activity)

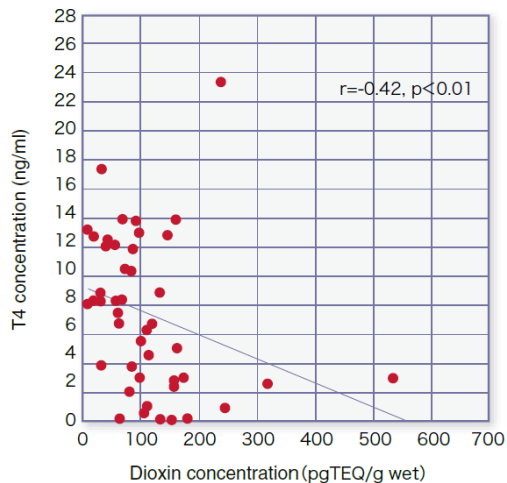


Figure 3-72 Negative correlation between dioxin concentrations in livers and thyroid hormone (T4) levels in periferal blood in great cormorants

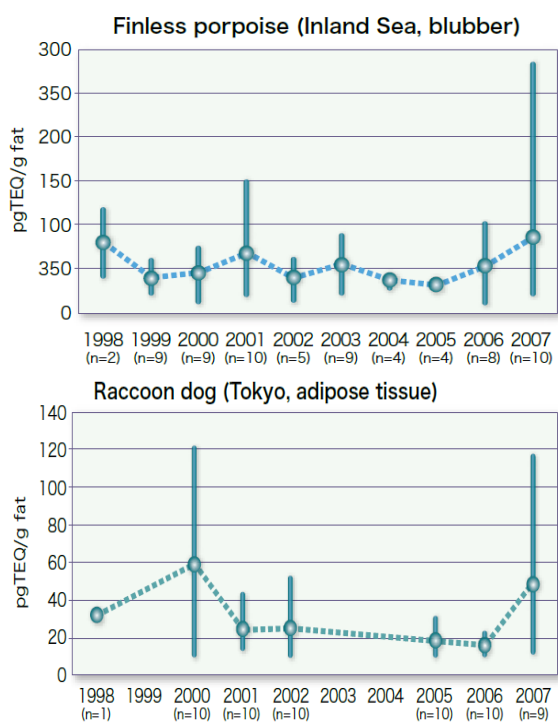


Figure 3-73 Temporal trends of dioxin levels in a marine wildlife, finless porpoise (blubber), and a terrestrial wildlife, raccoon dogs (adipose tissue)

The dioxin concentrations found in the bodies of Japanese wildlife were not sufficiently high to provoke concern regarding the kind of serious impacts witnessed in some overseas cases. However, among higher order predators within the ecosystem, individuals with high concentrations have been found, and some eggs of great cormorants and large raptors in particular showed high enough concentrations to raise concern over abnormalities. It has been suggested that adult female mammals and birds are likely to have lower dioxin concentrations than males owing to elimination of dioxins through birth, lactation and egg-laying, and the findings of this survey also showed such a tendency in some species. Findings also revealed differences in concentrations within the same individual according to organs and tissues, with liver in particular showing high accumulation in certain species. No decline was observed in dioxin concentrations in the bodies of wildlife in the same location over time.

Detailed analysis of the survey results will require the controlled setting of conditions such as age, sex, location in which specimens are collected, type of organ or tissue, year collected and so forth, and the collection of a sufficient number of individuals. Furthermore, considerations are required for the fact that the concentration of dioxins in wildlife is a result of accumulation for several years, and for the movements of animals. This survey did not gather enough specimens to enable this kind of precise investigation, but it did collect important data in an aspect of Japan's nature that had not been sufficiently investigated, shedding enough light on the dioxin concentrations in Japanese wildlife to enable comparison with overseas cases, and showing the differences that exist between different species in dioxin concentrations and types.

Histopathological investigation of impacts revealed changes likely to have been caused by dioxins in some specimens, but since no causal relationship with concentrations was found, the impacts of dioxin accumulation was unclear. However, evidence of impacts was found in certain physiological functions such as drug-metabolizing enzyme activity and thyroid hormone concentrations. It is not known at the present time whether such evidence will lead to concrete toxic impacts, but this evidence indicates that further investigation is required. Impacts on immune functions and the central nervous system have been reported as effects of dioxin on wildlife, but methods of investigating such impacts in wildlife have yet to be established, and this survey was unable to investigate them. Concerning impacts on reproduction, it was not possible during this survey to conduct investigation of the relationship between dioxin concentrations in eggs and hatching ratios, and such areas need to be investigated in future.

This survey yielded important knowledge regarding the state of exposure of wildlife to dioxins, accumulation kinetics within the body, and changes over time. No declining trend in concentrations within the body indicates the need for examination of the effects of restriction of dioxin emissions through further investigation of specific species, age groups, sex, location, and types of organ or tissue. Elucidating the impacts of chemical substances on wildlife also requires systematic observation not only of exposure, but also of such factors as changes in wildlife numbers and presence of abnormalities in individuals. The accurate assessment of the risks to wildlife posed by chemical substances calls for integrated, systematic, long-term investigation, together with a consideration of coexistence with human beings.

3. Endocrine disruptive effects of chemicals (EDCs) investigated by the Ministry of the Environment, Japan (MOE (2010))

Among health effects of chemicals to human beings and wildlife, endocrine disruptive effects of chemicals, particularly their potential to affect off-springs in a trans-generation manner, attracted attention in recent decades in Japan as well as in other countries. Environment Agency published “The Environment Agency's Basic Policy on Environmental Endocrine Disruptors – Strategic Programs on Environmental Endocrine Disruptors: SPEED'98 –” in May 1998 (revised in November 2000), and promoted activities including studies on chemical effects on endocrine systems, environmental surveys and monitoring of chemicals, as well as test development and implementation through the Millennium Project. This resulted in the identification of chemicals having potential endocrine disrupting effects on fish (Medaka). Following this result, the Ministry of the Environment (re-organized from Environment Agency in 2000) published “MOE's Perspectives on Endocrine Disrupting Effects of Substances – ExTEND2005 –” in March 2005, and promoted activities such as observation of wildlife, fundamental studies, assessment of chemical substances, information sharing and risk communication. Under this framework, fundamental studies on endocrine disrupting effects were conducted, and development of test methods using animals including fish was promoted under international cooperation. In accordance with the international activities such as EU and OECD towards the 5-year termination of ExTEND2005 in March 2010, the MOE has reviewed its actions through the “Task

Force on Endocrine Disrupting Effects of Substances” and its four sub-committees under the framework of ExTEND2005 since November 2009, while considering principles for its future activities and identifying major issues to be addressed. The MOE’s further actions to endocrine disrupting effects of chemical substances have been summarized as ExTEND2010 (Figure 3-74).

Under SPEED'98, surveys of the effects of EDCs on wildlife were conducted. Abnormal sexual organ development with formation of male-type sex organs in females was widely observed in a kind of marine snail, the rock shell (*Thais clavigera*), over wide coastal areas of Japan. This effect was related to organotin compounds such as tributyltin and triphenyltin in the marine environment. Also a series of chemicals were selected as candidates of EDCs based on literature survey, and were tested their potential to disrupt hormonal activity. Among 36 test chemicals, it was strongly suggested that 4-nonylphenol (branched form) and 4-t-octylphenol have strong endocrine disrupting effects on Medaka at the concentrations determined considering those found in the environment. It was also suggested that bisphenol A and o,p'-DDT also have endocrine disrupting effects on Medaka. Followed to this activity, fundamental studies and research for biological observation of wildlife were conducted under ExTEND2005. Major outcome of the studies is summarized as follows:

- As several factors other than systemic insecticides might simultaneously affect the decreasing number of *Sympetrum* dragonflies, the same spots of numerous rice paddy fields were monitored. In addition to the potential effects of systemic insecticides, research results suggested the impact from the drying up procedure of rice fields one to two months after rice planting.

- As a plausible factor affecting the declining freshwater algae *Charales*, it was considered that a low level of pentachlorophenol (PCP) pesticide might cause growth inhibition of the algae by photosynthesis inhibition. It was recognized that improvement of the environment and the withdrawal of PCP have contributed to the recovery of *Charales*.

- It was revealed that male juveniles appeared when *Daphnia* (only females can appear normally via parthenogenetic development) were exposed to juvenile hormone-like compounds including insect growth regulators. Gene clusters that showed changes accompanying the phenomena were also identified.

- In experiments to study the effects of nonylphenol on crustaceans (mysid), it was observed that slightly higher concentrations of nonylphenol than ambient concentrations could cause growth inhibition by retardation of mysid moulting.

- Nonylphenol, octylphenol, and bisphenol A have already been suggested to have potential endocrine disrupting effects on fish (Medaka). In experiments to study the effects of those chemicals on Ascidiacea, none of them inhibited embryogenesis of *Ciona intestinalis*.

- It was discovered that about 1% of wild Medaka (including species in China and the Republic of Korea) were individuals (sex-reversed individuals) showing a phenotypic sex different from genotypic sex. It was also revealed that the emergence of sex-reversed individuals could be attributed to genetic mutation.

· It was revealed that juvenile male Medaka are highly sensitive to female hormone-like compounds. The mechanism to generate ova in genotypic male was also clarified.

· It was shown that estrogen receptor α from 9 fish species (Medaka, zebrafish, fathead minnow, stickleback, roach, carp, goldfish, bluegill, and guppy) has an almost identical response to estrogen (estradiol), but has interspecies difference toward DDT-related compounds, which were unused pesticides. Low sensitivity of carp and goldfish was also clarified.

Bilateral cooperative studies on EDCs between Japan and UK, US and Republic of Korea have been conducted to support these research activities.

In ExTEND2010, further research promotion on EDCs is planned as shown in the Figure 3-75. In short the following activities will be conducted under the program.

- 1) Promotion of research for biological observation of wildlife and fundamental studies
 - * Research for biological observations of wildlife
 - * Fundamental researches
 - : comprehension of chemical mechanism by individual- or population-level approach
 - : cells or molecular level approach
 - : fundamental studies conducive to test method development
- 2) Development of test methods and establishment of assessment framework
 - : test method development
 - : establishment of assessment framework
 - : human health effects assessment
- 3) Study on environmental concentrations and exposure assessment
- 4) Implementation of actions and effects assessment
 - : selection of chemical substances to be considered
 - : assessment of effects based on literature information
 - : test implementation and hazard assessment
 - : human health effects assessment
- 5) Risk assessment and risk management
 - : risk assessment
 - : risk management
- 6) Promotion of information sharing
 - : information sharing via websites
 - : hosting opportunities including research presentations
 - : others
- 7) Promotion of international cooperation
 - : consideration in the OECD
 - : Japan-UK joint research
 - : Japan-US partnership
 - : cooperation in regions including Asia

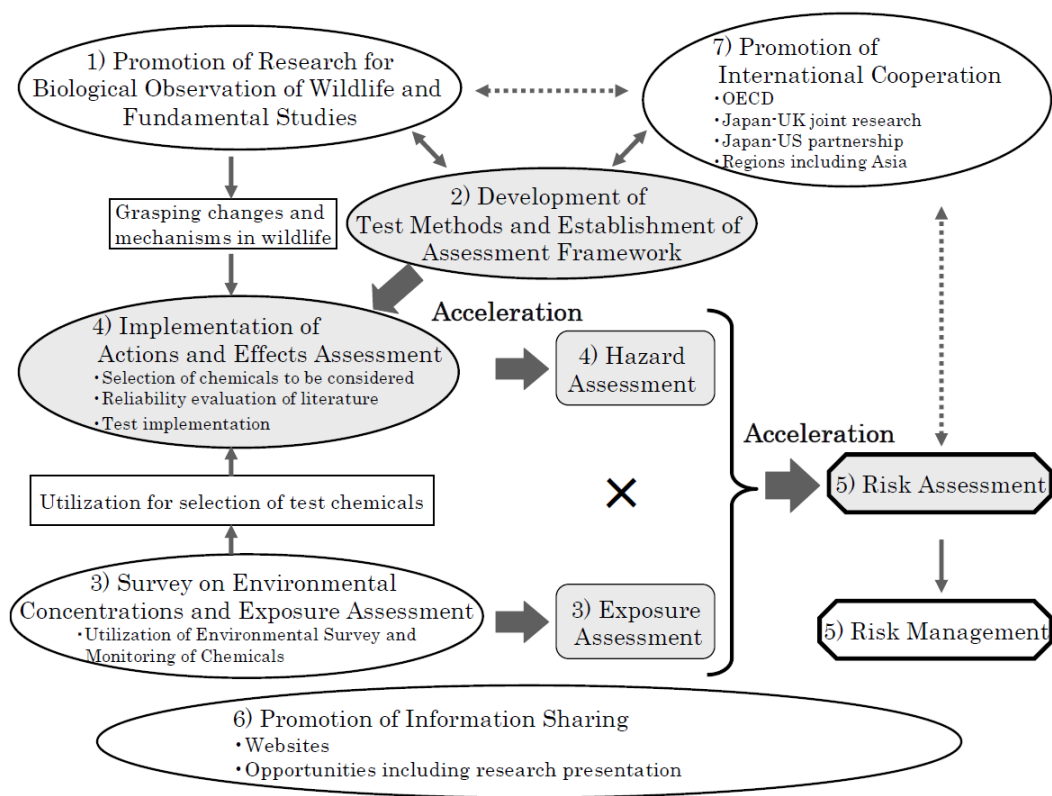


Figure 3-74 Outline of ExTEND 2010 (MOE (2010))

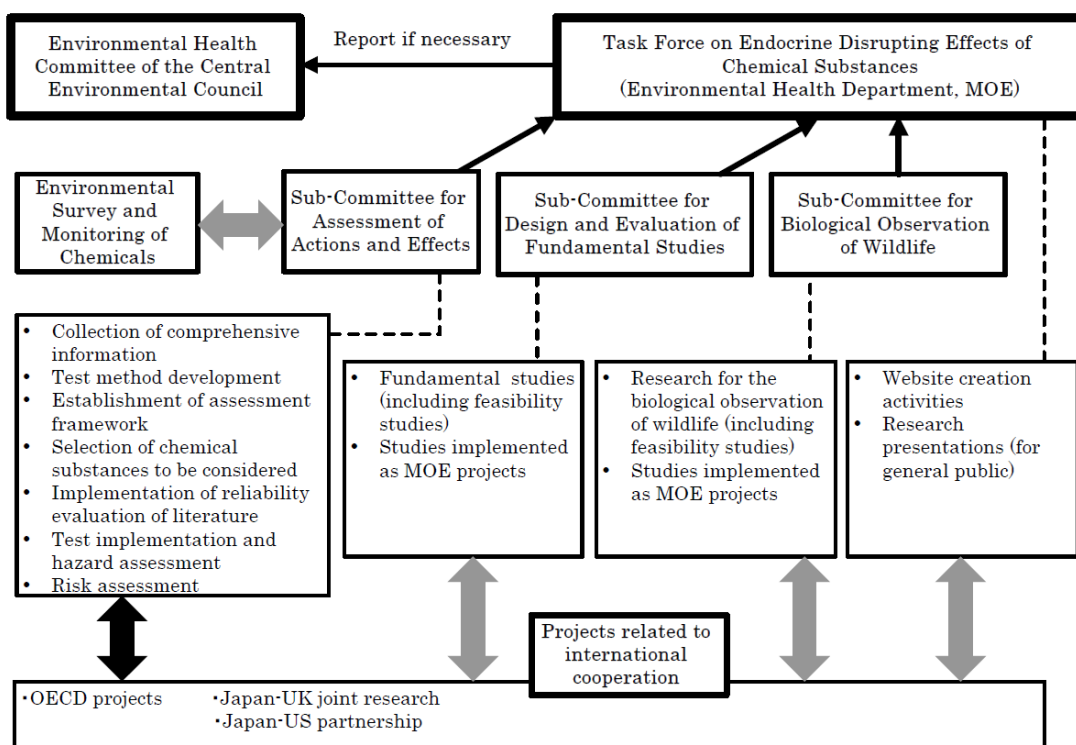


Figure 3-75 ExTEND 2010 framework to promote research and studies (MOE (2010))

4. EDCs and other related researches in Japan

Effects of organotins, antifouling reagent, to gastropod molluscs have been large environmental issues and research topics in Japan for around three decades from 1970's to 2000's, though production, import and use of these chemicals for ships and fishing nets were strictly regulated by legislation and government administrative guidance since 1990. In Japan, 39 gastropod species, including 7 mesogastropods and 32 neogastropods, were reported to be affected by organotins and showed characteristic imposex symptom (Horiguchi et al. (1997)). Rock shells, *Thais clavigera*, and a dogwhelk, *Nucella lapillus*, were among the most investigated snails in coastal region of Japan. The severity of imposex is represented by the relative length of penis induced on female gastropods compared with that on male, a so-called RPL (relative penis length) index = $[\text{average length}]_{\text{female}} / [\text{average length}]_{\text{male}} \times 100$. Based on extensive coastal field survey around all over Japan, Horiguchi reported that affected female *T. Clavigera* were detected in almost all sites except one point in a remote island, Sado, and that particularly severe effects, i.e., RPL = nearly 100, were observed around marinas and dockyards in early 1990's (Horiguchi (1994)). The authors also reported follow-up studies on the effects of organotins to *T. Clavigera* (Horiguchi et al, (2000)). During the survey between 1990 and 1996, all the females were healthy (without penis) in only 3 locations among 97 survey sites. During the survey between 1996 and 1999, all the females were found to be healthy at 6 locations among 93 survey sites. RPL index at severely polluted areas did not show clear improvements during the decade. The authors also showed a good correlation between TBT levels within the body and the RPL index value. The author further showed that TPT, in addition to TBT, could induce imposex in gastropod molluscs. In spite of such a severe imposex symptoms in the individual snails of *T. clavigera*, however, the gastropod molluscs were continuously found in many places in coastal Japan. This was thought to be attributable to the relatively long duration of planktonic stage of this species; i.e., during the planktonic stage, veliger larvae of *T. Clavigera* were expected to recruit from remote, less contaminated area to more severely affected area where majority of female apparently lost their fertility due to morphological changes by the exposure to organotins. Population-level effects of organotins, on the other hand, was observed in a different gastropod mollusc, ivory shell, *Babylonia japonica* (Horiguchi et al. (2006)). Although it is not clear whether the sensitivity against organotins are same between *B. Japonica* and *T. clavigera* or not, The authors suspected that the major reason of population effects found in *B. Japonica* seemed to be attributable to the differences in the duration of planktonic stage. *B. Japonica* had only 4-5 days of planktonic stage, which was too short for the species to recruit from less contaminated remote sites to severely affected areas. The effects of organotins to various gastropod mollusks in Japan were reported until middle of 2000's (for example, Fujinaga et al. (2006), and the references therein), while recent research activities have shifted on the mechanisms of imposex, including the hypotheses on effect to aromatase and RXR (retinoid-X receptor) (Nishikawa et al (2004), Horiguchi (2006), Horiguchi et al. (2010)).

