

HISTORICAL DEPOSITIONS OF DIOXINS AND FURANS IN LAGUNA de MIRAMAR, MEXICO

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Introduction

Thousands of chemical substances, including toxic, persistent, bioaccumulative substances (TPBS), are produced and used world-wide annually¹. These volatile and semivolatile TPBS may be transported by air both in gaseous phase and adsorbed to atmospheric particles² prior to deposition in soil and water. Due to the grasshopper effect, TPBS released may evaporate in warmer climates and be transported, reaching the colder air of polar regions or high mountains, where they are eventually deposited on land or water thousands of miles away. TPBS deposited on land may also end up in water bodies due to erosion and transport of soil particles that accumulate as sediments in lakes and reservoirs.

Due to the high K_{ow} and K_{oc} and low water solubilities, TPBS are principally associated with organic material and particles suspended in water. The mechanisms of removal of TPBS from the water column include sedimentation and accumulation in sediments. It has been determined that sediments act as a sink for these TPBS. Hence, the analysis of sediment cores in lakes and reservoirs represents a powerful tool for reconstructing historical deposition of persistent pollutants, particularly in countries like Mexico where monitoring programs for toxic, persistent, bioaccumulative substances (TPBS) such as dioxins and furans are absent. The historical deposition of dioxins and furans was evaluated in the remote Laguna de Miramar using sediment cores dated by ¹³⁷Cs and ²¹⁰Pb methods. Concentrations and selected isomer patterns of dioxins and furans in a sediment core are presented and discussed and compared with the results of ecological threshold values and data published for other lakes in the scientific literature.

Materials and Methods

Laguna de Miramar is the largest of a series of lagoons in the Montes Azules Biosphere Reserve of the southeastern state of Chiapas, Mexico. Physical and spatial characteristics of the lagoon are presented in Table 1. By the end of last century there were 34,000 people of different ethnic backgrounds living in small towns and unauthorized settlements within the reserve. The development of economic activities and the process of colonization or settlement of the region have had an impact on the ecosystem, gradually transforming the countryside as a result of changes in land use. The forest and other forms of wildlife have ceded land to the cultivation of basic grains, coffee, pastureland, cacao and chili. This process was intensified from the 1960's to the 1980's, leading to a significant reduction in the amount of wooded areas in the region.

Table 1. Summary of Data and Sampling in Laguna de Miramar. Adapted³

Parameter	Unit	Lagoon Miramar
Sampling year	-	2005
Latitude N	-	16°22'-16°26'
Longitude W	-	91°14'-91°18'
Altitude	M	200
Surface area	Km ²	22
Volume	Mm ³	-
Maximum depth	M	>120
Mean depth	M	-
Watershed area or sources of water	Km ²	76
Origin	-	Soluble limestone hollows
Climate	-	Humid, tropical
Mean annual precipitation	mm	2226
Main land use	-	High and medium Perennifolia forest
Mean annual temperature	°C	24.5
Length of analyzed core sample	cm	8

Sampling depth	M	37
Linear sediment accumulation rate (LAR)	cm yr ⁻¹	0.005
Mass accumulation rate (MAR)	g cm ⁻² yr ⁻¹	0.053

The sediment cores were obtained from deeper parts of the lagoon where undisturbed sediments were most likely to be found. The cores were extracted with a Wildco KB gravity corer (Model No. 2404) fitted with 4.7 cm by 76 cm cellulose-acetate-buturate (CAB) plastic core liners. To avoid mixing of sediments, the cores were immediately frozen with liquid nitrogen and stored vertically in a deep-freezer. In the laboratory, frozen sediment cores were cut along to observe stratification and possible local indicators, and horizontally to evaluate sedimentation rates as well as dioxins and furans concentrations. The length of sections for isotope dating was 1 cm.

The isotopes ¹³⁷Cs, ²¹⁰Pb, and ²²⁶Ra were analyzed by γ spectrometry based on ASTM methods C1402-98 and E181-98, similar to the methodology described by Fuller et al.⁴, van Metre & Fuller⁵, and Corbett et al.⁶. Excess ²¹⁰Pb was calculated as the difference between total ²¹⁰Pb activity and ²²⁶Ra activity. Sediment linear accumulation rates (LARs) and mass accumulation rate (MARs) were calculated using the constant flux-constant sedimentation (CF-CS) model⁷ and represent a maximum rate for the length of detectable excess ²¹⁰Pb in the core. Down-core ¹³⁷Cs activities were used to substantiate the ²¹⁰Pb-determined accumulation rates, and rates calculated with ¹³⁷Cs were typically within error of those determined by ²¹⁰Pb.

For dioxin analyses, a 25 g dry weight sample of each homogenized core section was spiked with the seventeen labeled dioxins and furans and twelve co-planar PCBs as isotope dilution internal standards and analyzed following a modified version of EPA Method 1613B⁸. Details of the method are described elsewhere by Ferrario et al.⁹. The concentrations of the congeners were determined using high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS).

Results and Discussion

Historical accumulation of dioxins and furans in the Laguna de Miramar sediment core are expressed on a toxic equivalents concentrations (TEQ), based on World Health Organization (WHO) toxic equivalent factors for fish (1998)¹⁰. The concentrations for the individual core segments are: 0.156 pg TEQ/g, d.w. (1997); 0.147 (1987); 0.148 (1971); 0.145 (1963); and 0.144 (1903), with an average of 0.148 pg/g TEQ, d.w. These values were lower than the Interim Sediment Quality Guideline (ISQG) established by the Canadian Council of Environmental Ministers (10) of 0.85 ng TEQ/kg and are significantly lower than the concentration recognized as the Probable Effect Level (PEL) (21.5 ng TEQ/kg).

