NATURAL FORMATION OF DIOXINS: A REVIEW OF TRENDS AMONG FOUR SITES

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Introduction

Recently, much attention has focused on the natural formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). In wetland or marine sediments, the nonanthropogenic PCDD pattern is dominated by OCDD, HpCDD and HxCDD, and very low or undetectable levels of PCDFs. Although there is substantial evidence that PCDDs can be formed naturally, the precursors and specific mechanisms and sources of formation remain unknown. This paper reviews the similarities among locations where naturally formed dioxins in sediments have been confirmed.

Naturally formed dioxins have been observed in sediments in South Mississippi, Queensland Coast, Australia, Mai Po Marshes, Hong Kong, and Lake Ahmasjärvi in Finland. Sediments from these locations contain elevated levels of the higher chlorinated dioxins, predominately OCDD, with decreasing concentrations with decreasing chlorine substitution, and low or undetectable levels of 2,3,7,8-substituted PCDFs. In addition, the HxCDD homologue in these samples is dominated by 1,2,3,7,8,9-HxCDD.

Discussion

In 1997, Rappe et al.,[1] reported PCDD/F results from an extensive study in southern Mississippi, USA. Sixty-one river sediment samples collected throughout the Leaf-Pascagoula River System were analyzed for PCDD/Fs. The Leaf-Pascagoula River System is in a remote area surrounded by wetlands and swamps, with parts flowing through the De Soto National Forest. High levels of OCDD and HpCDD were found in most river sediments. Based on loss of ignition (LOI), the OCDD concentrations ranged from 5,500 pg/g to 400,000 pg/g, with mean and median concentrations of 202,000 pg/g and 180,000 pg/g, respectively. The 1,2,3,4,7,8,9-HpCDD concentrations ranged from 240 pg/g to 15,000 pg/g LOI. The mean and median concentrations were 5,780 pg/g and 6,500 pg/g LOI, respectively.[2] The mean 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD ratio for all sediment samples was 2.05. The dioxin/furan ratio (D/F) for all river sediments ranged from 43 to 1,200, with a mean of 241 and median of 110, indicating the clear dominance of PCDDs. OCDD concentrations greatly increased after a creek passed through the De Soto National Forest, an area with wetlands and swamps.[1] The only known anthropogenic source in this area is the spraying of 2,4,5-T from 1954 to 1966, which cannot be associated with the high OCDD concentrations.

Elevated levels of PCDDs, in particular OCDD, have been detected along the Queensland, Australia coastline in sediment cores 350 years old.[3] Queensland Coast is a pristine environment that stretches more than 2000 km and includes the Great Barrier Reef. It is separated by the Great Dividing Range into two regions, the coastal plain to the east, which includes bushland and areas of intensive agriculture; and an arid inland area to the west, which includes bushland and extensive grazing activities.[4]

FORMATION AND SOURCES: FIELD CASES

Gaus et al.,[5] reported elevated OCDD concentration in Queensland. Marine and irrigation drain sediments and topsoil samples were collected from sites expected to be influenced by specific land-uses. High OCDD concentrations were detected in sediments collected near the mouth of rivers, which drain into large catchments in the tropical and subtropical regions. These sediments exhibit almost identical PCDD/F profiles along the entire coastline. The authors concluded that the PCDD/F profile of these samples strongly resemble those reported for river sediments from Mississippi. All samples were dominated by higher chlorinated PCDDs, with OCDD contributing 70-93 % to the ΣPCDD/F. Most samples contained very low or non-detectable PCDF concentrations. 2,3,7,8-TCDD was below the detection limit or not quantifiable in any of the sediments. The D/F ratios for all samples were high, ranging from >30 to >1090, with a median of 186. Like the Mississippi sediments, 1,2,3,7,8,9-HxCDD dominated the HxCDD homologue.

Later Prange et al.,[4] reported elevated OCDD concentrations in the coastal, mountainous and inland environment of Queensland. Distinct east-west gradients were detected in topsoil collected from various bushland regions. The authors concluded that the topsoil and river sediments collected in the Queensland coastal region suggest that elevated OCDD concentrations cannot be attributed to any of the known, land-uses or industries in this region. OCDD concentrations in the sediments ranged from 40 (sediment in a river passing through a national park) to 1,200 pg/g dm (sediment in a river which passes through a region dominated by bushland). As in the previous studies, 1,2,3,7,8,9-HxCDD dominated the 2,3,7,8-substituted HxCDDs, with the highest 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD ratio found in the bushland samples. The median D/F ratio was 400, which is consistent with the previous findings in Queensland samples and South Mississippi river sediments.