3.6. Overview of existing modeling approaches for PTS transport research

Under the Stockholm Convention, it is expected that long-term POPs monitoring is conducted by the Parties, preferably in regional basis, in order to evaluate the effectiveness of measures / countermeasures taken by the Parties under the Convention (Article 16). Basically the same approach was taken in Minamata Convention on Mercury (Article 22). In East Asia, atmospheric POPs monitoring program in background sites in East Asian countries has been conducted (Ministry of the Environment, Japan; <http://www.env.go.jp/en/chemi/pops/eaws.html>) in addition to the national POPs monitoring in some countries, like Japan, South Korea and China. The first phase data was compiled in Asia-Pacific regional report under the Convention, which will be a basis together with future monitoring data in order to evaluate the effectiveness of the Convention (downloadable from the homepage of the Convention; <http://chm.pops.int/Implementation/GlobalMonitoringPlan/MonitoringReports/tabid/525/Default.aspx>). It is essential to utilize the power of regional / global transport models as well as compilation of available inventory information in order to interpret and assess regional scale monitoring data properly, though lack of detailed and reliable emission inventory information on many of legacy POPs hampered the development of POPs models. Currently model development is more actively conducted on PAHs, which are unintentional products from current known sources.

There is another regional effort to control trans-boundary movement of POPs, such as 'Establishment of POPs Information Warehouse in East Asia', through which countries in the region share POPs monitoring data and cooperate for POPs control. For mercury, atmospheric mercury monitoring programs have been conducted in Japan (homepage of Ministry of the Environment on the data in FY2011 at Hateruma, Okinawa; http://www.env.go.jp/press/file_view.php?serial=21774&hou_id=16473 (in Japanese)), China and Korea, and there is an activity for the establishment of a network of atmospheric mercury monitoring in East Asian countries.

Several modeling studies based on Lagrangian model, Euler model, or their combination approach have been published in the literature. Woehrnshimmel et al. (2012) applied their multimedia model, BETR Research Model, for the understanding of POPs air movement among four areas in HTAP (Hemispheric Transport of air Pollution), i.e., North America, Europe, South Asia and East Asia. BETR is composed of 15 degree x15 degree grid with up-to-seven compartments (upper and lower atmosphere, vegetation, fresh water, surface ocean, soil, sediment) . They concluded that air pollution by PCBs in North America and Europe is consistently dominated by local primary and secondary emissions, whereas in East- and South-Asia extra-regional sources become major contributors. Contribution of sources within the region, on the other hand, is calculated to be dominant in the case of α -HCH in East Asia. Tian et al. (2009) treated the possible effect of East Asian summer monsoon to the movement of α -HCH by a three-dimensional regional scale atmospheric dispersion model, CanMETOP, coupled with a dynamic, three soil layers, Level IV fugacity-based soil/air exchange model and a two-film model to estimate water/air gas exchange. Their calculation showed that northeast China became a receptor of α -HCH where the net deposition of α -HCH took place. They concluded that the East Asian summer monsoon

delivered a significant amount of α -HCH laden air mass from southeast China, the major source region of the substance, to this region where colder temperature dominated. A multimedia model on geographical information system (GIS) is suitable to model environmental levels and behavior of variety of chemicals based on the information of surface morphology, riverline movements and major emission sources (such as PRTR information) (Suzuki et al., 2004). Their model, G-CIEMS, was applied to estimate distribution of air dioxin levels in all over Japan and exposure levels in population. The G-CIEMS approach showed significantly better agreement with the monitoring-derived EWAC (exposure-weighted averaged concentrations) than the generic model approach.

There are also studies on the inventories and models of PAHs in the East Asian countries. Global emission inventory of 16 PAHs from 1960 to 2030 was estimated and reported recently (Shen et al. (2013)). In this report, emission factor variations of PAHs among different countries and over time were newly estimated based on regression models and technology split method. PAH emissions in 2007 with spatial resolution of $0.1^\circ \times 0.1^\circ$ grids based on a newly developed global high-resolution fuel combustion inventory (PKU-FUEL-2007) estimated that the global total annual atmospheric emission of 16 PAHs was 504 Gg (331–818 Gg, as interquartile range), with residential/commercial biomass burning (60.5%), open-field biomass burning (13.6%), and on-road motor vehicles (12.8%) as the major sources. South (87 Gg), East (111 Gg), and Southeast Asia (52 Gg) were estimated to be the regions with the highest PAH emission densities, contributing half of the global total PAH emissions. Several modeling approaches to quantitatively interpret the monitoring data as well as to estimate movement of PAHs have been taken, including a multimedia fate model (Tao et al (2003)), a dispersion model (Tao et al. (2006), a potential receptor influence function (PRIF) probabilistic model(Lang et al. (2007)) and a regression model (Zhang et al. (2007)). The emission inventory (REAS-POP; Regional Emission inventory in ASia for Persistent Organic Pollutants version), concentration levels and transboundary transport of PAHs in North East Asia was reported recently (Inomata et al. (2012)). The developed transport model (Regional Air Quality Model ver2 for POPs version, RAQM2-POP) together with the inventory REAS-POP could simulate the levels of nine PAHs well. Based on the report as well as monitoring in sea water in NOWPAP region, they made a tentative estimate of PAH budget into the central NOWPAP as shown in the Figure 3-76.

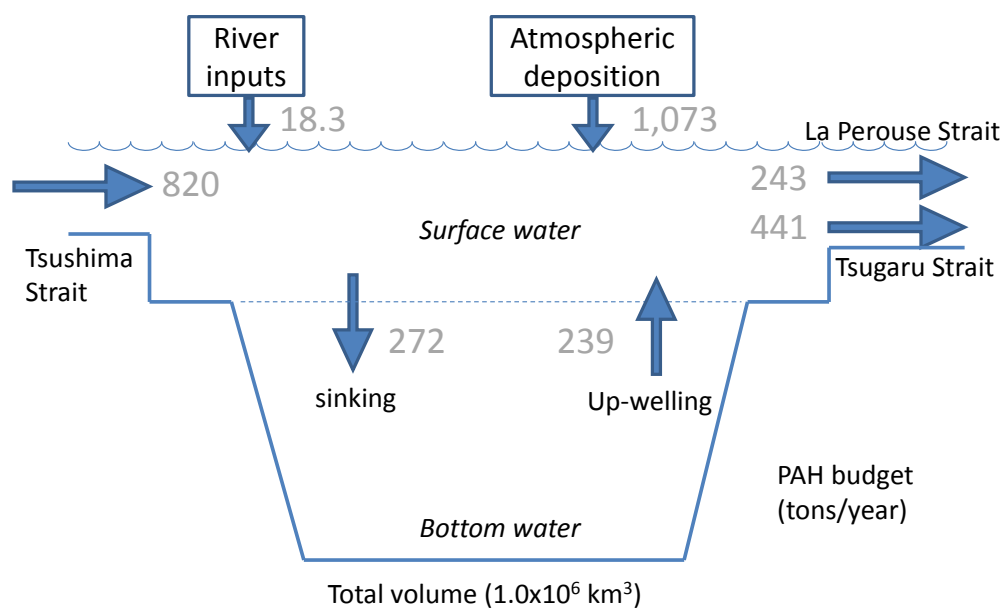


Figure 3-76 Tentative budget of PAHs in the central NOWPAP ocean (re-drawn from the original figure by Hayakawa (2011))

The limited coverage of the Russian area of NOWPAP region by a monitoring network does not allow to make the assessment of PTS contamination based only on monitoring data. On the other hand, modeling methods need monitoring data for model evaluation and formulation. Hence, for assessment of PTS contamination in the NOWPAP region, an integrated measurement/modeling approach is highly recommended.

In the European part of Russian Federation, the EMEP/MSCE-POP model has been utilized to predict transboundary transport of pollutants (<http://www.msceast.org>). This model is a multicompartment one describing processes in and exchange between basic environmental compartments (atmosphere, soil, seawater, vegetation).

MSCE-POP model is being developed and used for the following purposes:

- evaluation of atmospheric transport and deposition of POPs on regional (EMEP) scale
- evaluation of transboundary transport of POPs
- evaluation of POP partitioning between main environmental compartments (atmosphere, soil, vegetation, and seawater)
 - assessment of temporal and spatial trends
 - projection of future levels of POP contamination and trends under various emission scenarios
 - estimation of long-range transport potential and overall persistence of new substances candidates to POPs.

Following the prevailing large-scale circulation, receptor regions are generally located 'downwind' of areas of major usage of POPs. For example, the Northern Pacific

Ocean, including Russian zone of NOWPAP region, is expected to receive long-range transport from East Asia. In contrast to zonal transport and transport from mid to high latitudes, interhemispheric transport is less significant. All transport can be subject to considerable interannual variability

In particular, apart from atmospheric transport, the model takes into account the transport of pollutants by sea currents. This is essential for pollutants which tend to accumulate in the marine environment (e.g. HCB and γ -HCH). Model parameterization has been carried out for PAHs, (B(a)P), HCHs (γ -HCH), PCBs, HCB, and PCDD/PCDF. In the model, media such as atmosphere, soil, and sea are separated vertically into a number of layers to describe the vertical transport of a pollutant in question. To describe variability of the properties in the horizontal direction the corresponding land-use and leaf area index information is taken into account.

Due to large accumulation capacities of bottom sediments and sea water compartments and long periods required for establishing equilibrium, for correct evaluation of POP environmental pollution levels long-term calculations are to be performed. At present the discrepancies between measured and calculated data for all the pollutants considered are within the order of magnitude.

Data of previous studies have shown that for marine areas of NOWPAP regions including Russian area atmospheric transport dominate for all toxic substances compared with river input (NOWPAP POMRAC, 2006). The role of atmospheric inputs for coastal marine areas was determined by the ratio of concentrations of these substances in the rain/snow and in river water as well as by the ratio of river run-off and the amount of precipitation. In offshore regions and for entire basins, atmospheric inputs are dominant and additional attention is needed for any potentially dangerous substances migrating via atmosphere fluxes.

Investigation of PTS concentrations in the atmospheric air over the Asian part of Russia including Primorsky krai and Vladivostok show the PTS levels corresponding both to background world levels and to the largest values of POPs in major industrial cities of the world. Either polybromdiphenyl ethers (PBDEs) were not detected in the atmospheric air overall the study territories or they were not revealed in trace amounts. Concentrations of the other POPs did not exceed MPCs and safe reference levels of impact (SRLI) as adopted in Russia. In 2008- 2009 POPs concentration in the air near Vladivostok varied in winter or summer: PCB – 100-300 pg/m^3 , sum DDT - 1000-9600 pg/m^3 , HCH – 415 pg/m^3 , and hexachlorbenzol 40-50 pg/m^3 . The quantitative and qualitative compositions of POPs are conditioned to exchange processes in the soil–atmospheric air system due to the action of negative and positive temperatures, temperature inversions, atmospheric precipitation and other depositions, transboundary atmospheric transport and contemporary local sources of pollution (Mamontova et al., 2012). In general, atmospheric input is an important source .in PTS transport in this region as well as in other temperate and polar regions.

It is possibly assess the significance of direct input of some chemical substances with wastewater. PTS level in wastewaters is not registered, but increased DDT and

HCH concentrations in bottom sediments in coastal ecosystems testifies pesticides input and accumulation in the sites of wastewater discharge (see Chapter 3.4).

Specific features of PTS transport on the Russian coast of NOWPAP region is a biotransport by Pacific salmon. Many species of animals shift their habitat during their life cycle. In anadromous fish such as salmon, spawning and rearing occur in freshwater, whereas the adult life stage is spent in the ocean. Before they migrate, such species generally accumulate lipids for both energy use and gonad development during migration. With this buildup of lipids occurs a concomitant accumulation of lipophilic pollutants. Accordingly, migrating animals can act as vectors of organic pollutants between ecosystems, and fish have been shown to transport pollutants from the tropical and subtropical regions to the temperate areas. The organic pollutants that the salmon accumulate during their ocean life stage are not eliminated during the spawning migration, and the pollutants are transported to the spawning rivers and springs and possibly deposited there. As the pollutants reach coastal and terrestrial ecosystems, they accumulate in biota because of their lipophilic and persistent properties. The geographic distribution of Pacific salmon extends from San Francisco Bay, in California, northward along the Canadian and Alaskan coasts to rivers draining into the Arctic Ocean, and southward down the Asian coastal areas of Russia, Japan, and Korea. Most probably, all seven species of Pacific salmon are “biotransporters” of pollutants from the Pacific Ocean to their spawning sites in freshwater. The extent of this process is determined by pollutant exposure in their foraging areas, food choice, and the structure of the ecosystem at the spawning sites. If we know average pesticides concentration in fish body and number of fish reaching the spawning we can calculate total pesticides amount in the coastal ecosystems of NOWPAP region transported by salmon.

Table 3-91. Salmon catch and pesticides amount transported by salmon in the Russian area of NOWPAP region (Lukyanova et al., 2012)

Area	2010		2011	
	Catch, t	Pesticides, g	Catch, t	Pesticides, g
Southern-western Sakhalin Is.	3962	200	1234	62
Khabarovskiy kray	6077	304	155,6	7,8
Primorsky kray	2428	120	135,1	6,8

A large catch of salmon occurs on the Russian coast of NOWPAP region last years. Salmon’s spawning grounds are located along the shorelines in Khabarovskiy krai, Primorsky krai, and southern-western Sakhalin Island. Salmon’s catch in 2010 and 2011 was estimated (Table 3), and according to the expert evaluations the similar amount of salmon pass to the spawning rivers and springs and spawn and die there. Pesticides accumulated in salmon’s body remain in freshwater ecosystems and transfer through food web. Average pesticide concentrations in salmon’s body (*Oncorhynchus keta*) were estimated as 30 ng/g wet weight for HCH and 20 ng/g for DDT. Total

pesticide amount transported by Pacific salmon to the Russian coast of NOWPAP region was estimated as 624 g in 2010 and 77 g in 2011. These circumstances could cause an environmental risk for local ecosystems.

Hence, the main factors determining PTS transport in the Russian area of NOWPAP region are the atmospheric transfer, wastewater discharges, river input and salmon's biotransport.

Few reports were found about the modeling approaches for PTS transport research. In literature, the mass transport budgets of p,p'-DDT and BDE-209 in the Pearl River Delta, South China were calculated based on previously collected data (Zhang et al., 2011). Residual p,p'-DDT, mostly related to historical use, has largely settled into soil (780,000 kg), while the soil BDE-209 inventory (44,000 kg) is considerably smaller. Conversely, large amounts of BDE-209 currently used in numerous commercial products have resulted in a much higher atmospheric depositional flux of BDE-209 (28,100 kg/yr) relative to p,p'-DDT (310 kg/yr). The soil inventory of p,p'-DDT is predicted to decrease to half of its current value after 22 years, and the percent area containing soil p,p'-DDT at levels exceeding the effects range-medium (27 ng/g) will decrease from 40% to 20%. Finally, soil BDE-209 inventory will reach an equilibrium value of 940 tons in 60 years, when BDE-209 levels in 50% of soil will be above an equivalent risk guideline value (125 ng/g).

LRT dynamics of POPs can be predicted and evaluated by environmental multimedia modeling (MMM). The models with different spatial scale such as POPsME, EDCSeoul, and KoEFT-PBTs have been developed to predict the fate and transport of classical POPs or VOCs in multimedia environments (Lee et al., 2004; NIER, 2001, 2002, 2003; Lee, 2005). These models are considered to serve as a basis for the future development of LRT models of the north-east Asian region.

For example, Multimedia mass balance models (MMMs) have proven to be a powerful tool in the exposure or the risk assessment process. The performance of MMMs was often evaluated by comparing their prediction with field measurements for PCDD/Fs in Korean environment (Lee et al., 2007). Used sampling map and resolution is presented in Figure 3-77. POPsME was evaluated for its performance to assess the fate and transport of 2,3,7,8-substituted PCDD/F congeners in a multimedia environment of South Korea. Particular attention was paid to assessing quantitatively the effects of the grid size and the homogeneous mixing assumption on the bias of model predictions. As PCDD/Fs were predominantly emitted from point sources (i.e., waste incinerators), the problem of homogeneous mixing assumptions, if they exist, was anticipated to be prominent. Also, attention was paid to the nature of the monitoring data that were compared to the model prediction. The results on comparisons between predicted total PCDD/Fs concentrations and those measured in each medium are presented in Figure 3-78.