If one examines the data in Table 2, it is obvious that the dioxins/furans and co-planar PCBs demonstrate a remarkably consistent pattern and concentrations in all of the samples. Most of the PCBs were below the detection limits except for PCB 169 which had an average concentration of 0.051 ppt. The detection limits for the co-planar PCBs ranged from 0.04 ppt for PCB 126 to 20 ppt for PCB 118 and were based on background blank levels, except for PCB 169. The vast majority of the 2,3,7,8 Cl-substituted furans were also at or below the detection limits. Only one congener, 1,2,3,4,6,7,8-HpCDF, was detected in all the samples and again, only slightly above the detection limits. Most of the 2,3,7,8-Cl substituted dioxins were detected in the samples except for 2,3,7,8-TCDD, which was detected at approximately 0.02 ppt in two samples. The OCDD was by far the major congener present with an average concentration of 280 ppt followed by the 1,2,3,4,6,7,9-HpCDD at approximately 21.8 ppt and the hexa-dioxins at 8.1 ppt. Interestingly of the toxic hexa 2,3,7,8-Cl substituted congeners, the 1,2,3,7,8,9-HxCDD was the congener found at the highest concentration in all the samples. The relatively high octa-dioxin concentration and low to non-detectable levels of furans led to high dioxin/furan (D/F) ratios ranging from 374 to 2269 with an average of 1450. It is interesting to note the similarity of several of the characteristics of the congener profiles seen in these Mexican core samples to those seen in ball clay and old sediment samples from Queensland Australia: dominance of the OCDD and 1,2,3,7,8,9-HxCDD among the toxic hexa-dioxin isomers and relatively low to non-detectable furans. Also noteworthy is the prevalence of the 1,4,6,9,- substituted dioxin congeners and the higher concentration of

1,2,3,4,6,7,9-HpCDD as compared to the 1,2,3,4,6,7,8-HpCDD and the implication of the presence and relative concentrations of the isomers regarding dechlorination preferences as discussed by Gaus et al.¹¹.

Table 2. Summary of the Sediment Core Average Results

Description	Laguna de Miramar	
Matrix	Sediment	
	Average Core Value	RSD
Quantity (g) Analyzed	~ 25 g	
Concentration	(pg/g), dry wt	%
2,3,7,8-TCDF	ND (0.0133)	7.39
1,2,3,7,8-PeCDF	ND (0.0148)	13.2
2,3,4,7,8-PeCDF	ND (0.0163)	14.2
1,2,3,4,7,8-HxCDF	ND (0.0168)	22.5
1,2,3,6,7,8-HxCDF	ND (0.0161)	17.7
2,3,4,6,7,8-HxCDF	ND (0.0140)	6.00
1,2,3,7,8,9-HxCDF	ND (0.0196)	16.1
1,2,3,4,6,7,8-HpCDF	0.0419	16.1
1,2,3,4,7,8,9-HpCDF	ND (0.0184)	20.4
OCDF	ND (0.0442)	18.8
2,3,7,8-TCDD	ND (0.0140)	25.0
1,2,3,7,8-PeCDD	0.0379	14.8
1,2,3,4,7,8-HxCDD	0.0685	7.72
1,2,3,6,7,8-HxCDD	0.134	10.8
1,2,3,7,8,9-HxCDD	0.357	20.8
1,2,3,4,6,7,8-HpCDD	5.86	11.6
OCDD	279.6	8.50
Total Tetrafurans	0.504	33.4
Total Tetradioxins	1.11	27.1
Total Pentafurans	0.0142	15.2
Total Pentadioxins	0.944	16.3
Total Hexafurans	0.0337	40.5
Total Hexadioxins	8.10	20.3
Total Heptafurans	0.0897	11.5
Total Heptadioxins	27.7	13.6
Total Octafurans	0.0442	18.8
Total Octadioxin	280	8.50
Total Furans	0.360	81.4
Total Dioxins	317	8.96
Ratio (D/F)	1450	63.9
PCB 169	0.0510	6.60
	(pg TEQ/g, d.w.)	
Total Dioxins & Furans	0.148	3.38

Again, these consistent concentrations and congener patterns over the past approximately 100 years are unlike others reported in the literature. Most notably, they do not demonstrate the dramatic increase in concentration from the late 1940s to the late 1970s as reported by Zennegg et al.¹² in a small shallow lake of the Swiss Plateau, Greifensee, Switzerland or in Lake Constance in southwestern Germany as reported by Hagenmaier and Walczok¹³ where the peak concentration was observed in 1975. Also, there was no increase in the D/F ratio around 1940 as observed in both of these studies and the TEQs from this study are much lower except those

from the earliest samples. The consistency of the concentrations and congener profiles shown here are also in contrast to patterns observed by Kjeller and Rappe¹⁴ in cores from the Baltic Proper where they note that the congener pattern could be divided into three main groups: the old, middle and recent periods. Interestingly, there are similarities to cores taken by Czuczwa et al.¹⁵ from a lake in North America, Lake Siskiwit. It is located on Isle Royale, Lake Superior which receives inputs from only atmospheric deposition. These sediments also showed a predominance of OCDD at a surprisingly similar average concentration (335 ppt) and similar concentrations of 1,2,3,4,6,7,9-HpCDD and 1,2,3,4,6,7,8-HpCDD as was shown from these sediments. The historical patterns seen here and the similarity of the concentrations and congener profiles at the different depths are also similar to those observed in other Mexican core samples¹⁶ and support their position that the profiles reflect differences in the industrial development of Mexico as compared to other more developed countries. Further investigations are underway to both confirm these results by analyzing cores taken in parallel with those reported on here and to subsequently conduct a more thorough examination of the literature. Perhaps these additional studies can better inform the discussion as to the sources of these contaminants.

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