PCDDs and PCDFs in the Environment.
Historical Trends and Budget Calculations

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Abstract

A decreasing trend of PCDDs and PCDFs has been found for guillemot eggs from the Baltic Proper and in pike muscle from a remote lake in northern Sweden. Archived soil and herbage samples show a rapid increase 1940 - 1970 followed by a decrease. A sediment core from Japan shows a maximum for the late 60s and early 70s, but hepta- and octa CDD could be found in deeper sediment, about 8000 years old. Sediments from Baltic Proper also show a maximum for the 70s. The pre 1940 samples show a great influence of burning and incineration, the post 1940 samples are also highly influenced by impurities found in commercial pentachlorophenol. Budget estimates indicate a larger deposition than the amount that could be explained by known sources indicating the importance of long range transport. Natural formation of PCDDs and PCDFs via photolytic and enzymatic reactions can also explain this discrepancy.

Introduction

The polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have been found to be ubiquitous in our environment today. They have been in the scientific and general interest for decades, and several countries have introduced various regulations to reduce the release of these compounds in the environment. Due to the high toxicity, US EPA has introduced a guideline called the virtually safe dose (VSD) of a daily intake of 2,3,7,8-tetraCDD or Toxic Equivalents of 0.006 pg/kg b.w., day which means zero emissions of identified anthropogenic sources. A similar value is also discussed in the reassessment of the risks of exposure to dioxins presently performed by US EPA. Governments and regulatory agencies can regulate the release of PCDDs and PCDFs from anthropogenic sources, but the situation is more complicated if PCDDs and PCDFs also have natural non anthropogenic origin. In the present paper we will briefly discuss and review the literature concerning historical trends, budget calculations and non-anthropogenic sources of PCDDs and PCDFs.

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Historical Trends

Extensive analyses of human samples, primarily in Germany and USA, indicate a decrease in the body burden of PCDDs and PCDFs in these countries (1,2). In this section we will discuss the historical trends found in environmental samples.

Biota

The decreasing concentrations of 2,3,7,8-tetra CDD in herring gull eggs from Lake Ontario and other of the Great Lakes are well established (3,4). This decrease is associated with the cleaning of specific point sources, which directly contaminated these lakes.

A decreasing trend has also been found for the concentrations of PCDDs and PCDFs in guillemot eggs from a colony in the Baltic Sea (Baltic Proper). During the period 1969-1992, the concentrations of PCDDs and PCDFs counted as I-TEQ decreased by a factor of 3 in this matrix (5). During this period most identified fugative and point sources of PCDDs and PCDFs around the Baltic Sea were reduced as halogenated scavengers in petrol, MSW incineration and bleaching of pulp using chlorine gas. In addition the use of chlorinated phenols, 2,4,5-T and PCB was banned in the Nordic countries and in Germany . Of special interest is the decreasing concentrations of 1,2,3,7,8-penta CDD and 2,3,4,7,8-penta CDF in the biota. These two congeners contribute by more than 60% to the TEQ value, but they have not been clearly associated with any specific known source. However, these congeners can be found among others in commercial chlorophenols and in emissions from various incinerators (6,7,8).

Analyses of pike samples from a lake in the remote part of Lapland in northern Sweden show decreasing concentrations of PCDDs and PCDFs as well. This is a clear indication of decreasing amounts of PCDDs and PCDFs undergoing long range transport, since the major input of PCDDs and PCDFs into this remote lake is via long range transport (5).

Abiotic samples

Kjeller et al. (9) have studied the increase of PCDDs and PCDFs in soil and vegetation since the 1840s. Archived soil and herbage samples from the same semirural plot in southeast England have been analyzed, the soil samples covered the period 1846-1986 and the herbage samples 1891-1988. Atmospheric deposition has been the major source of PCDDs and PCDFs to the site over this time. Both PCDDs and PCDFs were found to be present in all samples including 2,3,7,8-tetra CDD, 1,2,3,7,8-penta CDD and 2,3,4,7,8-penta CDF in the oldest samples. The concentrations were found to

increase over time with the exception of the 1979-1988 herbage sample, which contained lower concentrations of PCDDs and PCDFs than the sample from 1960-1970 (9).