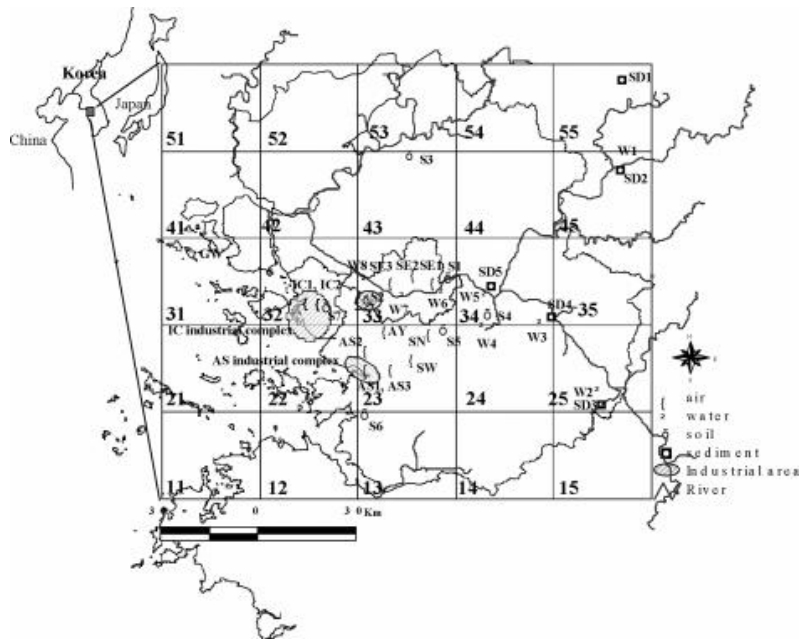


Figure 3-77. Study area with the cells used in POPsME and the locations of the industrial complex and monitoring sites. The cell numbers are at the bottom left of each cell (Lee et al., 2007).

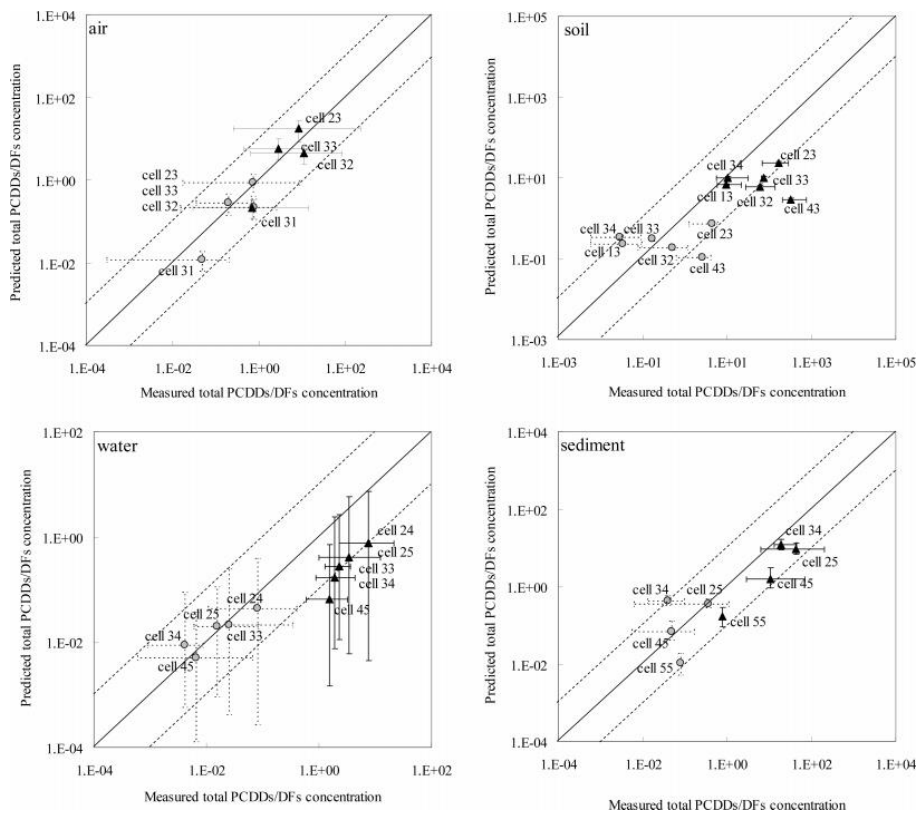


Figure 3-78. Comparisons between predicted total PCDD/Fs concentrations and those measured in each medium. The measured concentration is the averaged value of the measurements in each cell. Data are mean and the range. Triangles mark the mass-

based concentrations (air, pg/m^3 ; water, pg/L ; and soil and sediment, pg/g dry weight soil or sediment), and circles present the TEQ-based concentrations (air, $\text{pg I-TEQ}/\text{m}^3$; water, $\text{pg I-TEQ}/\text{L}$; and soil and sediment, $\text{pg I-TEQ}/\text{g}$ dry weight) (Lee et al., 2007).

LRT of atmospheric pollutants has become a concern in South Korea partly because release of numbers of pollutants in eastern China may be a potential source of air pollution in South Korea (Kwon et al., 2002). Studies of LRT, however, have focused on suspended particulate matter such as PM_{10} or $\text{PM}_{2.5}$ (Lee et al., 2006), particle-associated heavy metals (Han et al., 2002), or acidic air pollutants (Park and In, 2002). Since Gosan in Jeju Island is used as a reference site for ACE-Asia (Asian-Pacific Regional Aerosol Characterization Experiment) project in 2001, many studies are performed for LRT of pollutants from East Asia. Ghim et al. (2003) reported the variation in atmospheric concentrations of POPs including PCDDs/DFs, dioxin-like PCBs, OCPs, and PAHs in Asian dust at the reference site, Gosan. Little increase in atmospheric concentrations of POPs was observed during the Yellow Sand season except for PAHs. Another study measured atmospheric bulk deposition of PCDDs/DFs in urban and suburban areas in South Korea during one year including periods of Asian dust. Elevated levels were not also observed in the presence of Asian dust (Moon et al., 2005). Instead, they reported the effect of Asian dust on South Korean air by using the specific congener patterns observed during the period, clearly differing from those of other seasons. These studies were, however, restricted to a short term. Thus, further long-term studies are needed on trans-boundary LRT of POPs in this region (Kim et al., 2007).

Considerable efforts have been conducted in Japan in order to develop useful models for PTS in the environment, including multi-media model development (such as G-CIEMS), inventory compilation (dioxins survey, PRTR, etc.), process research including bioconcentration / accumulation efficiencies, and synthesizing these efforts together with GCM (global circulation model). In addition, extensive environmental monitoring activities have been conducted and are used for validation and improvement of the models. Detailed description of these activities is omitted here as many of them have been described in the previous sections.

3.7. Data gaps and needs

Majority of PTS, including legacy POPs, lack detailed information on emission inventories in NOWPAP region as well as in the global scale. Also environmental monitoring data is scarce, particularly in the central NOWPAP region. For many of industrial chemicals, it is not easy to get information on, or estimate usage amounts in particular locations / areas in the region. Under such circumstances, compilation of monitoring data in terrestrial as well as coastal environment, particularly air and river water as well as effluents from factories and waste water treatment plants (sewage treatment plants), is valuable to estimate input of PTS to the central NOWPAP region. As pointed out in the previous sections, it is highly recommended to take integrated measurement / modeling approach in order to elucidate the status and assess risks of PTS contamination in the NOWPAP region. Furthermore, ecological effects of many of PTS are still not clear. It is important to develop methods and conduct ecotoxicological / ecological risk assessment by the combination of eco-toxicological data and exposure levels as well as by the careful monitoring of the status of ecosystem or wildlife in the regional environment.

There is a scarcity of reliable data on the sources of PTS in the Russian area of NOWPAP region. Little information is available on the quantity and location of obsolete pesticides. Monitoring services in Asian part of Russia control 6 organochlorine pesticides only: α -HCH, β -HCH, γ -HCH, DDT, DDD and DDE. Other new pesticides, industrial compounds and unintentional by-products are not control. The list of PTS monitored is often shorter than the Stockholm Convention's list of 12 POPs, resulting in data gaps. There is almost a complete lack of data on HCB, PCB, PCDD/PCDF stocks and occurrence. Data are inadequate to monitor and/or model results or to identify specific source locations and PTS transport pathways. Inadequate methods are usually used for pesticides analysis in sea water, bottom sediments and biota.

Key information gaps on PTS issues in the Russian area of the NOWPAP region include:

- Inadequate information to determine the significance of regional chemicals: Polybrominated Diphenyl Ether (PBDE), Pentachlorophenol (PCP), Organic Mercury Compounds,
- Inadequate information on PTS accumulation mechanisms in the biota and their effects on biota. There is also a concern with the stability of some PTS in the marine environment given the very slow degradation rate of such PTS (PCBs for example) in marine ecosystems;
- Poor understanding of the sources of regionally significant PTS affecting marine and coastal environments.
- Lack of Advanced or Best Available Technology
- Insufficient Knowledge and Training of Special Personnel

It is need to harmonize methodologies and procedures for monitoring water quality among NOWPAP countries.

Enhance efforts to obtain reliable data on PTS level in marine environment and biota at the national and regional levels.

At present, except that the Trustworthy Food and Drug Project of the State Council and the Action Plan for Food Safety of the Ministry of Health have definitely decided to include food pollutants across the country in their plans and to conduct monitoring of such POPs as DDT, PCBs and Dioxins, China has not carried out a nationwide systematic assessment of POPs release monitoring, environmental impacts and impacts on human health. All existing data come from scientific research reports involving a small number of regions, and lacks a systematic nature (NIP of China, 2007).

Although China has carried out the above monitoring and research work, POPs-related monitoring data is still deficient and information disclosure and sharing mechanisms have not been well established, neither the comprehensiveness of data nor the geographic range covered by the data can meet the requirements for assessing POPs risks and their hazards to the environment.

At present, monitoring units below the provincial level have insufficient hardware for POPs monitoring, and the standards and systems for monitoring POPs have yet to be established and improved. Normative management of laboratories needs to be further strengthened and their technological capacity has yet to be improved, particularly, their lack of simple testing technologies for Dioxin in China.

China has begun to be able to produce pesticide POPs alternatives. However, China needs to strengthen its capability for independent development and focus on research and development of efficient, low-toxicity, environmentally sound and cost-effective alternatives and alternative technologies, particularly IPM (Integrated Pest Management) technologies, because the alternatives require relatively high costs and their performance cannot meet the requirements for substitution.

Study on risk assessment and effective pollution control is ecologically important to understand the bioaccumulation and biomagnifications of POPs in both aquatic and terrestrial food chains. Many researchers in foreign countries studied the bioaccumulation and biomagnifications of POPs in aquatic food chain. However, only a few researchers focused their studies on terrestrial food chain, and even fewer researchers did on the both food chain. There is little information on the bioaccumulation and biomagnifications of POPs in food chain in China. Therefore, it is necessary to study the bioaccumulation and biomagnifications, as well as the related treatment models of POPs in food chains when the POPs are now becoming more and more harmful to the environment and human health.

As above mentioned, the NIER (or MoE) and NFRDI (or MOF) have launched the monitoring program for POPs and related compounds in terrestrial and marine environment of Korea, under Stockholm Convention. Many studies have reported on legacy POP contamination, source characterization and temporal trends for Korean environments. However, a few studies on emerging POPs such as PBDEs and PFCs in

terrestrial and marine environment are available. In particular, long-term temporal studies on emerging POPs will help to establish management strategy for these contaminants in terrestrial and marine environment. Although some studies found ecotoxicological implications for residue levels of POPs in Korean cetaceans, no long-term trend studies on POPs in cetaceans from Korea are available. In 2009, some chemicals were designated as new POPs. PBDEs and PFCs are relatively studied by many researchers associated with nationwide monitoring program. However, almost no data are available on the other chemicals such as hexabromobiphenyl, pentachlorobezene, chlordecone and endosulfan (designated as new POPs in 2011) in Korean environment. In addition, some chemicals regarded as POPs candidates (HBCD and short chained chlorinated paraffins, SCCPs) should be included as target compounds in the nationwide monitoring programs. To document these emerging contaminants in Korea, the standard methods including sampling sites, preparation methods, instrumental analysis and QA/QC protocols should be established. In addition, long-term studies are needed on trans-boundary LRT of POPs in South Korea.

Extensive environmental monitoring and inventory compilation activities as well as toxicological / ecotoxicological studies have been conducted in Japan in order to establish sound chemical management system. There still remain gaps, however, as for toxicity / ecotoxicity information on current use chemicals, and lack of such information might cause unattended pollution of new chemicals. Intensive researches have been conducted to develop analytical methods for newly added POPs under the Stockholm Convention, though further development of rapid, sensitive, reliable and cost-effective monitoring methods are needed to monitor vast number of chemicals of potential adverse effects to human beings and the environment. Proper control / management of chemicals like carcinogens or endocrine disruptors need particular attention due to significance of their adverse effects, difficulties to assess their toxicity / ecotoxicity, and their delayed effects long after their exposure. Long term storage of representative portion of environmental monitoring samples (environmental specimens) for future retrospective studies, a so-called Environmental Specimen Banking (ESB), will supplement the gaps and support establishment of sound chemical management systems, and ESB is now recognized as indispensable tool under the global monitoring plan (GMP) for the effectiveness evaluation of the Stockholm Convention. In Japan, pilot ESB was established at the National Institute for Environmental Studies (NIES) in 1979 and up-graded to full-scale system from 2004 by the completion of Environmental Time Capsule Facility at NIES, including liquid-nitrogen cooled insulating tanks, -60 C cold rooms and -80 C freezers. Now an extensive sampling and archiving of environmental samples, particularly mussels and oysters along the coastline of Japan, is on-going under the "Environmental Time Capsule program". In addition, environmental monitoring samples (biological samples and sediments) under "The Chemicals in the Environment" program by the Ministry of the Environment Japan has been archived in the facility (from 1978 until present for biological samples). Another large ESB was established in Ehime University in 2005 and is archiving variety of wildlife and human samples collected from various places in the world by the researchers in the university. In South Korea, an ESB was constructed at NIER and is collecting various environmental samples in selected locations in South Korea every year. Another ESB is recently established in Shanghai, China, for collecting and archiving samples mainly in

Yangze river delta. Harmonization of ESBs among the countries as well as between environmental monitoring activities will further support sound chemical management process in NOWPAP region.

4. Regulatory frameworks and capacity building

4.1. Existing laws and regulations

<China>

The Environmental Protection Law of China is a comprehensive law on environmental protection. Article 48 of the law is directly related to POPs management, which stipulates that “production storage, transportation, sale and use of poisonous chemicals and goods containing radioactive substances must abide by related national stipulations to prevent environmental pollution”. The Law on Water Pollution Prevention and Control, the Law on Air Pollution Prevention and Control, the Law on Marine Environmental Protection, the Law on Environmental Impact Assessment, and the Law on Solid Wastes Pollution Prevention and Control, all stipulate pollution prevention and control requirements from different perspectives, which can be used for POPs management, see Tab. 12. (NIP of China, 2007). Currently, China does not have any law or regulation specifically addressing POPs.

Table 12 Departmental Regulations on Management of Hazardous Chemicals and Pesticides

Name	Issuing department	Effective Date	Relevance to POPs management
<i>Measures for the Administration of Operating Licenses for Hazardous Chemicals</i>	The former State Economic and Trade Commission	2002	Management of business licenses related to POPs
<i>Implementation Measures for Safety Production License of Hazardous Chemical Production Enterprises</i>	State Administration of Work Safety State Administration of Coal Mine Safety	2004	Management of the qualifications of enterprises engaged in POPs production
<i>Management Measures on Production of Packages and Containers for Hazardous Chemicals in Designated Enterprises</i>	The former State Economic and Trade Commission	2002	Management of designated manufactures of packaging and containers for hazardous chemicals
<i>Measures for management on Registration of Hazardous Chemicals</i>	The former State Economic and Trade Commission	2002	POPs registration management
<i>Details Rules for Registration of Hazardous Chemicals (Trial)</i>	The former State Economic and Trade Commission	2000	
<i>Implementation Measures for Safety License of Hazardous Chemicals Construction Projects</i>	State Administration of Work Safety State Administration of Coal Mine Safety	2006	Safety check of POPs production and storage enterprise
<i>Regulations on</i>	State Environmental	1994	Import and

<i>Environmental Management of the First Import and Export of Toxic chemicals</i>	Protection Administration General Administration of Customs The former State Economic and Trade Commission		export management related to POPs
<i>Detailed Rules on Registration for Environmental Management on the First Import Chemicals and the Import and Export of Toxic Chemicals</i>	The former SEPA	1995	
<i>Provision on Safe Use of Chemicals in Workplaces</i>	The former Ministry of Labor, The former Ministry of Chemical Industry	1996	Safety management related to POPs production sites
<i>Measures for management on Production license of Industrial Products</i>		2002	Production license management related to POPs
<i>Regulations for the Safe Use of Pesticides</i>	The former Ministry of Agriculture, Animal Husbandry and Fishery, Ministry of Health	1982	management related to the use of POPs
<i>Regulations on Prevention of Termites in Urban Housing</i>	Ministry of Construction	1999	management related to the use of POPs
<i>Management Regulations on Railway Transportation of Hazardous Goods</i>	Ministry of Railways	1996	management related to the transportation of POPs
<i>Regulations on Waterway Transportation of Hazardous Goods</i>	Ministry of Communications	1996	management related to the transportation of POPs
<i>Regulations on Road Transport of Hazardous Goods</i>	Ministry of Communications	1993	management related to POPs
<i>List of Chemicals with Severe Toxicity (Amended in 2002)</i>	State Administration of Work Safety Ministry of Public Security, SEPA Ministry of Health State Bureau of Quality Supervision and Inspection Ministry of Railways Ministry of Communications, General Administration of Civil Aviation	2002	Includes POPs
<i>List of Hazardous Chemicals</i>	The former State Administration of Work Safety	2003	Includes POPs
<i>Reference No. of Dangerous Goods and Classification GB 6944-2005</i>	SEPA	2005	Includes POPs

<Japan>

Chemical management by the government of Japan has been conducted in several separate categories, including pharmaceuticals, agrochemicals including pharmaceuticals for veterinary uses, and general industrial chemicals. Pharmaceuticals and agricultural chemicals are primarily controlled by Pharmaceutical Affairs Law (Ministry of Health, Labour and Welfare), and Agricultural Chemicals Regulation Law or Fertilizer Control Law (Ministry of Agriculture, Forestry and Fisheries), respectively. Their residual levels as well as other additives in foods are controlled under Ordinance for Enforcement of the Food Sanitation Act. Majority of industrial chemicals, on the other hand, is controlled by the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. (Chemical Substances Control Law), which is jointly controlled by the Ministry of Economy, Trade and Industry, Ministry of Health, Labour and Welfare, and Ministry of the Environment (MOE). Other laws or regulations of environmental concern include Air Pollution Control Law, Water Pollution Control Law, Soil Contamination Countermeasure Act, Law Concerning Special Measures against Dioxins, Law on Waste Disposal and Cleaning, Law for the Control of Export, Import and Others of Specified Hazardous Wastes and Other Wastes, and Law Concerning Reporting, etc. of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management (PRTR) (MOE). Some specific chemicals are controlled by other law systems, including Poisonous and Deleterious Substances Control Law, Stimulant Drug Control Law, and Narcotics and Psychotropics Control Law.