Recently, Müller, et al.,[6] reported on the natural formation of dioxins in the Mai Po Marshes Nature Reserve, Hong Kong. The Mai Po mudflats consist of approximately 1.8 km^2 which were formed largely as a result of sediments deposited from the Pearl and Shenzhen River. Fourteen sediment samples were collected from four sites in the Mai Po Marshes Nature Reserve and from six sites in Victoria Harbor and along the Hong Kong coastline. PCDD/Fs were detected in all samples collected in the Mai Po Marshes and other sites from Hong Kong. No significant differences in PCDD/F profiles in surficial sediments from the four sampling locations along the Mai Po mudflats were observed. Moreover, there were no significant differences in the PCDD/F concentrations with sediment depth at the one site where a depth profile was determined.[7] PCDD/F profiles in all samples were dominated by OCDD, which contributed 94-97 % to the Σ2,3,7,8-PCDD/F in the samples from the Mai Po Marshes, and 84-95 % in all other samples. PCDF concentrations were only measured in two samples, which were collected in Victoria Harbor. All samples have a HxCDD profile that is dominated by 1,2,3,7,8,9-HxCDD.

Recently, Isosaari et al.,[8] reported PCDD/F concentrations in a sediment core from Lake Ahmasjärvi, Finland. The deepest strata was from a depth of 4 meters and was determined to be more than 8,000 years old. PCDD/F concentrations from the surface strata represent low levels of industrial contamination. The authors reported that the PCDD/F profile from earlier studies that exhibit the natural dioxin formation was found in all pre-industrial sediment strata. Specifically, the concentrations were OCDD>1,2,3,4,6,7,8-HpCDD>1,2,3,7,8,9-HxCDD>1,2,3,4,7,8,- HxCDD>2,3,7,8-TCDD. The highest PCDD/F concentrations were found in the surface sediments, where most 2,3,7,8-substituted PCDD/Fs were detected, and OCDD and OCDF were the dominant congeners. The second highest concentrations were at a depth of 124-157 cm, which corresponded to 3,418-4,350 years ago. PCDD/F profiles at this depth and below were similar, and reflect apparent background levels from pre-industrial periods. Low levels of dioxins were detected but most furans were absent. The oldest sample exhibiting the natural formation profile was more than 8,000 years old.

In the Mississippi study, Rappe et al.,[2] analyzed 28 sediment samples from 15 lakes in rural areas in south Mississippi with no known anthropogenic sources of PCDD/Fs. OCDD and 1,2,3,4,6,7,8,-

HpCDD dominated in all lake sediments. Based on LOI, OCDD concentrations ranged from 11,000 pg/g to 640,000 pg/g, with a mean and median of 182,000 pg/g and 130,000 pg/g LOI, respectively. Concentrations of 1,2,3,4,6,7,8-HpCDD in the lake ranged from 4.7 pg/g to 510 pg/g LOI. Mean and median concentrations of 1,2,3,4,6,7,8-HpCDD were 135 pg/g and 510 pg/g LOI, respectively. Of the 2,3,7,8-substituted HxCDDs, 1,2,3,7,8,9-HxCDD dominated all samples analyzed with a mean and median 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD ratio of 2.2 and 2.3, respectively

Among the Mississippi, Queensland Coast, Mai Po Marshes and Lake Ahmasjärvi sediments, there are distinct similarities. In particular, all have high concentrations of OCDD, and very low or undetectable levels of PCDFs. Not surprisingly, all have high D/F ratios, with the majority of the PCDD/F concentration coming from OCDD, which is not found where anthropogenic sources are evident. Likewise, there are clear similarities in the geography of the Queensland Coast, Mai Po Marshes, and Southern Mississippi. Wetlands and swamps are associated with all these sites. Mangrove forests occur along the Queensland Coast and the fringe of the mudflats in the Mai Po Marshes.[9, 10] The similarities between these sites is essential to understanding the natural formation process(es) and modifications which occur in marine and wetland sediments.

Tests are being conducted to understand better the processes with respect to the production, modification and transport of dioxins in marine and wetland sediments. Capacity and release kinetics will be determined by sorption-desorption experiments with sediment samples impacted with dioxins. Data from this study will help determine if sediments can act as a source and sink for dioxins under natural conditions. In addition, combustion studies are planned to investigate varying parameters (e.g., temperature, amount of oxygen, residence time, natural organic matter) of the destruction and formation of dioxins using, 1) sediment samples impacted with dioxins and 2) different types of vegetation found in the geographical areas described in the four different sites.

Conclusions

1. Sites where the natural formation of dioxin has been confirmed exhibit a PCDD/F profile that is unlike any known anthropogenic sources. This profile contains high levels of OCDD and HpCDD, and very low or undetectable levels of PCDFs. Further the HxCDD homologue is dominated by 1,2,3,7,8,9-HxCDD.
2. The existence of PCDDs has been confirmed in a sediment core dated more than 8000 years ago, supporting the theory of natural formation of dioxins.
3. The geography at locations where naturally-formed dioxins in sediment have been observed have similar characteristics. In particular wetlands and forests may play a role in understanding the formation mechanisms.
4. Further experiments are needed and currently under way, which should give us a better understanding as to the role wetland and marine sediments play in the formation, modification and transport processes of dioxins.

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