In the herbage samples and, to a lesser extent, in the soil samples we observed an interesting shift in the ratio of PCDDs to PCDFs. In the pre-1950 samples the values of sum PCDFs were higher than the sum PCDDs, but in the samples collected after 1950 there is a dominance in the hepta- and octa CDDs. This is a clear indication of two different sources for this background contamination of PCDDs and PCDFs. In the pre-1950 samples the PCDD/PCDF ratio, the congener group profile and the congener pattern indicate various incineration processes to be the ultimate source, while the post-1950 samples with the dominance of hepta- and octa CDDs have a much larger similarity with the pattern both found in samples of commercial pentachlorophenol as well as from burning and incineration of pentachlorophenol in smaller and larger units. The pattern found for the lower chlorinated congeners still indicates a contribution of various combustion sources also for the post-1950 samples (9). The concentrations found in the oldest samples are around 10 - 20% of the concentrations found in the samples from the 1980s. This can be interpreted that around 80-90% of the present contribution is related to the chlorine based industry, while 10-20% is not related to this type of industry.

An interesting difference was found between the soil and herbage samples from the pre 1940 period. For the soil samples the proportion of octa CDD was around 50% of the total Cl_4 - Cl_8 PCDDs, while in the herbage sample the proportion is only 15-20%. This could be explained in three ways. One way could be by a much longer halflife of octa CDD as compared to the other congeners found in the soil. The other explanations could be by a non-anthropogenic formation of primarily octa CDD in the soil or a reduced absorption of octa CDD on plants. Pentachlorophenol was first synthesized by Merz and Weith in 1872 (10), and the commercial introduction in Europe was during the late 1930s.

Sediment samples have been found to be a useful matrix to study historical trends of PCDDs and PCDFs. Hites and co-workers have reported that concentrations of PCDDs and PCDFs in dated sediment cores have increased greatly since 1940s in the Great Lakes and in Lake Siskiwit, a remote site on Isle Royal in Lake Superior, which only received inputs via deposition from the atmosphere (11,12). The trend was almost identical in sediment cores from three lakes in Switzerland (13). In pre-1940 cores the values were not significantly greater than the laboratory blanks.

Hashimoto et al. (14) have reported on the analysis of two sediment cores from the coastal areas of Japan and one core from a remote lake in Japan. No PCDDs or PCDFs could be found in the lake sediments, but both PCDDs and PCDFs could be

found in the coastal sediments. The highest concentrations were found in sediments from the late 60s and the early 70s, the same was found for PCDDs as well as PCDFs. Around 1980 the concentrations had decreased by a factor of 2 to 5, the PCDFs decreasing more than the PCDDs. In fact no PCDFs could be found in one of the surfacial sediments. Hashimoto et al. also report that PCDDs primarily octa CDDs and hepta CDDs (ratio 6:1) but no PCDFs could be found in the deep sediments, even in the sediments dated to be more than 8000 years old (14). Cross-contamination during sampling can be ruled out due to the different ratio between PCDDs and PCDFs found in different disks of the sediment cores.

Smith et al. (15) have studied sediment core samples from Green Lake, a small lake east of Syracuse, NY, USA. They also report that the concentrations increased during the 1940s and 1950 reaching a sharp peak in the 1960s and then declining. In the 1980-90 core the concentrations were around 50% of the peak concentrations. The homolog distribution profiles were also found to change. Since around 1970 there is a dominance by octa CDD. Prior to that the lower chlorinated congeners were relatively more abundant. In the 1943 core the tetra CDFs were the most abundant congener group of the PCDFs (15). This is in agreement with the findings from the archived soil and herbage samples discussed above.

A laminated sediment core from the Baltic Sea (Baltic Proper) has been studied by Kjeller and Rappe (16). The sediment was sliced into nine dated disks ranging from 1880's to the present time. A full range of PCDD and PCDF congeners were detected in all disks, including the disk from 1880s. Up to 1962 the concentrations are quite low and they were found to increase slowly, the PCDDs slower than the PCDFs. The concentrations were found to increase in the 1970 and 1978 disks. Once more the PCDDs increased more rapidly than the PCDFs. In the 1985 disk there is a very small decrease for the PCDDs, but a more pronounced decrease for the PCDFs. Inspection of the congener patterns and profile indicate that combustion/incineration is the major source in the pre-1970 sediment, while the post-1970 sediment is related to pentachlorophenol (16).