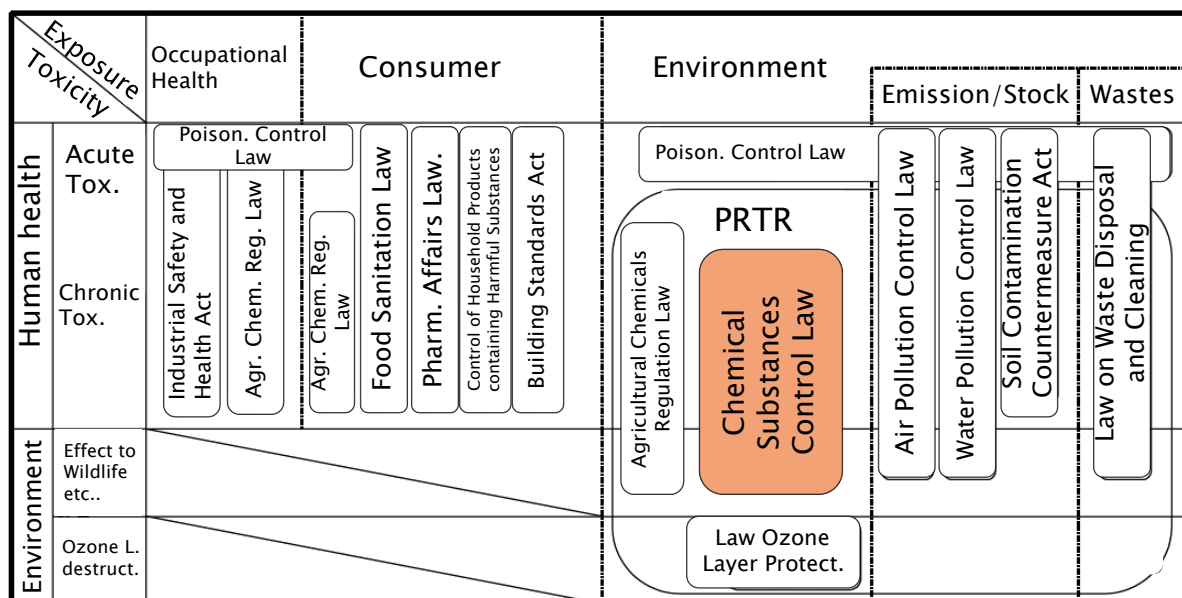


Figure 1 Outline of chemical management system in Japan.
Chemical Substances Control Law (CSCL) is marked in orange color.

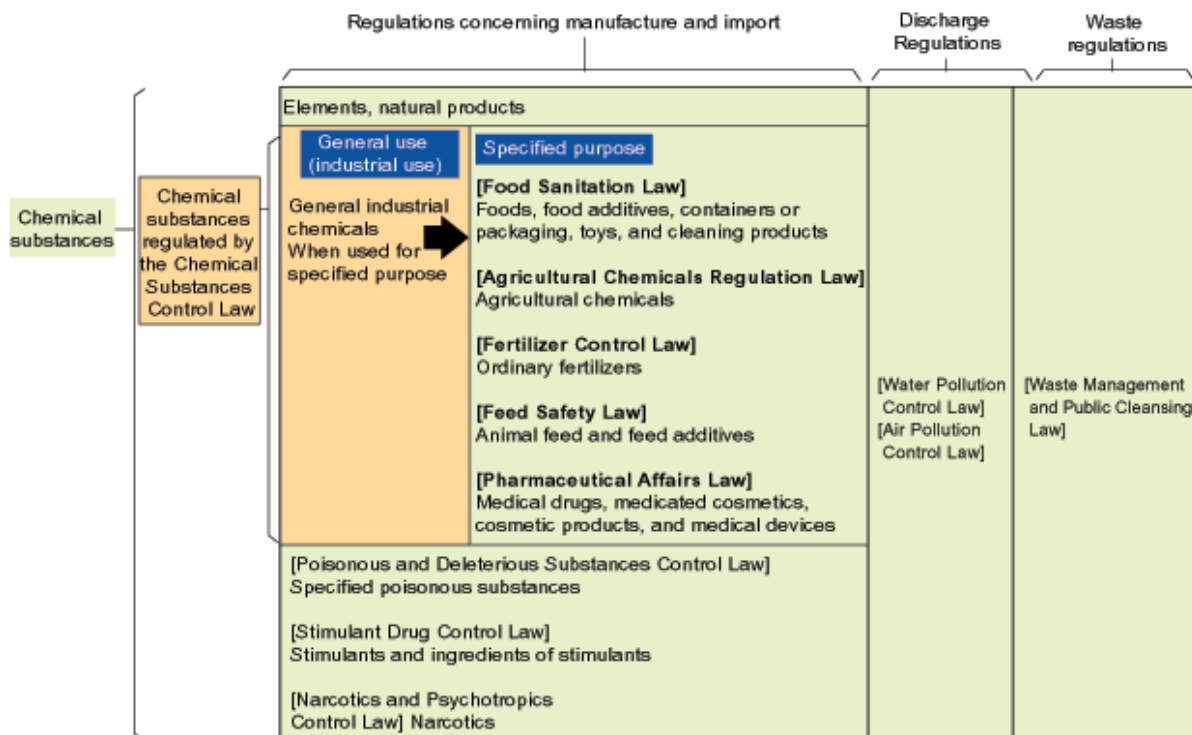
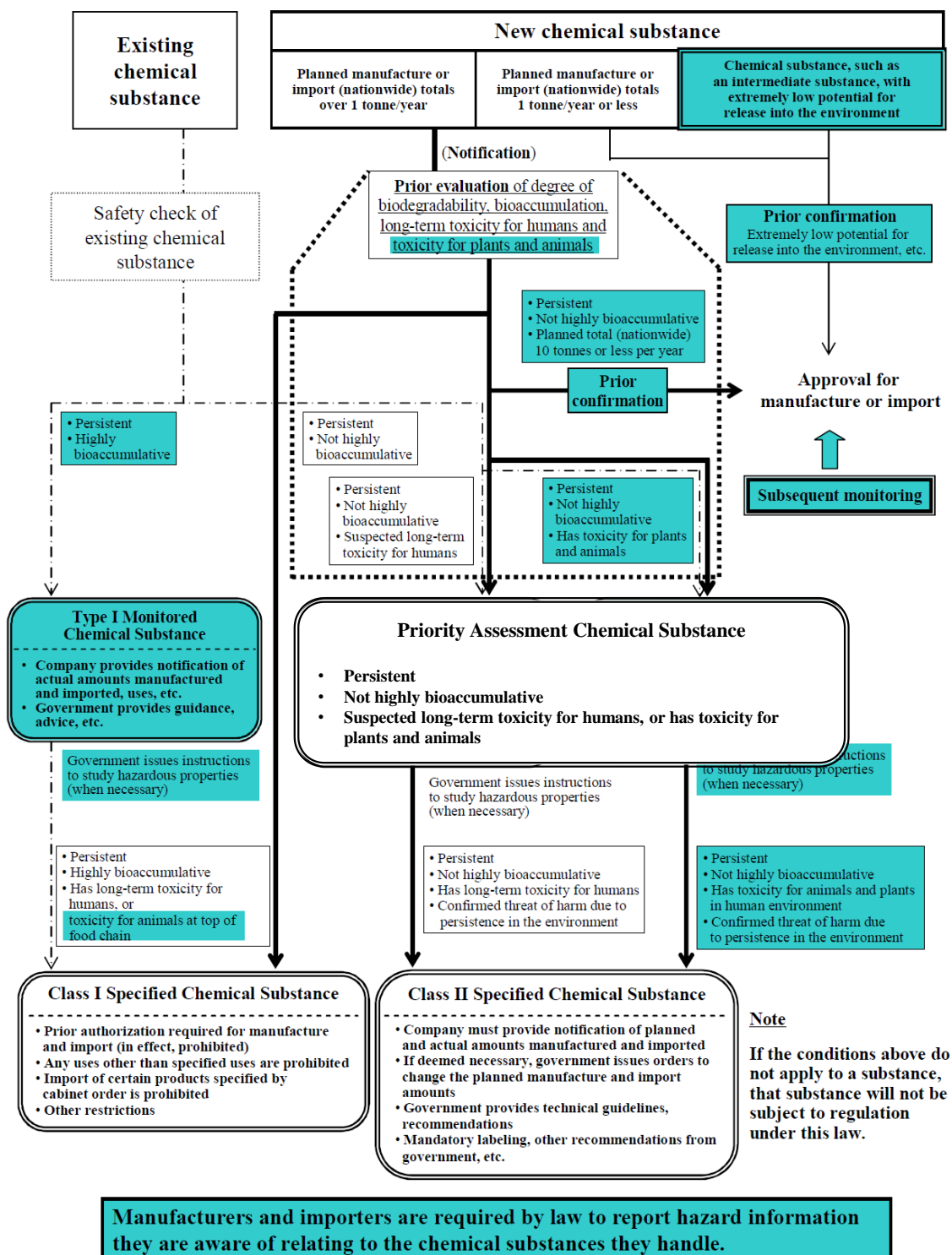


Figure 2 Chemical Substances Subject to the Regulations of the Chemical Substances Control Law (Relationship with other Laws)

As the Chemical Substances Control Law (CSCL) deals with not only production but also import / export and usage of the chemicals, majority of POPs chemicals, including industrial and agricultural chemicals, are controlled under the CSCL in Japan. Unintentionally produced chemicals, including chlorinated dioxins and furans, however, are outside of the scope of CSCL, which deals with intentionally produced substances. Therefore another special law was established in 1999 in order to control production and emission of dioxins and related chemicals, including dioxin-like PCBs (*dl*-PCBs). Environmental and emission standards are set for dioxins (sum of TEQs of PCDDs, PCDFs and *dl*-PCBs) and PCBs. Waste management and recycling including their international transport is controlled by another law systems under Waste Management and Recycling Division of MOE. PCBs-containing materials, with levels equal or higher than 50 micrograms of PCBs per gram, have to be treated by either of the designated non-combustion, chemical destruction procedures operated at five PCB-destruction factories in Japan.

Outline of Chemical Substances Control Law (CSCL)

- Framework for Evaluation and Regulation of Chemical Substances in Japan -



(Most recent amendments to the law are indicated by shaded text.)

Figure 3 Structure of Chemical Substances Control Law in Japan (modified from the figure in homepage of MOE according to recent amendment of the Law)

<Korea>

Ministry of Environment made Korean POPs law entitled 'Special Persistent Organic Pollutants Control Act' in 2007, after ratified a global treaty for the Stockholm Convention. The purpose of this Act is to prescribe matters necessary for controlling persistent organic pollutants, including dioxin etc., which are prescribed in the Stockholm Treaty on Persistent Organic Pollutants, in order to implement the Stockholm Treaty on Persistent Organic Pollutants, and thereby to protect the health of the people and environment from harm caused by persistent organic pollutants and to promote international cooperation. This Act involves regulation and activities to reduce exposure to POPs including: (1) prohibition and restriction of production, distribution, and use of POPs; (2) establishment of environmental quality guidelines (EQGs) in each compartment, human tolerable daily intake (TDI), standard operation procedure (SOP), and regular monitoring system; (3) emission control including establishment of emission guidelines and emission inventories; (4) management of POPs containing waste; and 5) protection of POPs contamination of soils and restoration of POPs-contaminated soils.

Establishment of emission and/or discharge guidelines for each source and environmental quality criteria for each compartment are legal regulations that have been established to reduce environmental exposure to POPs. South Korean guidelines and quality criteria are applied to dioxins from municipal waste incinerators, and waste and environmental quality guideline for PCBs (Table 3). Regulatory controls of POPs-containing raw materials or wastes in South Korea are based on eight individual acts (Table 3). In 2005, one POPs specific ordinance was presented for registration to effectively enact the use, distribution, emission/discharge, environmental residual levels, and treatment and management over the whole life cycle. The early regulation was focused on classical POPs, namely, the OCPs (Table 3). Like many other developed countries, almost all OCPs were banned from use in South Korea, during the early stages of POPs control in the late 1960s. The AgroChemical Management Act (ACMA) banned the registration of OCPs in 1969, which implies the ban of import, manufacture, and sale. After the ban of other OCPs, heptachlor and toxaphene were widely used as alternatives. However, in 1980, these two pesticides were also banned from use in South Korea. HCB and mirex were neither imported nor produced in South Korea as pesticide. Endosulfan has not been banned and is still being used. It is known that OCPs were imported and used illegally for a few years even after the ban. Furthermore, some OCPs are known to have been used as a non-food additive agent. For example, chlordane was used as an adhesive for plywood and DDTs as an intermediate in the production of dicofol. It was not until the 1990s that regulation of OCPs in South Korea was mandated by the Toxic Chemical Control Act (TCCA).

PCBs were imported from abroad and their use was legally regulated for the first time in 1979. The Electricity Business Act (EBA) prohibited the use of electric heaters with PCB-containing dielectric fluids. However, existing PCB-containing articles were allowed to be used for other purposes until 1996 when production, import, and use of articles containing concentrations of PCBs greater than 50 ppm were banned by the TCCA. Waste containing concentrations of PCBs greater than 2 ppm was classified as

specific hazardous wastes was treated by special methods listed in the law, and should be reported to and confirmed by the KMOE. According to the Stockholm Convention, PCB-containing equipments such as capacitors, condensers, and transformers should be forbidden from use by 2025 and are recommended to be treated by environmentally sound methods by 2028 (Stockholm Convention on Persistent Organic Pollutants, 2001). The South Korea Ministry of Environment (KMOE), South Korea Electric Power Corporation (KEPCO) and six electric power companies, and three non-governmental organizations (NGO) reached a cooperative and administrative agreement in 2004 for the removal of PCBs in South Korea by 2015. An investigation of the domestic status of PCB-containing articles is currently being conducted. In spite of the regulations, government actions on POPs began practically only after a public concern on the dioxin release in waste incinerators in 1997. Since then, the emission of PCDDs/DFs was included in regulations. Recently, in response to the Stockholm Convention, periodic monitoring has been conducted in South Korea.

Waste incineration is a known source of dioxins and other dioxin-like compounds. As a part of change in waste management policy since the early 1990s, many incinerators have been constructed. The number of incinerators in South Korea reached a maximum of about 16,000 in 1998 (from only 100 in 1993). However, it has decreased noticeably to ~5000 in 2003 since an introduction of stringent dioxin emission regulations for the incinerators in 1997. Large-scale incinerators have been required to restrict emission of dioxins to less than 0.1 ng I-TEQ Nm³. Subsequently, medium- and small-scaled incinerators have been included in these regulations (Table 4). All the incinerators are required to reduce emissions of dioxins to less than 0.1–10 ng I-TEQ m³. Under the Waste Control Act (WCA), facilities that incinerate less than 0.025 ton/h are no longer allowed (Kim et al., 2007). Another provision of the WCA is that all incinerators are obliged to conduct regular monitoring for dioxin-like compounds: semiannually, annually, and biannually for large, medium, and small scale, respectively. Since these regulations went into effect, the best available technologies (BAT) such as spray absorber/bag filter (SDA/BF) with lime and activated carbon mixture sprayed into the SDA have been applied to incinerators and the number of smaller, less economically feasible incinerators has greatly decreased. In addition to regulations on waste incineration, discharge/emission guidelines for dioxins released from industrial sources, such as metallurgical plants, are expected to be established in 2006.

Table 3. Regulatory action on POPs in South Korea (Kim et al., 2007)

Pollutant category	Major use in Korea	Regulatory action						Food residual level ⁱ
		ACMA ^a	ISHA ^c	ISHA ^c	EBA ^d	CACA ^e /WQCA ^f /SECA ^g	WCA ^h	
PCBs	Dielectric fluid etc.	–	Ban ('96 >50 ppm, '99)	Ban ('03)	Ban ('79)	Specific hazardous chemical	Hazardous waste (> 2 ppm) ^k	–
OCPs ^j								
DDTs	Insecticide	Ban ('69)	Ban (> 1%, '91)	Ban	–	–	–	<0.1 ppm
Chlordanes (CHLs)	Insecticide/additive agent	Ban ('69)	Ban (> 1%, '99)	Ban	–	–	–	<0.02 ppm
HCHs	Insecticide	Ban ('69)	Ban (> 1.5%, '91)	Ban	–	–	–	
Aldrin	Insecticide/additive agent	Ban ('69)	Ban (> 0.1%, '99)	Ban	–	–	–	<0.01 ppm
Endrin	Insecticide/additive agent	Ban ('69)	Ban (> 1%, '99)	Ban	–	–	–	<0.01 ppm
Dieldrin	Insecticide/additive agent	Ban ('70)	Ban (> 1%, '99)	Ban	–	–	–	<0.01 ppm
Heptachlor	Insecticide/additive agent	Ban ('79)	Ban (> 6%, '99)	Ban	–	–	–	<0.01 ppm
Toxaphene (Camphechlor)	Insecticide	Ban ('82)	Ban (> 1%, '91)	Ban	–	–	–	–
Endosulfan	Insecticide	–	Ban (> 1%, <'03)	Ban	–	–	–	–
Tetrachlorobenzene (TeCB)	Intermediate in pesticide	–	–	–	–	–	–	–
Pentachlorobenzene (PeCB)	Intermediate in pesticide	–	Ban (> 1%, <'03)	Ban	–	–	–	–
Hexachlorobenzene (HCB)	Domestic no use	–	–	–	–	–	–	–
Mirex	Domestic no use	–	–	–	–	–	–	–
PCDD/Fs	Domestic no use	–	–	–	–	–	Restricted release('97)	–
Coplanar PCBs (coPCBs)	By-products	–	–	–	–	–	–	–
Hexachlorobenzene (HCB)	By-products	–	–	–	–	–	–	–
PBDEs	Flame retardant	–	–	–	–	–	–	–
Perfluoroalkyl acids (PFAs)	Acids offluoropolymer, rust/oil/ water retardant	–	–	–	–	–	–	–
PAHs		–	–	–	–	–	–	–

^aACMA (Agrochemical Management Act); the ban of registration of pesticides, indicating implicitly the ban of import, manufacture, and selling.

^bTCCA (Toxic Chemical Control Act); the restricted use (until '90) and the ban (from '91) of manufacture, import, and use of non-food additive agent.

^cISHA (Industrial Safety and Health Act); the same legal action as TCCA was enacted in 2003.

^dEBA (Electricity Business Act); the ban of use for electric heater of facilities used PCB -containing dielectric fluid.

^eCACA (Clean Air Conservation Act); the specific air hazardous chemical.

^fWQCA (Water Quality Conservation Act); the water quality criteria of PCBs as specific water hazardous chemicals.

^gSECA (Soil Environment Conservation Act); the air quality criteria of PCBs as specific water hazardous chemicals.

^hWCA (Waste Control Act); the restriction of waste treatment.

ⁱGuideline of Korean Food and Drug Administration.

^jOCPs (Organochlorine Pesticides).

^kPCBs as specific hazardous waste should be treated in separated and specific method and reported and confirmed by KMOE administrator.

In 2005, an administrative agreement on reduction of dioxin emission through

industrial processes was adopted by among Ministry of Environment, NGOs, and four industries, including the iron & non-iron metal industry, cement industry, and chemical industry. The groups agreed to reduce dioxin emission to 70% of that estimated for 2001 by 2008 and 50% by 2010. To achieve this goal best environmental practice (BEP) in addition to BAT will be adopted.

In 2009, Ministry of Ocean Fisheries made ‘Enforcement Decree of Marine Environment Management Act’ to protect marine ecosystem from anthropogenic activities such as various kinds of pollutants from development coastal regions and industrial complex. This Act contained operation of the POPs monitoring network, environmental standard of POPs and ban on POPs and related compounds in marine environment. To date, no available guidelines or environmental standards for POPs in marine environmental media in Korea.

Table 4. Guideline of dioxins release from waste incinerators (ng I-TEQ m³) (Kim et al., 2007)

Waste type	Incinerator size		Guideline and application date			
			New incinerator		Existing incinerator	
Municipal solid waste	Category	Capacity/application	From Jul./97	To Jun./99	To Jun./03	From Jul./03
	Large	> 50 ton/day	0.1	0.5	0.5	0.1
Other all wastes	Category	Capacity/application	From Jan./01	To Dec./02	To Dec./05	From Jan./06
	Large	4 ton/hr	0.1	20	20	1
		2–4 ton/hr	1	40	40	5
	Medium/small	0.025–2 ton/hr	5	40	40	10
Hospital/medical waste	Category	Capacity/application	From Aug./04	To Dec./05	To Jun./06	From Jul./07
	Large	4 ton/hr	0.1	0.1 ^a (20) ^b	0.1 (1)	0.1 (1)
		2–4 ton/hr	1	1 (40)	1 (5)	1 (5)
	Medium	1–2 ton/hr	1	5 (40)	5 (10)	1 (5)
		0.2–1 ton/hr	5	5 (40)	5 (10)	5 (5)
	Small	0.025–0.2 ton/hr	5	–	10 (10)	10 (10)

^aFor hospital/medical waste incinerators installed between Jan./01 and Jul./04.

^bFor hospital/medical waste incinerators installed before Jan./01.

<Russia>

The Russian Federation takes an active part in the international cooperation in the field of environmental protection. Russia is a member of several international organizations and a party to many multilateral and bilateral conventions and agreements directed at solution of worldwide and regional environmental problems. A basis for current Russian environmental legislation is provided by the Constitution of the Russian Federation. There is a well-developed system of normative and legal documents represented by legislative acts as well as by their by-laws namely the Presidential and Governmental Decrees, Acts of federal executive bodies, Orders etc.

The Environmental Doctrine of the Russian Federation approved by Prescription of the Government of the Russian Federation N 1225-r, dated August 31, 2002 considers the control of use and distribution of toxic substances as one of the priority directions of activity in providing the environmental safety of Russia.

Major Laws and Regulations Concerning PTS in Russia:

1. Federal Law on Environment Protection (2002)
2. The Earth Code (2001)
3. The Water Code (2006)
4. Federal Law on Air Protection (1999)
5. Federal Law about Sanitary – Epidemiological Well-being of the Population (1999)
6. Federal Law about Safe Handling with Pesticides and Agrochemicals (1997)
7. Federal Law “On the food safety”, 2000-2008.
8. Act of the Russian Government “State monitoring of water biological resources”, 2008
9. Order of Federal Fisheries Agency “Monitoring of marine biological resources and environment quality in fisheries areas” 2009, 2010.

One of the major conceptual legal documents on issues concerning marine activities of the Russian Federation is the *Maritime Doctrine of the Russian Federation for the present period to the year 2020*.

Legal status of the economic activities in the Far Eastern Seas is determined by the following: *The Federal Law on Russian Continental Shelf*;

The Federal Act on the Internal Maritime Waters, Territorial Sea and Adjoining Zone of the Russian Federation;

The Federal Law on the State Border of the Russian Federation;

The Federal Law about Exclusive Economical Zone of the Russian Federation.

Russia signed the Stockholm Convention on POPs in 2002. Federal Law on 27.06.2011 № 164-FZ “Ratification of Stockholm Convention about POPs” was ratified by the Government of Russian Federation and President of Russian Federation in 2011.

In 2012 Russia acceded to the International Convention on the Control of Harmful Anti-fouling Systems on Ships, which prohibits the use of harmful organotins in anti-

fouling paints, used on ships and establishes a mechanism to prevent the potential future use of other harmful substances in anti-fouling systems. Convention covers not only ships entitled to fly the flag of the Parties but ships touching at ports of the Parties. The Russian Maritime Register of Shipping has made demands on anti-fouling systems in its rules. The Ministry of Transportation will check ships for their use of anti-fouling systems that meet international standards.

Russian basic legislative acts and their by-laws with short summaries aimed at ensuring the PTS control are listed below:

1. The Federal Law of the Russian Federation “On the Conservation of the Environment” N 7-FZ, dated January 10, 2002. It is legally concerned with the state environmental policy on ensuring the maintenance of favorable environment state and natural resources to meet the demands of recent and future generations, strengthen the law and order on environmental protecting and ensuring the ecological safety.

2. The Federal Law of the Russian Federation “On Fishery and Conservation of Water Biological Resources” N 166-FZ, dated December 20, 2004. It directed to preserve the water living resources *viz.* to maintain or restore the water living resources to a such level when their maximal stable catch and biological diversity can be ensure by means of scientifically substantiated implementation of measures on research, protection, reproduction and rational use of water living resources as well as protection of their habitat.

3. The Federal Law of the Russian Federation “On Ecological Expertise” N 174- FZ, dated November 23, 1995. It directed to prevention of negative environmental impact of economic activity including that which assumed to realize on specifically protected natural areas on the land and in the seas.

4. The Federal Law of the Russian Federation “On the Internal Waters, Territorial Sea, and Contiguous Zone of the Russian Federation” N 155-FZ, dated July 31, 1998. It determines ensuring the toxicological safety of the marine environment of the internal waters and territorial sea, prohibition or restriction on economic and other activity in specifically protected natural territories and fisheries protected areas of internal waters and territorial sea as the basic principles of protection and conservation of the marine environment and natural resources of internal waters and territorial sea.

5. The Federal Law of the Russian Federation “On the Continental Shelf of the Russian Federation” N 187-FZ, dated November 30, 1995. It regulates an economic activity on conservation and protection of marine environment and optimum use of living water resources on the continental shelf of the Russian Federation.

6. The Federal Law of the Russian Federation “On the Executive Economic Zone of the Russian Federation” N 191-FZ, dated December 17, 1998. It directed at protection and conservation of the marine environment of the exclusive economic zone.

7. “The Regulations on State Control of Environmental Protection (The State Ecological Control)” approved by Resolution of the Government of the Russian Federation N 53, dated January 27, 2009. It lays down an order of exercising the state control of environment protection (the state ecological control), which carries out to execution of environmental legislation and observe demands on environmental protection as well as ensure the ecological safety by public authorities of the Russian

Federation and subjects of the Federation as well as local bodies, artificial and natural persons.

8. “The Regulations of Formation of Fisheries Protected Areas” approved by Resolution of the Government of the Russian Federation N 603, dated August 12, 2008. It establishes a procedure of formation of fisheries protected areas which are the water bodies with fishery capabilities or their parts with adjoining territory, where special regime of economic and other activity is established to conserve the economically important water species and to create the favorable conditions for fishery and fish-breeding development excepting commercial one.

9. “The Regulations of Determination of Fisheries Conservation Areas” approved by Resolution of the Government of the Russian Federation N 743, dated October 6, 2008. It lays down the procedure of determination of fisheries conservation areas which are the territories adjoining the water bodies with fishery capabilities, where restrictions are introduced and special regime of economic and other activity is established to maintain the favorable conditions for the water living resources reproduction.

4.2. Existing management structures

<China>

In the central government, apart from the State Environmental Protection Administration, departments involved in POPs management include: the Ministry of Foreign Affairs, the National Development and Reform Commission, the Ministry of Science and Technology, the Ministry of Public Security, The Ministry of Civil Administration, the Ministry of Finance, the Ministry of Construction, the Ministry of Railways, the Ministry of Communications, the Ministry of Agriculture, The Ministry of Commerce, the Ministry of Health, the General Administration of Customs, the State General Administration for Quality Supervision and Inspection and Quarantine, the General Administration of Civil Aviation, the State Administration of Work Safety and the State Electricity Regulatory Commission.

Further, as the national coordination mechanism of the Chinese government for implementation of the Stockholm Convention, the National Coordination Group for Convention Implementation (NCG) is responsible for reviewing and implementing national guidelines and policies on POPs management and control, and coordinating important issues related to POPs management and convention implementation.

As the office under the NCG, Office of the National Coordination Group for Convention Implementation (CIO) is acting as the focal point for China’s implementation of the Stockholm Convention.

Based on the NIP and taking into consideration local needs, the local governments formulate related local policies and plans and organize their implementation, investigate into and deal with non-compliance activities; organize publicity, education and training

on local convention implementation activities; and assist in preparation and implementation of national projects relate to the convention implementation.

<Japan>

Under the Chemical Substances Control Law (CSCL), any producer or importer of a new industrial chemical with production and/or import amount of more than 1 ton per year has to submit information on the bio-degradability (stability under incubation with sewage), bioaccumulation (BCF data under standard protocol using fishes), toxicity (28 days repeated administration test to experimental animals, and mutation and genotoxicity tests using bacteria and mammalian cell lines, respectively) and ecotoxicity (acute or sub-acute toxicity against microalgae, daphnia and/or fishes) to a governmental committee. Based on the submitted information, the committee assessed the potential of risks of the proposed chemical to human beings and wildlife, and categorized the chemical to either of the following groups;

- 1) General Industrial Chemical Substances with no particular regulations on their manufacture or import,
- 2) Priority Assessment Chemical Substances, which are not considered to have low enough risks against human beings or wildlife, and are asked to provide their production / import amounts as well as their usages,
- 3) Class II Specified Chemical Substances, which are bioaccumulative and toxic chemicals and are asked to report their production / import amounts as well as to regulate their usages,
- 4) Class I Specified Chemical Substances, which are persistent, bioaccumulative and toxic, and are banned or strictly restricted their production / import / usages. However, even when chemicals are designated as Class I Specified Chemical Substance, they still can be used under stringent control if no alternatives exist and their uses would not threaten human health.

In addition to them, risk assessment of existing chemicals have been being conducted to reduce potential risks of using chemicals in modern society further. The whole chemical management system of Japan and the structure of CSCL are summarized in the Figures 2 and 3, respectively.

Measures under the Pharmaceutical Affairs Law:

Item 3, Paragraph 2, Article 14 of the Pharmaceutical Affairs Law (including cases where it shall read and apply pursuant to the provisions of the Article 83) stipulates that drugs, quasi-drugs and medical devices (hereafter referred to as drugs etc.), may be approved for marketing only after evaluation of their name, ingredients, composition, structure, dosage and administration, indications and usage, performance, side-effects etc.. Currently no drugs etc. containing the chemicals whose manufacture etc. is prohibited under the Stockholm Convention, are approved inside Japan.

Measures under the Foreign Exchange and Foreign Trade Law:

The Export Trade Control Ordinance under the Foreign Exchange and Foreign Trade Law stipulates that POPs are subject to the requirement of export approval under Article 2 of the ordinance as goods listed in 2.35.3 of the schedule of the said ordinance. Under the Stockholm Convention not only the export of POPs themselves but also products containing POPs are subject to export control. The Operational Notification of the Export Trade Control Ordinance specifically defines the scope of products which shall be subject to the requirement of export approval. Its Cautionary Notes on export set forth the conditions of export approvals such as the prohibition of the export of products containing PCB. Furthermore, the chemicals designated under the Stockholm Convention are itemized on the Published List of Imports as goods being subject to the requirement of import approval under the Import Trade Control Ordinance under the Foreign Exchange and Foreign Trade Law and their import is virtually prohibited. The Import Trade Control Ordinance regulates the import of POPs as a legal framework complimentary to the domestic laws governing the import of POPs (the Chemical Substances Control Law, the Agricultural Chemicals Regulation Law and the Pharmaceutical Affairs Law). The Export Trade Control Ordinance and the Import Trade Control Ordinance stipulate that the POPs wastes shall be subject to the requirement of import or export approval. These Ordinances, together with the relevant laws (the Waste Management Law and the Law for the Control of Export, Import and Others of Specified Hazardous Wastes and Other Wastes (Law No. 108 of 1992) etc.) ensure that stockpiles and wastes are disposed of in an environmentally sound manner in compliance with paragraph 1 (d) of Article 6 of the Stockholm Convention.

<Korea>

Ministry of Environment (MoE), National Institute of Environmental Research (NIER) and Korea Environment Cooperation (KECO) are involved in the POPs monitoring for terrestrial environment of Korea. Ministry of Environment (MoE) are managing the monitoring network for POP in Korea and providing information on POPs data public society through homepage website. National Institute of Environmental Research (NIER) is supporting this program as aspects of data analysis (spatial distribution and temporal trends), QA/QC protocol and standard method establishments. Korea Environment Cooperation (KECO) has performed the sampling, preparation and instrumental analysis of POPs in Korean environment.

Ministry of Ocean and Fisheries (MOF), National Fisheries Research and Development (NFRDI) and Korea Marine Environment Management Cooperation (KOEM) are involved in the POPs monitoring for marine environment of Korea. MOF is managing the POPs monitoring network, and the NFRDI had been performed the POPs monitoring during 2001-2009. KOEM has been responsible for the POPs monitoring since 2010. In the present, KOEM is supporting this program as aspects of data analysis (spatial distribution and temporal trends), QA/QC protocol and standard method establishments.

<Russia>

In the Russian Federation a number of federal executive bodies perform functions on ensuring the environmental protection and sustainable nature management.

The Ministries/ Agencies/ Committees Concerning PTS:

1. Ministry of Natural Resources
2. The Federal Supervisory Natural Resources Management Service
3. Ministry of Health
4. Ministry of Emergency Situation
5. Russian Federal Service on Hydrometeorology and Environmental Monitoring
6. The Federal Agency for Fishery of the Russian Federation

The Ministry of Natural Resources and Environmental Protection of the Russian Federation [www.mnr.gov.ru] is a basic federal executive body performing the functions on drafting the state policy and normative and legal regulation in the sphere of the environmental protection and conservation including the specifically protected natural areas as well as in the sphere of study, use, regeneration, and conservation of wildlife resources and their habitat.

The Federal Supervisory Natural Resources Management Service [<http://rpn.gov.ru>] is under the authority of the Ministry of Natural Resources and Environmental Protection of the Russian Federation. The Federal Supervisory Natural Resources Management Service is a federal executive body performing control and supervision functions in the sphere of nature management. This Service exercises control and supervision in the field of preservation, use, and reproduction of wildlife and wildlife habitat; in the sphere of the observance of legislation of the Russian Federation and international rules and standards concerning the marine environment and natural resources of internal seas, the territorial sea, exclusive economic zone, and on the continental shelf

The Federal Agency for Fishery of the Russian Federation [<http://fish.gov.ru>] is a federal body of executive authority performing functions on draft and exercise of state policy and legal regulation in the sphere of protection, rational use, research, preservation, and reproduction of marine living resources and their habitat. .

Monitoring programs of marine environment in the coastal zones of the Russian area of the Sea of Japan are operated by the State Environmental Monitoring Center (EMC) of Territorial Offices of Russian Federal Service on Hydrometeorology and Environmental Monitoring in Primorsky krai, Khabarovsk Krai and Sakhalin oblast.

Quality of marine environment and commercial fish and seafood safety in fisheries areas are estimated by the research institutes of the Federal Agency for Fishery: Pacific Research Fisheries Centre (TINRO-Centre) in Vladivostok, Khabarovsk Branch of TINRO-Centre in Khabarovsk, Sakhalin Research Fisheries Centre in Yuzhno-Sakhalinsk.