Alkylsubstituted PCDFs can be used to estimate the transport time from the coastal zone to the sampling station, a distance of about 150 km, since these compounds are indicators of pulp bleaching using free chlorine, a process which started in the early 1950s (17). These compounds have also been found as large peaks in the upper sediment disks and the transport time from the coast to the station is approximately 30 years. Taking this into account, there is a good agreement between the changes in patterns and profiles in this sediment core, the soil and herbage and the commercial introduction of pentachlorophenol. The difference in patterns and the alkyl-PCDF in the upper layer can rule out bioturbation and cross-contamination as artifacts.

Budget calculations

A few attempts have been made to perform national budget calculations on sources and deposition of PCDDs and PCDFs. A few countries have performed national source inventories. The first country to do so was Sweden (18) and the most detailed inventory has been made by the Netherlands (19). Other countries with dioxin inventories are the former West Germany (BRD) (20) and United Kingdom (21). Deposition measurements have been performed in Sweden (22,23), Germany (24) and USA (15). In all cases where budget comparisons have been performed, the deposition seems to be larger than the known emissions to the atmosphere counted as TEQ. Calculations on hepta- and octa CDDs show an even larger discrepancy between emissions and deposition. Such calculations give a clear indication of the importance of atmospheric long range transport.

It has also been reported that the atmospheric lifetime for PCDDs and PCDFs increases with increased number of chlorine atoms, the longest lifetime is reported for octa-, hepta- and hexa CDFs, followed by octa CDD (25).

Here we seem to have a dilemma. Combustion and incineration result in the formation of PCDDs and PCDFs, and normally the emissions of PCDFs are higher than the emissions of PCDDs by a factor of 2-3. The atmospheric lifetime should be longer for PCDFs than for PCDDs but samples of air, soil, vegetation, sewage sludge and sediments are all dominated by hepta- and octa CDDs, which might be transported bound to particles.

Again we arrive at the conclusion that the lower chlorinated PCDDs and most PCDFs are formed by combustion incineration processes, while the source of hepta- and octa CDD is commercial pentachlorophenol or burning of pentachlorophenol.

However, it cannot be completely ruled out that there is a natural formation of hepta- and octa CDDs in the environment. Octa CDD was the dominating congener group in the 1846 soil sample followed by hepta CDDs. These samples were collected almost 100 years before the commercial introduction of pentachlorophenol. The 8000 years old Japanese sediments also contained octa- and hepta CDDs.

Vollmuth et al. recently reported that photolysis of purified pentachlorophenol in water resulted in the formation of octa CDD (26). In spite of a widespread ban on pentachlorophenol, this compound is still frequently used for impregnating textiles, primarily cotton (27). Lamparski et al. (28) have also found that octa CDD could be formed by photolytic reactions. They found a formation of octa CDD when they irradiated (mercury low-pressure lamp) wood treated with purified pentachlorophenol.

A biochemical formation of primarily octa CDD from pentachlorophenol takes place in sewage sludge (29), and composting of garden wastes results in increased concentrations of PCDDs and PCDFs primarily octa CDD (30,31).

Conclusions

1. PCDDs and PCDFs have been found in a series of historical samples, the primary source is incineration and combustion

2. Post 1940 samples are influenced by the contamination of hepta- and octa CDD found in commercial pentachlorophenol which was introduced at that time.

3. Combustion and incineration is the major source for the lower chlorinated PCDDs and PCDFs both in pre and post 1940 samples

4. The environmental concentrations peaked in the 1960 and early 1970 and they are now decreasing

5. Vegetation and sediments from the 19th century was also contaminated by PCDDs and PCDFs including 2,3,7,8-tetra CDD

6. The contamination in the 19th century has very likely resulted in contaminated food (milk, fish) and exposure to humans

7. Budget calculations clearly show the importance of long-range transport of PCDDs and PCDFs

8. Natural formation of PCDDs and PCDFs can occur via photolytic and enzymatic reactions and could contribute to the dominance of hepta- and octa CDD found in many abiotic environmental samples

9. The reduction of the anthropogenic sources has not yet resulted in concentrations typical for samples from the 19th century.

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