4.3. Monitoring methods, objects and standards

<China>

In China, HCHs and DDTs are covered in most state-level environmental standards, e.g. Environmental Quality Standards for Surface Water (GB 3838-2002), Quality Standard for Ground Water (GB/T 14848-9), and Environmental Quality Standards for Soils (GB 15618-1995), PCBs are included in Environmental Quality Standards for Surface Water (GB 3838-2002), BaP and Heavy metals such as Mercury, are included in Sea Water Quality Standard (GB 3097-1997), while other POPs are not contained yet. Accordingly, promulgated standard methods on POPs monitoring are limited, such as Water Quality- Determination of BHC and DDT - Gas Chromatography (GB7492 -87), Standard Examination Methods for Drinking Water Organic Parameters (GB5750.09-2006), the Specification for Marine Monitoring Part 4: Seawater Analysis (GB 17378.4-2007), Soil Quality- Determination of BHC and DDT - Gas Chromatography (GB/T 14550-93) and Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-p-furans by Isotope Dilution HRGC/HRMS (HJ 77-2001), etc., and most of them focus on water bodies. Amounts of analysis methods on other POPs are in process in China. For the early reported and published data about POPs levels in water, sediment and soils, various methods for sampling and analysis of POPs have been applied, so as that analytical procedures, criteria of QA/QC and data validation were quite different. In detail, many extraction methods, such as liquid-liquid extraction, solid-phase extraction, Soxhlet extraction, automatic Soxhlet extraction, supersonic extraction, microwave assisted extraction, and accelerated solvent extraction, were applied for POPs in water, sediment, soil and particulate matter. Common clean-up steps were to use sulfuric acidified silica gel cartridges, multiple layer chromatography columns and GPC. GC/MS-EI, GC/MS-NCI, HRGC/HRMS and GC/MS/MS were effective for organochlorinated pesticides, PCBs, PCDD/PCDFs and PBDEs measurement respectively in environmental background samples. HPLC/MS/MS with solid phase extraction was developed for analyzing perfluorinated alkyl acids, sulfonates and their salts.

Atmosphere is regarded to be an effective environmental media for monitoring of POPs at global/regional scale. In the global monitoring programs for POPs, the recommended methods for sampling and analysis of POPs in the air and human samples were provided as "Guidance on the Global Monitoring Plan for Persistent Organic Pollutants". And PAS is becoming more and more an effective complementary sampling technique for the conventional hi-volume atmospheric sampling, with its extraordinary advantage in synchronic monitoring of POPs in the atmosphere across vast territories.

<Japan>

In Japan, environmental monitoring started in 1974 when Environment Agency was established. The monitoring was shifted to yearly monitoring from 1978 with respect to wildlife, and updated from 1986 to include water and bottom sediment with a

view to understanding and monitoring long term trends of persistence of chemical substances in the environment. Considering the accumulation and continuity of such data, the measurement has been conducted, in principle, using the same sampling and analytical methods with occasional minor adjustments as necessary. A major revision and up-dating of the long term monitoring program was conducted in 2002 to cover basically all POPs except for unintentionally produced dioxins/furans/*dl*-PCBs, which were conducted independently under the different law, by using high resolution GCMS in order to reveal baseline levels of POPs in Japan before entry into force of the Stockholm Convention. This investigation aims to monitor the quantity of POPs in Japan and verify the effectiveness of the measures for eliminating and reducing their emission in the implementation procedure of Stockholm Convention. Currently four environmental media, i.e., air, water (both terrestrial water and coastal sea water), sediments and biota (fishes, bivalves and birds) are the target of the monitoring. The sampling sites are selected in order to reveal yearly changes in general environmental condition of Japan; i.e., each site is expected to represent local background levels rather than the emission from particular hot-spots. C.a. 35 air sampling sites are set all over Japan at around 100 km interval between the sites, and POPs in the air has been collected twice a year (late summer and early winter) by high volume sampler for the consecutive three days (1,000 m³/day x 3), or seven days sampling with reduced rate (1,000 m³/week x 1). For the water POPs monitoring, typically 20 L of water was sampled and passed through a C18 disk to trap POPs. Sediment samples and biological samples were extracted with organic solvent, and all the extracts were analyzed by high resolution GCMS after appropriate clean-up procedure. The data was evaluated by expert committee including QA/QC procedures, and approved data was reported every year from MOE (“Chemicals in the Environment”, or so-called “black book (KUROHON in Japanese)”).

Development of analytical methods has also been conducted to monitor various chemicals including POPs, newly added POPs and their candidates. Developed methods are assessed of their performance, applicability and validity by the committee of experts in environmental analysis, and approved ones are compiled as a book and published every year by MOE (called “white book”).

Marine environment monitoring has been conducted by another section of the MOE Japan. In addition to this, Japan Coast Guard has been conducting ocean pollution survey along several transects from coastal environment to the peragic regions surrounding Japan archipelago. Both of the data were compiled in the previous section on environmental monitoring of PTS. The nationwide monitoring of dioxins started in 1985 with respect to bottom sediment and aquatic animals in the rivers, lakes, marshes and sea waters and in 1986 with respect to the ambient air. In 1998, water and soil as well as wildlife (fishes, amphibian, birds, terrestrial and marine mammals) also became subject to nationwide monitoring of dioxins. In the same year, dioxins levels in human samples (bloods) and foods were analyzed, and these samples have been monitored continuously from 2002. In human blood monitoring, PFOS and PFOA were added in 2008. In 2011, total mercury analysis in blood, and total cadmium and arsenic speciation analysis as well as metabolites of pesticides and plasticizers analysis in human urine were added in the program, and all the original POPs were analyzed together in human blood samples in 2012. Some of the human monitoring data until

middle of 2000's were compiled and reported in the first regional report of Asia / Pacific under the Stockholm Convention. Since 2000, local public authorities have been implementing a larger scale monitoring as a continuous monitoring under the Dioxins Law. Summary of these monitoring data were described in “Section 3.4. Current status and temporal trends of PTS concentration in the environment”.

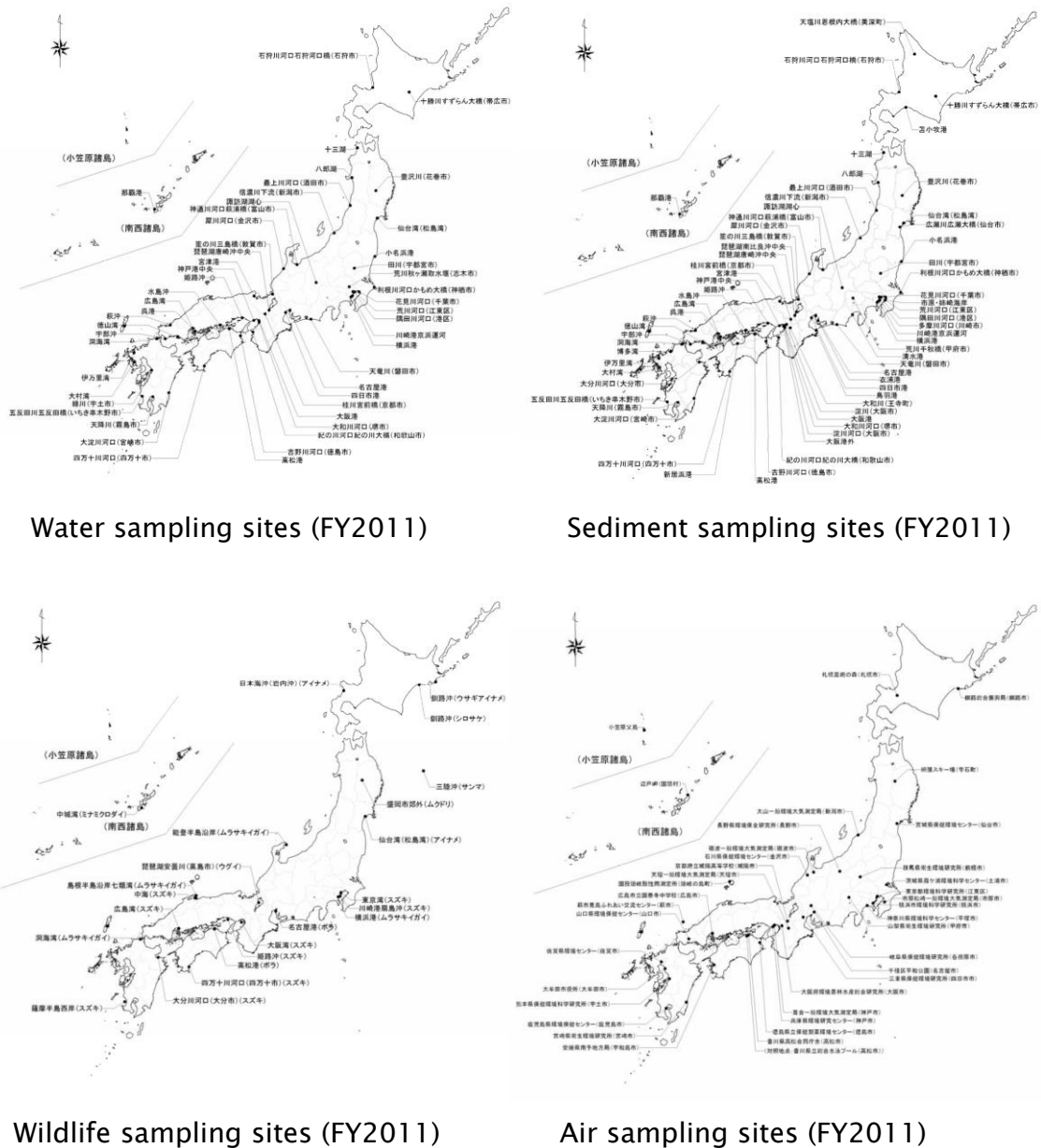


Figure 20. Yearly POPs monitoring sites under “Chemicals in the Environment” program by the Ministry of the Environment, Japan

The local public authorities monitor PCB in addition to other chemicals, heavy metals and other elements, and indices of water qualities, such as BOD, COD, DO etc., in the rivers, lakes, reservoirs and sea waters as part of the regular-observation for the public water quality under the Water Pollution Control Law 14 (Law No.138 of 1970). PCB standards have a long history (established in 1971) and the monitoring method based on a traditional packed column GC-ECD has not been changed due to its clarification criteria (“not detectable” by the designated method). ECD detector and mass spectrometry show different sensitivity profiles against PCB congeners; for example, ECD has generally lower sensitivity against lower chlorinated congeners among PCB than mass spectrometry. Therefore these two detectors are not comparable, and may provide us with quantitatively different data against the same sample. A modern GC/MS technique has been used for environmental monitoring, emission inventory analysis as well as wastes measurements so that even lower chlorinated PCBs, such as mono- / di-chlorinated PCB, will be sensitively detected and controlled appropriately. In fact, there have been several PCB and other POPs contamination incidents detected by the modern analytical method. Recent detection and notification of PCB contamination in commercial products include the cases of chlorinated paraffins (Takasuga et al. 2012), pigments (Anezaki & Nakano, 2013), and silicone-based glues (Anezaki & Nakano 2013, METI 2013).

Among POPs chemical substances, environmental standards and emission standards have been set for dioxins and PCB. The Japanese environmental standards are compiled in Table 7. The standards for dioxins were set based on TDI (tolerable daily intake) = 4 pg-TEQ/kg/day, and the analysis of dioxins are conducted based on high resolution GC/MS method (hrGC/hrMS).

Chemicals	Media	standard	unit	Method
Dioxins*	Ambient air	0.6	pg-TEQ/m ³	QFF+PUF, hrGC/hrMS
	Water	1	pg-TEQ/L	JIS-K0312
	Sediments	150	pg-TEQ/g dry	Soxhlet ext, hrGC/hrMS
	Soils	1,000	pg-TEQ/g dry	Soxhlet ext, hrGC/hrMS
PCB	Water	not detected		packed GC-CED
	Ground water	not detected		packed GC-CED
	Soils	not detected		water ext, GC-ECD

*: Total TEQ of all TEF-assigned PCDDs, PCDFs, dl-PCBs

The standards of dioxins in emissions to the air and effluent water are compiled in Table 8-9. In the emission to the air, different standard values were set to different industrial activities and facility types according to their total activities in order to reduce total dioxins emission to the environment in efficient manner. In the regulation of effluent water, specific types of facilities with higher tendencies / risks of dioxins emissions are list-upped and regulated. The same standard, 10 pg-TEQ/L, is also applied to the waste water from the terminal waste disposal facilities.

Table 8. Emission standards of dioxins to the air from facilities (pg-TEQ/m³)

Type of Specified Facilities	Scale of facilities (Capacity of incineration)	Standards for new facility	Standards for existing facility
Waste incinerators (hearth area is more than 0.5 m ² or capacity of incineration is more than 50 kg/h)	More than 4t/h	0.1	1
	2t/h - 4t/h	1	5
	Below 2t/h	5	10
Electric steel-making furnaces		0.5	5
Sintering facilities for steel industry		0.1	1
Facilities for recovering zinc		1	10
Facilities for manufacturing aluminum base alloy		1	5

Table 9. Effluent water standards of dioxins in the specified facilities (pg-TEQ/L)

Type of Specified Facilities	Standard
<ul style="list-style-type: none"> · Bleaching facilities using chlorine or chlorine compounds used for manufacturing sulfate pulps(kraft pulps) or sulfite pulps. · Cleansing facilities for acetylene used for manufacturing acetylene by carbide method · Cleansing facilities for waste gas used for manufacturing potassium sulfate · Cleansing facilities for waste gas used for manufacturing alumina fiber · Cleansing facilities for waste gas which is released from firing furnaces used for manufacturing supported catalysts (limited to those that use chlorine or chlorine compounds) · Cleansing facilities for dichloroethane used for manufacturing vinyl chloride monomer* · Sulfuric acid concentration facilities, cyclohexane separation facilities, and waste gas cleansing facilities used for manufacturing caprolactam (limited to using nitrosyl chloride) · Water washing facilities and waste gas cleansing facilities used for manufacturing chlorobenzene or dichlorobenzene · Filtration facilities, drying facilities and waste gas cleansing facilities used for manufacturing sodium hydrogen 4-chlorophthalate · Filtration facilities and waste gas cleansing facilities used for manufacturing 2,3-dichloro-1,4-naphthoquinone · Nitro-derivative and its reductant separation facilities, nitro-derivative and its reductant cleansing facilities, dioxazineviolet cleansing facilities, and hot-air drying facilities used for manufacturing dioxazineviolet · Cleansing facilities for waste gas and wet dust collecting facilities relating to roasting furnaces, melting furnaces or dry kilns used for manufacturing aluminum or aluminum-base alloy · Refining facilities, waste gas cleansing facilities, and wet dust collecting facilities used for recovering of zinc (limited to zinc recovery from dust that is generated from electric steel-making furnaces and collected by dust-collector) · Filtration facilities, refining facilities and waste gas cleansing facilities used for collecting metals from spent supported catalysts (excluding collection methods that treat catalysts with sodium carbonate in a roasting furnace or extract metals with alkalis (limited to those that do not treat in a roasting furnace)) · Cleansing facilities, wet dust collecting facilities, and ash storing facilities which are related to waste incinerators (hearth area is more than 0.5m² or capacity of incineration is more than 50 kg/h) and discharge sewage or waste solution* · Resolving facilities for waste PCB or PCB-processed products · Cleansing facilities for PCB contaminated matter or PCB-processed products · Plasma reactors, waste gas cleansing facilities, and wet dust collecting facilities used for breaking down chlorofluorocarbons or hydrochlorofluorocarbons (limited to those employing the plasma reaction, waste mixed combustion, submerged combustion, or superheated steam reaction method) · Facilities for disposing water discharged from plants or business places with facilities mentioned above · Terminal treatment facilities for sewerage relating to facilities mentioned above 	10

<Korea>

Tables 5 and 6 are showing the nationwide monitoring program of POPs in terrestrial and marine environment of Korea. For terrestrial environment, Ministry of Environment (MoE) has been responsible for POPs monitoring program. Ministry of Ocean and Fisheries (MOF) and the National Fisheries Research and Development Institute (NFRDI) have monitored the POPs and related compounds in marine environment. Because TBT and polycyclic aromatic hydrocarbons (PAHs) are conventional contaminants in coastal environment, these contaminants were included as monitoring components. However, MoE, NIER and KECO are only watching POPs under Stockholm Convention. In recent years, both ministries (MoE and MOF) are trying to add emerging POPs such as polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs) as nationwide monitoring components, because these contaminants are included as new POPs in 2009. Sampling locations for terrestrial and marine environments are showing in Figures 18 and 19, respectively.

Table 5. Nationwide monitoring program for POPs in Korean environments

	Atmosphere	Soil	Freshwater	Freshwater sediment
Sampling sites	37	57	36	30
Frequency	4 times/year	1 time/year	2 times/year	1 time/year
Survey period	4 seasons (Spring, summer, autumn, winter)	April to May	April to May October to November	November to December
Monitoring items	Polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans (PCDD/Fs) ¹ , Polychlorinated biphenyls (PCBs) ² , DDTs and metabolites ³ , Hexachlorobenzene (HCB), Aldrin, Dieldrin, Toxaphene, Mirex, Heptachlor, Chlordanes			

¹2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF.

² Dioxin-like PCBs (PCB congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189).

³ *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDT, *o,p'*-DDT.

Table 6. Nationwide monitoring programs for POPs in marine environment of Korea

Environmental media	Monitoring items	Sampling period	Sampling intervals	Sampling locations
Seawater ¹	Polychlorinated biphenyls (PCBs) ² , Tributyltin (TBT)	February to May	1 time/year	25 coastal sites
Marine sediment	Polychlorinated biphenyls (PCBs), DDTs and metabolites ³ , Hexachlorohexanes (HCHs) ⁴ , Hexachlorobenzene (HCB), Polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans (PCDD/Fs) ⁵ , Tributyltin (TBT), Polycyclic aromatic hydrocarbons (PAHs) ⁶			
Marine bivalves (Mussels or oysters)	Polychlorinated biphenyls (PCBs), DDTs and metabolites, Hexachlorohexanes (HCHs), Hexachlorobenzene (HCB), Polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans (PCDD/Fs), Tributyltin (TBT), Polycyclic aromatic hydrocarbons (PAHs)			

¹Seawater monitoring was stopped since 2010.

²IUPAC No. CBs 8, 18, 28, 29, 44, 52, 87, 101, 105, 110, 118, 128, 138, 153, 170, 180, 187, 194, 195, 200, 205 and 206.

³*p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDT, *o,p'*-DDT.

⁴ α -HCH, β -HCH and γ -HCH (lindane).

⁵16 non-alkylated PAHs recommended by the US EPA: Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene.

⁶2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF.

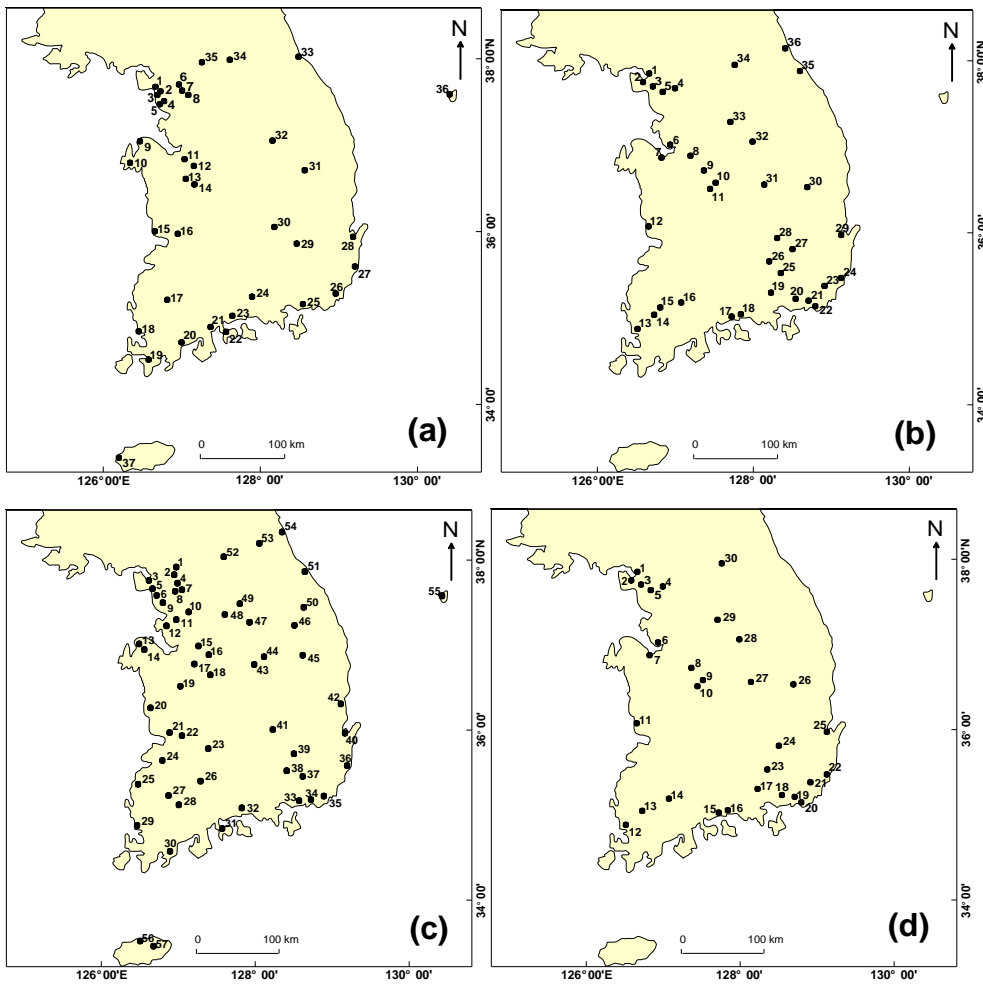


Figure 18. Nationwide monitoring map for POPs in (a) air, (b) water, (c) soil and (d) sediments from Korea (KMOE, 2001, 2002a,b, 2003a,b, 2004a,b,c,2005a,b,c).

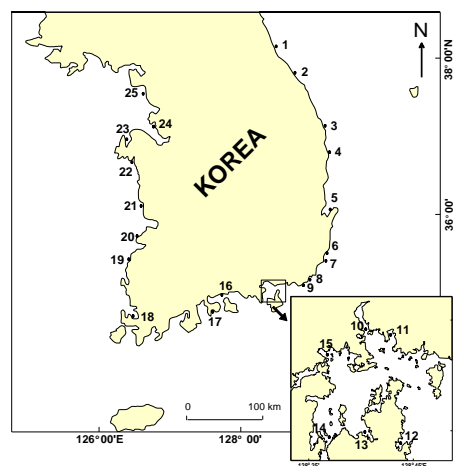


Figure 19. Nationwide monitoring map for POPs in marine sediments and bivalves (mussels and oysters) collected from Korean coastal waters (Moon et al., 2007; Choi et al., 2010a, 2011b).

<Russia>

In the Russian area of NOWPAP region sea water and bottom sediments sampling is conducted quarterly (4 times/yr) on 28 stations reported in the Peter the Great Bay, in Amur River mouth and in the coastal waters of Sakhalin Island.. Monitoring items include α , β , γ -HCH and DDT, DDD, DDE in seawater and bottom sediments.

In offshore zones of the central region of NOWPAP monitoring items include HCH, DDT and PCB in seawater, commercial fish, crabs, shrimps and seaweeds.

Methods of pesticides extraction include some steps: homogenization of frozen tissues, extraction by organic solvents, clean with sulphuric acid and concentration by evaporation.

The main methods for HCH, DDT and PCB determination in sea water and bottom sediments are Gas Chromatography (GC), in biota – GC and GC-MS.

Sampling and chemical analysis are carried out according to official recommendations of the State Committee of Russia on Standards, Metrology and Certification No. 52.24.509-96, “Implementation of Measures Regarding the Quality of Hydrochemical Information”, and No. 52.18.599-98 “Implementation of Inspections of the Accredited Laboratories (Centers)” and various Guidelines (1977; 1993), and Procedures (1979; 1982; 1984) recommended by Federal Service on Meteorology and Environmental Monitoring.

Table 10. Major Environmental Standards (Maximal Permitted Concentrations) on PTS in Russian Federation

Object	DDT	HCH	PCB	Dioxin	Org.Hg	Heptachlor
Drinking water	absent	absent	0,5 mkg/l	–	–	-
Freshwater	absent	absent	0,5 mkg/l	20 pg/l	0,1 mkg/l	0,001 mg/l
Water on fishing areas	10 ng/l	10 ng/l	10 ng/l			
Fish and seafood	200 mkg/kg	200 mkg/kg	100 mkg/kg.	88 ng/kg lipids	0,5 mg/kg	absent

(Maximal permitted concentrations of pollutants for fisheries waters...1999)

Maximal permitted concentrations (MPC) on POPs in bottom sediments in Russian Federation are not developed.

Main objects of monitoring in coastal areas in the Russian area of NOWPAP region are seawater and bottom sediments and some species of marine organisms: laminaria, mussels, crabs, shrimps, and commercial fish: flounders, Pacific herring, Walley Pollack, Pacific salmons, Pacific cod, Safrá cod and Saury. MPC for some PTS are presented in Table 10.

4.4. Measures to reduce intentionally and non-intentionally produced PTS

<China>

The Chinese government solemnly commits to fulfill the relevant responsibility specified by the Convention, comply with the national strategy of sustainable development and incorporate requirements of Convention implementation into the relevant plans of the state, given the support by the Conventions's financial mechanism and technology transfer mechanism. Additionally, China commits to establish and improve corresponding administration systems, develop and implement related policies and necessary action measures so as to achieve the control objectives required by the Convention, i.e., to reduce or eliminate the production and use of pesticide POPs, to eliminate the use of PCBs, to reduce or eliminate releases of unintentionally produced POPs, and to gradually take measures to reduce or eliminate POPs releases from POPs stockpiles, wastes and contaminated sites.

China will, by combining actions for Convention implementation with the objectives of “promoting the optimization and upgrading of industrial structure” and “constructing a resource-saving and environment-friendly society” set out in the Outline of the Twelfth Five-Year Plan, adjust product and industrial structures, promote cleaner production, develop a cyclic economy, boost effective utilization of resources, create new economic growth openings, increase employment opportunities, improve the environmental awareness of the whole society and the level of public participation, and ultimately promote sustainable development.

In addition to the aforementioned, China will, based on its actual situation, improve policies and regulations designed to fulfill the objectives of Convention implementation, strengthen institutional capacity building, take relevant strategies and actions, and carry out Convention implementation activities by stage, region and industry, so as to achieve the following objectives:

(1) Prohibit and prevent the production and import of aldrin, dieldrin, endrin, heptachlor, hexachlorobenzene, toxaphene and PCBs; begin to eliminate the production, use, import and export of chlordane, mirex and DDT by 2009, except for the production and use of DDT as limited intermediate in a closed-system site and for acceptable purposes; and achieve the environmentally sound management of currently used equipment containing PCBs in demonstration provinces and identified high-risk equipment containing PCBs currently used by 2015;

(2) Apply BAT/BEP measures for new sources in key sectors with unintentional POPs release by 2008, and apply prioritized BAT/BEP measures for existing Dioxins release sources in key sectors of key regions, and basically control the increasing trend of dioxins release by 2015;

(3) Improve support systems for the environmentally sound management and disposal of POPs wastes by 2010 and begin to achieve the environmentally sound management and disposal of identified POPs wastes by 2015.

<Japan>

1. Regulation of production, use, import and export. Production, use, import and export of the chemicals designated under the Stockholm Convention are prohibited or strictly regulated under the Chemical Substances Control Law, the Agricultural Chemicals Regulation Law, the Pharmaceutical Affairs Law (Law No. 145 of 1960), the Export Control Ordinance (Ordinance No. 378 of 1949) and the Import Control Ordinance (Ordinance No. 414 of 1949) based on the Foreign Exchange and Foreign Trade Law (Law No. 228 of 1949). These measures will be described for detail in Section 3 of Chapter 3. Currently all the POPs (original 12 and newly added ones) and organotins (TBTO, TPT) are designated as Class 1 specified chemical substances and are either prohibited or strictly regulated its production, import and use.

2. Measures regarding unintentional production. In Japan under the Dioxins Law, PCDDs, PCDFs and coplanar PCBs are defined as the dioxins. Environmental quality standards, tolerable daily intake (TDI) and emissions standards for effluent water and emission gases from specified facilities are set forth. A government plan to reduce the release of dioxins is established, and various release reduction measures are promoted in a comprehensive manner. According to the current scientific knowledge, the source categories and the formation processes of PCB and Hexachlorobenzene (HCB) are considered to be similar to those of dioxins. Therefore, it is assumed that the release of PCB and HCB has also been reduced through the dioxins reduction measures. Efforts to increase accuracy of emission inventories of dioxins, PCB, HCB and PeCB as well as to assess efficiencies of reduction by different techniques have been conducted by analyzing emission data in selected sources from major source categories every year. Under the Law concerning Reporting etc. 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 PCB are subject to the requirements of the PRTR (Pollutants Release and Transfer Register) system.

3. Measures regarding stockpiles and wastes.

(1) Collection and detoxification of agricultural chemicals containing POPs

It is prohibited to distribute or use agricultural chemicals containing 14 chemicals listed under the Stockholm Convention or endosulfan as the active ingredient, respectively. Additionally, manufacturers and the like have collected these agricultural chemicals and have either stored them safely or detoxified them. In Japan, organochlorine agricultural chemicals including certain POPs (aldrin, dieldrin, endrin, DDT and BHC; hereafter referred to as "POPs agricultural chemicals") used to be stored under the ground. According to a survey done by the Ministry of Agriculture, Forestry and Fisheries, the total amount of stored POPs agricultural chemicals and the number of the stored places identified were 4,400 tons and 168 places, respectively. Approximately 4,000 tons of these POPs agricultural chemicals were already excavated and handled properly by February 2011.

(2) Study for proper disposal of POPs wastes

Stored POPs agricultural 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 of under the Dioxins Law and the Waste Management and Public Cleansing Law (Law No.137 of 1970, hereafter referred to as the Waste Management Law). Wastes containing PCB are disposed of under the PCB Special Measures Law. In 2009, “Guideline for detoxifying waste electrical machinery etc. contaminated by small amount of PCB – incineration” and “Guideline for collecting and transporting waste electrical machinery etc. contaminated by small amount of PCB (Revised August 2011)” were issued to promote safe and definite detoxification, collection and transport of waste electrical machinery etc. contaminated by small amount of PCB. To understand the actual wastes emissions and formulate their disposal standards, etc. for other POPs wastes, “Technical Documents on Treatment of Agricultural Chemicals containing POPs” and “Technical Documents on Treatment of Wastes containing PFOS” were formulated based on the outcomes of the above mentioned development of detoxification methods etc. for agricultural chemical wastes containing POPs and wastes containing perfluorooctane sulfonic acid (PFOS) or its salts.

<Korea>

In principal, intentional byproducts such as organochlorine pesticides have been banned for production and use in South Korea. However, trace levels of OCPs (e.g. DDT and HCHs) are still detected in Korean environment. With public concern, international conventions (Stockholm Convention) to reduce or eliminate emissions of POPs in South Korea took effect in May 2004. The South Korean Government, as a signatory participant of the Stockholm Convention on POPs, plans to ratify the convention. Then the government is obliged to submit a National Implementation Plan (NIP) to minimize POPs emission and update the plan and provide a status report every two years from the time of ratification (Stockholm Convention on Persistent Organic Pollutants, 2001). Therefore, it is inevitable that a scientific assessment and review of the domestic status and history of the POPs pollution including emissions, contamination levels (or distribution), exposures, and risks will be needed. This information will be disseminated to the public and also used to develop efficient control strategies to minimize exposure of humans and the wildlife to the POPs.

<Russia>

The main ways to reduce or eliminate emissions of intentionally produced PTS:

1. Substitutes can be identified, so that the production or use of PTS can be prohibited.
2. If substitution cannot completely replace a PTS, its use can be restricted to only essential applications.
3. Certain PTS components in products may be banned, so as to reduce or eliminate PTS components entering the environment.

Unintended byproduct emissions may be reduced through the implementation of stricter environmental standards.

5. Recommendations for future regional activities and priorities

East Asia is rapidly developing its economy in terms of industry as well as agriculture, fishery and mining/oil production activities to support large human population. Production and usage of variety of chemicals as well as unintentional products, particularly those in the PTS group, have been increasing in East Asia dramatically, and they have strong potential to affect the NOWPAP region. Establishment of sound chemical management in the region is of utmost importance, and harmonized, well organized environmental monitoring, inventory compilation, model development and toxicological/ecotoxicological research on PTS chemicals are urgently needed. There still remain large gaps in terms of:

- Harmonized environmental monitoring covering the whole NOWPAP region;
- Emission inventory of PTS in the region;
- Models of PTS covering entire region;
- Toxicity/ecotoxicity data, particularly on wildlife species in the region, of PTS and other chemicals.

In the NOWPAP region, continuous and nation-wide environmental monitoring of POPs has been conducted in Japan and South Korea. Environmental monitoring plays key role in the chemical management procedure: to know the status of the environment, to identify emerging chemicals of concern, to improve reliability and to assess validity of a model, and to evaluate effectiveness of current chemical management procedure. Development of cost-effective sampling and analytical methods for variety of PTS is important, and environmental specimen banking will be efficient and effective supplementary activity to support environmental monitoring. In Japan, all the biological samples and sediments so far collected and analyzed are archived in ESB at NIES; previous data can be confirmed/validated in the future by more advanced analytical procedures, and temporal trends of newly identified pollutants can be revealed by retrospective analysis of archived samples. Construction of ESB has been conducted in other countries in the region, and a net of ESBs in the region as well as in global scale will further improve the effectiveness of environmental monitoring in the region.

Development of proper models reliably describing fate of chemicals in the environment is also important and will help and support establishing sound chemical management in the region. Compilation of reliable inventory information is indispensable to use such models for estimating fate and designing proper management strategy for chemicals. Major difficulties may come from rapid development and continuous changes in regional economy and industries, which will accompany with continuous changes in the emission inventory of many chemicals. Efforts will be needed to establish mechanism to capture the industrial activities and their changes in the aspect of usage of chemicals simultaneously. Some of the PTS chemicals show large LRT potential, far exceeding the size of the NOWPAP region; in such cases, the boundary condition, i.e. the flow of chemicals from the outside of the region, should also be carefully evaluated and included in the consideration. Other chemicals may affect the region by trading activities rather than natural transport phenomena, and thus need

detailed information on the lifecycle and international trade of products and wastes containing such chemicals for proper management.

Detection and assessment of ecotoxicological effects of chemicals to the wildlife species are difficult and challenging research topics. There have been international efforts to establish test methods of ecotoxicity of chemicals under the OECD but these are primarily aiming to assess the ecotoxicity of individual chemical, and assessment of ecotoxicity by a mixture of chemicals is still a formidable task. Various candidates of “endpoints” by the effect of particular type of chemicals to organisms have been proposed based on basic research on the mechanisms of toxicity, although many of them have been recognized as exposure marker rather than toxic effect marker, and proper interpretation of their levels in wildlife species awaits further basic research on the topic. Toxicity/ecotoxicity data are needed to prioritize chemicals to be controlled/monitored, and encouragement of relevant research in the region as well in the world is recommended. Considering difficulties and time-consuming nature of such research, proper and harmonized use of precautional approach (or precautional principle) in chemical management procedure is also needed.

Future activities proposed from each member country are listed below.

1. Monitoring parameters, methodologies and technical standards/criteria based on studies from NOWPAP member countries need coordination. Each NOWPAP country currently conducts its own pollution monitoring. However, for some PTS, especially trans-boundary pollutants, identifying their sinks and sources, as well as their environmental impacts, is difficult without an integrated, regional monitoring network that is staffed with trained technical personnel. Regional research is necessary on deposition of contaminants into marine and coastal environments. Standardization of monitoring methodologies and detection limits may be the initial steps towards capacity strengthening of monitoring of PTS.
2. It would be desirable to create a database on PTS in the framework of NOWPAP POMRAC.
3. Studies on the effects of different PTS on sensitive animal species are also essential. Development of various biomarkers could provide with effective early warning systems.
4. Researchers of each country might determine PTS levels in mussels from coastal areas. Comparison of the results could form the basis of Joint International Project “The current PTS levels in mussels from coastal waters in NOWPAP countries” which provides new information on PTS level and trends in the NOWPAP region.
5. It would be helpful to conduct a joint Russia-Korea-Japan-China workshop on PTS problems and to share available information.

Capacity building priorities of **China** on the Stockholm Convention for the near future (2007-2010) were identified (NIP of China, 2007), and include activities in several directions:

(1) Strengthening the capabilities of Convention implementation institution, which in turn includes:

a) Strengthen the decision making and coordination capabilities of the NCG, so as to promote scientific decision making on Convention implementation from such aspects as policies, technology and fundamental research;

b) Strengthen capabilities of the members of the NCG regarding policy making, basic investigation and research, data collection, information exchange and communication, and supervision and management;

c) Improve the implementation capabilities of the Convention Implementation Office;

d) Improve Convention implementation awareness at the local level, strengthen capabilities for developing relevant local policies, regulations and plans, and enhance capabilities for implementation of activities for Convention implementation, fund procurement, basic investigation and research, and information collection and reporting;

e) Strengthen the capabilities of industrial associations regarding organization, coordination and publicity relating to Convention implementation in relevant fields.

(2) Improvement of the regulatory framework. Pursuant to requirements of Convention implementation, draft plans for the development or revision of relevant laws, rules and regulations, and incorporate them in the relevant legislative calendars of the state to make regulations on such aspects of POPs as production, use, import and export, waste and release; and develop/revise standards and technical specifications pertaining to POPs.

(3) Establishment of economic policies and financial mechanisms on Convention implementation. Establish and improve economic policies that help to prevent, reduce and eliminate POPs hazards, as well as environment protection input and operational mechanisms, aiming at ensuring the implementation of action plans for Convention implementation.

(4) Improvement of POPs monitoring capacity. Improve the existing system of monitoring networks, include POPs in monitoring targets, establish standard analysis methods for POPs, and build quality control and management systems for POPs laboratories, thus forming the capacity for conducting nationwide monitoring of POPs and for getting a grip on the status of POPs release and pollution, so as to provide a scientific basis for the management and control of POPs and to evaluate objectively the effectiveness of Convention implementation.

(5) Acceleration of technological development and promotion.

a) Evaluate the technological requirements for Convention implementation, identify economically and technically feasible technologies, and establish a technology assessment system and a technology transfer center;

b) Develop systems on technological registration, certification and incentives, thus promoting the independent development and broad application of alternatives/alternative technologies for POPs which urgently need to be phased out, waste treatment and disposal technologies, and BAT/BEP for the control of Dioxins releases.

(6) Conducting publicity and education on Convention implementation. Carry out publicity and educational activities relating to the hazards of POPs and to national Convention implementation actions, aiming at decision-making levels (government departments at all levels and concerned ministries and commissions), technology levels (industries and associations involved in projects), groups directly involved in the production, distribution and use of POPs, and the public in regions with relatively intensive releases of POPs, so as to begin to create a social atmosphere that all people have a deepening understanding of POPs, from attention to concern and from understanding to cognition, and to create conditions for winning wide-ranging support for China's Convention implementation actions from all ranks at home and abroad.

Based on nationwide monitoring program, more comprehensive monitoring strategies for POPs would be strongly needed. For instance, the emerging POPs such as polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs) should be included as nationwide monitoring component in **Korea** environment. In addition, the international cooperation has to be considered, as an aspect of a contribution to the international monitoring of global scale. Therefore, continuous monitoring and ecotoxicological studies are required to understand the contamination status of POPs and emerging contaminants in marine ecosystems and to accurately evaluate the potential risks to marine mammals in Korea from exposure to these contaminants. As well, long-term studies are needed on trans-boundary LRT of POPs in South Korea.

6. Conclusions

PTS chemicals are present in the environment for a long time after their release. During that time, PTS are transported over long distances from the emission sources in gaseous, dissolved and particulate forms through air and seawater at regional and global scales. In addition, many of PTS have been used in commercial products, and thus transported through international trading activities among countries as products and/or wastes containing PTS. Transboundary transport and subsequent spread of pollution in various countries are important issues in PTS management. These are major reasons why international and regional activities are required to manage and control PTS in an appropriate manner.

PTS chemicals are persistent, toxic, and bioaccumulative, and thus have to be controlled properly. Many of them, on the other hand, have been used as beneficial chemicals supporting our daily life, and are already present in our houses, towns, around factories, waste dumping sites, and even natural environment. On the one hand, it is necessary to conduct careful check and elimination of PTS from industrial/commercial products regularly in order to prevent PTS production and their use. On the other hand, it is necessary to conduct careful environmental monitoring, identification of emission sources, toxicological studies and risk assessment procedures in order to protect wildlife and human health from the PTS exposure. In particular, it should be noted that there is huge human population in/around the NOWPAP region. There are also agricultural/industrial activities as well as international trade in order to support the human population and their life. Thus there is a high demand of beneficial chemicals, such as agrochemicals, pharmaceuticals and personal care products, plastics and their additives including plasticizers and flame retardants, UV filters, synthetic masks, etc., in/around the NOWPAP region. Another issue is that the central NOWPAP region is semi-enclosed in terms of seawater circulation. Once the chemicals flow into that central region from surrounding environments and long range atmospheric transport, the PTS will stay for long-term periods and be accumulated and biomagnified in the marine food web, including top predators.

Large amounts of data concerning POPs and other PTS levels in the environment from the NOWPAP region have been documented. In addition, information on source inventory has been accumulated, and measures/countermeasures have been set in the NOWPAP countries. The data and information are summarized in this publication. There still remain large gaps and needs, however, to further harmonize and coordinate environmental monitoring, to gather inventory information more comprehensively, and to develop reliable models of PTS in the region. Such activities enable us to grasp the current status of emissions, environmental levels and ecological risks of PTS in the region, to accurately predict future status and trends, and to establish more efficient chemical management system in the region. Toxicological/ecotoxicological data of PTS is indispensable information for the risk assessment, and should be accumulated properly and promptly in internationally harmonized manner. The studies for proper endpoints or outcomes, such as induction of particular enzymes, genes, metabolites etc., through the detailed studies on toxicological mechanisms, will be valuable and useful to develop biomarkers for exposure/toxicity assessment in wildlife species. Other

important and challenging topics are to detect and assess total toxicity/ecotoxicity of environmental specimens containing a variety of toxic chemicals from the natural environment. This topic has been a matter of discussion among researchers working on chemical toxicity/ecotoxicity, but may need to be addressed from other aspects, including, for example, detailed discussion and collaboration among professionals of diverse scientific fields in the course of the development of research and management framework on ecosystem health. Capacity building and enhancement procedures are indispensable to fill the gaps and coordinate the related activities in the region more systematically. On the other hand, differences and specificities among the countries compiled in the following paragraphs should also be taken into consideration in order to design and conduct relevant NOWPAP activity in efficient and harmonized manner.

PTS and POPs such as heavy metals, PAHs, organochlorine pesticides (mainly HCHs and DDTs), PCDD/Fs and PBDEs are of concern in the NOWPAP areas in **China**, due to their highly toxic nature and historical production and usage.

In China, POPs monitoring in recent years found that the concentration of residual pesticide POPs is relatively high in water bodies of a small number of estuaries, and that the level of pollution caused by POPs is relatively high in the soils of wastewater irrigated farms, vegetable plots and sites of pesticide POPs production and storage. Relatively high concentrations of Dioxins were detected in the organisms, sediments and soils around a few lakes in central and east China, the sediments of some maritime zones of the East China Sea and Yellow Sea, and the schistosomiasis affected areas in south China. Dioxins levels in human blood samples and human breast milk in sodium pentachlorophenol contaminated areas and schistosomiasis affected areas, were found to be higher than those in persons in other areas. But due to lack of the systematic monitoring and risk evaluation of POPs impacts on the environment and human health, it is still hard to determine impacts of POPs on China's ecological environment and public health.

About the emerging POPs in China, most research on PBDEs has been conducted in the e-waste dismantling sites in Guangdong and Zhejiang provinces, where PBDE levels in the environmental matrices and human bodies are high. The PBDEs levels within the NOWPAP regions in China are at a moderate or low level. PFOS/PFOA levels are relatively low in environmental matrices and human bodies in China, perhaps because of less usage compared with that in North America. Few studies on the pollution status of DPs and SCCPs have been reported in China. Long-term temporal variations of the levels of such pollutants in China remain unclear because all available data are reported only in very recent years.

Although China has carried out the monitoring and research work of PTS, data is still deficient and information disclosure and sharing mechanisms have not been well established, neither the comprehensiveness of data nor the geographic range covered by the data can meet the requirements for assessing POPs risks and their hazards to the environment. The capacity building for POPs monitoring programs in China remains to be top priority and recommendation. More reliable data on PTS and POPs concentrations are needed in order to obtain the whole picture of basic background of

POPs. In particular, resources are required to improve analytical skills and facilities and relevant QA/QC protocols for the determination and verification of PTS and POPs.

Japan has a long history of conducting environmental monitoring as indispensable tool for the proper management of chemicals. Understanding the current environmental status is a first step to identify potential problems, to know status of environmental standards, and to assess effectiveness of the measures/countermeasures. Japan has been conducting yearly environmental monitoring of POPs from 1978 until present together with the sample archiving activity: environmental specimen banking at the National Institute for Environmental Studies. Official or standard analytical methods have been established for each environmental chemical, and data evaluation including QA/QC procedures is conducted every year before opening the data to the public. Further efforts, such as translation of the sampling/analytical manuals into English, training and QA/QC procedures, as well as information transfer of long-term experiences and the efficient management system to other countries, may support the regional/international activities and improve and strengthen harmonization.

In recent years, with the rapid economic development in **Korea**, the effects of POPs and PTS on terrestrial and marine ecosystems have caused increasing concerns among scientists and administrators in South Korea. Due to the hazardous effects of these contaminants to terrestrial and marine ecosystems, including aquatic organisms, a number of monitoring and research projects on POPs and PTS in the environment have been performed by Korean government institutes. Due to their persistent, bioaccumulative, and toxic properties, POPs are worldwide categorized as priority pollutant group to be prohibited in their use and distribution, or removed from environment. Long-range transport of POPs has resulted in relevant international efforts such as Stockholm Convention. South Korean government has followed actively the needs of the convention: 1) regulation in use, distribution, and treatment of POPs substances itself and/or POPs-containing facilities and wastes; 2) development and application of BAT and BEP to reduce POPs release; and 3) monitoring and investigation of POPs contamination nationwide.

Preliminary emission inventory in Korea was estimated by use of the top-down approach for by-product POPs. Over 90% of the total emission for PCDD/Fs was determined to be from two major sources, via waste incineration and steel industry, suggesting the necessity of control focused on corresponding sources. Due to the governmental regulatory action, during the recent years, the emissions of PCDD/Fs have been significantly reduced and the atmospheric PCDD/Fs levels decreased gradually from 1999 to 2013. However, the concentrations trends of PCDD/Fs in marine environment seemed to be less clear compared with that of atmospheric PCDD/Fs trends. In the case of TBT, seawater, bivalves and cetaceans showed clearly decreasing temporal trends, due to the ban on the anti-fouling paints. Besides dioxins, contamination of other classical POPs (including PCBs and OCPs) were localized in hot spots, such as coastal industrial areas and/or big harbors and waste incineration areas. In some of these areas, concentrations of residues exceeded corresponding environmental quality criteria such as ERL and ERM.

In contrast to classical POPs, environment in Korea was observed to be relatively more contaminated with emerging POPs, than were other countries. This is likely due to the recent dramatic economic growth of South Korea. However, to evaluate emission status and trends of contamination in South Korea, further monitoring efforts should be performed, especially for the emerging pollutants such as PBDEs, PFCs, SCCPs and DPs. Considering the current deficient efforts (expressed as fund and participant numbers) for Korean environment, more comprehensive monitoring strategies for POPs and PTS would be strongly needed. For instance, the emerging POPs should be included as nationwide monitoring component in Korea. In addition, the international cooperation has to be considered, as an aspect of a contribution to the international monitoring in a global scale. In particular, long-term studies are needed on trans-boundary LRT of POPs in South Korea. Consequently, continuous monitoring and ecotoxicological studies are required to understand the contamination status of PTS and emerging contaminants in Korean environments and to accurately evaluate the potential risks to terrestrial and marine ecosystems in Korea from exposure to these contaminants.

Russia has some shortage of reliable monitoring data on the PTS, programs on emission control, and adequate data quality control. Environmental management of chemicals and relevant research began some time ago. Russia signed the Stockholm Convention in 2002 and ratified in 2011, and now Russia do not produce or use prohibited chemicals. Government monitoring services in the Asian part of Russia control 6 organochlorine pesticides only: α -HCH, β -HCH, γ -HCH, DDT, DDD and DDE. Other new pesticides, industrial compounds and unintentional by-products are determined in the environment during the restricted number of scientific research. The list of PTS monitored in Russia is often shorter than the Stockholm Convention's list of 12 POPs, resulting in data gaps.

Total amount of pesticides in the marine environment in the Russian part of the NOWPAP area (Peter the Great Bay) decreased during the last two decades (1990-2010), but long-term presence and new input of PTS to marine, coastal and estuarine ecosystems has been established. In general, atmospheric input is an important source in PTS transport in this area as well as in other temperate and polar regions. Typical sources of coastal water pollution are domestic wastewaters, industrial and agricultural wastewaters. The agriculture, coal production and transport become most significant sources of pollution, excluding of power generation and municipal water usage. In 2000 - 2012 some new enterprises of oil and gas industry have been built in the region. These plants are able to produce PTS as components of wastewaters and atmospheric emissions. Large volumes of wastewater get into marine environment untreated. Sewages contain many domestic and industrial pollutants, including pesticides. Razdolnaya River and Tumen River bring various pesticides coming from agricultural regions. Detectable concentrations of DDTs, HCHs and PCBs were revealed in bottom sediments of estuaries of several rivers running into the sea. Data on PTS in river and marine waters are limited, while data on PTS concentrations in sediments and marine organisms are more readily available. Regular monitoring of PCBs in marine environment in Russia is not carried out. However, some data indicate a long presence

of detectable amount of PCBs in the bottom sediments in estuaries of the Razdolnaya and other rivers.

Federal Fisheries Agency of Russia carries out monitoring of pesticides in commercial fish and shellfish since 2010. HCH and DDT concentrations in seafood didn't exceed sanitary norms established in the Russian Federation - 200 ng/g wet weight. Mussels, mysid shrimps, and flounders (widespread in adjacent seas of the Russian Far East) were used as the main bioindicators. Pesticides concentrations in mussels increased from 5 to 10 times from 1996 to 2004. The highest concentrations were determined in mussels from the south-western part of the Peter the Great bay, near the border with North Korea and China. Total pesticides concentration in mussels from Peter the Great Bay was lower than in mussels from Hong Kong, China and Vietnam. But HCHs level in soft tissues of mussels from Peter the Great Bay was higher than DDTs concentration, on the contrary to mussels collected in the other Asia-Pacific countries where DDTs is dominating pesticide. Positive correlation between activity of molecular biomarkers of oxidative stress and pesticides concentration in mussels and flounders was revealed.

Generally, PTS are not dominated contaminants in marine pollution in the Russian part of NOWPAP region. Biological effects are not specific mainly and are caused by combined interaction of different pollutants in wastewaters being discharged to coastal ecosystems.

Monitoring and assessment of ecotoxicological effects of chemicals is still a big challenge in the NOWPAP region as well as in the world. Monitoring parameters, methodologies and technical standards/criteria based on studies from member NOWPAP countries need coordination. There have been several related activities in the past, including imposex monitoring and other endocrine disruptive chemicals research, monitoring of dioxins levels in wildlife, including marine mammals and raptors, together with their health status examination, and development of several short-term assay systems, such as reporter gene assays, for particular type of chemicals. Majority of these methods focused on specific type of chemicals or toxicity mechanisms, however, and more comprehensive assessment procedure need to be developed. Test battery approach, i.e., combination of different test methods for assessing various toxicities simultaneously and development of WET (whole effluent toxicity) method have been conducted from experimental toxicity testing groups. Use of same biological species for both testing chemicals and environmental biomonitoring is another way to realize such an assessment procedure.

It should be pointed out that the exposure levels of chemicals in the toxicity tests are generally higher than their levels in the natural environment. In other words, we need to detect subtle and earlier effects of chemicals in wildlife/ecosystem in natural environment before the appearance of their major toxicity like in the case of toxicity testing where clear toxic effects should be detected in small number of testing organisms. Although it is generally considered that effects at molecular levels precede those in cellular and organisms levels, it should also be taken in mind that toxic effects or biomarkers of chemicals at low levels might be different from those at higher doses.

Clearly detailed basic research on toxicity mechanisms of chemicals are needed to establish appropriate assessment procedures, and information exchange and sharing among NOWPAP countries are indispensable and very useful to develop sound chemical management system in the region.

Comprehensive approaches have already been developed and providing new insights in both toxicological research (toxicogenomics, -proteomics, -metabolomics) and pollutant analysis (GC-GC/TOF and LC-TOF for comprehensive organic pollutant analysis, and multi-elemental analysis by ICPMS and ICPAES), and development and establishment of comprehensive approaches in effect monitoring of chemicals to wildlife and community/ecosystem are strongly awaited. Combination of advanced molecular toxicological methods and information with conventional ecosystem health assessment approach, such as benthos or microbial community research, may open new windows for the assessment of total effects of chemicals to ecosystem. Furthermore, combination of comprehensive approaches in different fields, such as comprehensive pollutants analysis and comprehensive toxicity testing procedures, will be valuable to establish sound chemical management in future.

In conclusion, establishment of sound chemical management system, particularly on PTS, is important and urgent in the NOWPAP region, where effects of human activities including PTS influence on the semi-enclosed marginal seas are observed. Environmental monitoring is indispensable as a primary tool to reveal the temporal and spatial trends of PTS, to identify their sources and hot-spots, and to assess effectiveness of regulations. Establishment of regional monitoring network taking into account specific needs and status of each country is a crucial next step. Environmental chemodynamic models of PTS are needed to assess environmental/ecological risks, to predict future status, and to design better management system. Information collection on inventory of PTS emissions to the environment as well as detailed monitoring data is critical for proper design, improvement and use of models. Toxicological/ecotoxicological data on PTS are also needed to assess their risks properly, and collection and sharing relevant information in the NOWPAP region will support better PTS management. Proper assessment of risks of total exposures to PTS and other chemicals for the wildlife and human beings is a real challenge in the NOWPAP as well as in the world, and long-term strategy to tackle these issues will be needed.

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Научно-справочное издание

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На английском языке

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