On the potential origin of dioxins and furans from surface sediments and fish tissues from four regions in Mexico.

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Introduction.

Dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs), are recognized as pollutants with a wide distribution showing persistent and toxic behavior (Müller *et al*., 2002). We measure the most toxic congeners in core sediments and fish tissue on four regions of Mexico. The sites included areas on the Pacific Ocean, the Gulf of California, the Gulf of Mexico and Patzcuaro lake. Due to the lack of identical species at all sites, we selected similar trophic levels for fish with similar feeding modes. The fish selected for this study were *Caranx caninus, Caranx hippos* and *Chirostoma estor estor.* One of our objectives for this work was to try to identify possible sources for these dioxins and furans. For this purpose, we selected from the core samples only the top cm to analyze the particular congener profile to look for similarities from potential sources previously reported from around the world.

Material and methods.

The sediment core from Ensenada (Pacific Ocean) was collected using a 50 x 50 cm stainless steel box corer. From the box, an individual polycarbonate core was obtained. Sediment cores from Guaymas Basin (Gulf of California) and Paraiso (Gulf of Mexico) were collected using a piston corer. The core from Patzcuaro Lake was collected by scuba diving. The sediment cores were frozen until their analysis in the laboratory. Fish samples were commercially available and obtained during September-December of 2005 at Ensenada, El Barril, Carmen City and Patzcuaro lake in Mexico. Sampling sites for cores and fish are shown in Figure 1.

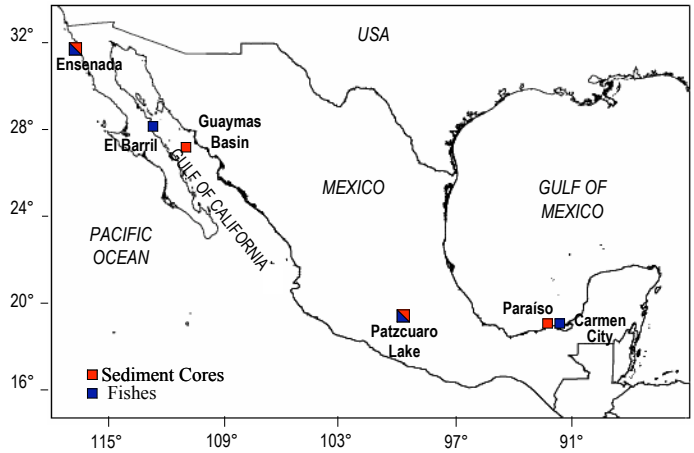


Figure 1. Sampling sites for sediment cores and fishes.

In the laboratory, sediment cores were sectioned each 1.0 or 2.0 cm intervals using a piston extruder. Each was freeze-dried and analyzed for 2,3,7,8-substituted dioxins and furans content, organic carbon content, grain size and dating using ^{210}Pb.

A sample batch included a method blank (MB), a recovery and precision blank (OPR), a certified reference material DX-2 (Wellington Labs) and up to nine samples. A 10 g dried sediment sample was toluene extracted for 16 h in a soxhlet extraction device. We used quartz white sand (60/70 mesh) heated to 450°C for 4 h for MB and OPR.

Before the extraction, samples, reference material, MB and OPR received a mixture of isotopically labeled ($^{13}C_{12}$) dioxins and furans (EPA-1613 LCS, Wellington Labs). Only the OPR was added with a known amount of native Standard (EPA-1613 PAR, Wellington Labs). Once extracted, 20 µL of a purification standard was added (EPA-1613CSS, Wellington Labs) to the extract, concentrated to about 2 ml and cleaned up as described in the method.

For fish tissue, ~25 g sample size were homogenized and mixed with anhydrous Na_2SO_4. It was soxhlet extracted with dicloromethane:hexane (1:1 v/v) for 16 h. After adding the purification standard, the extract was concentrated and solvent exchanged. For purification we used three glass columns, packed with: GSAB, acidic alumina and a mixture of 18% CarbopackB/Celite, respectively.

The concentrations of the 17 PCDD/Fs 2,3,7,8-substituted compounds were measured by the isotopic dilution method of the US Environmental Protection Agency. Method 1613 (US EPA, 1994) using a high resolution Mass Spectrometer.

Results and discussion.

Figure 2 shows the homologue comparison in percentage between sampled sites for both the surface sediments and the fish tissue samples.

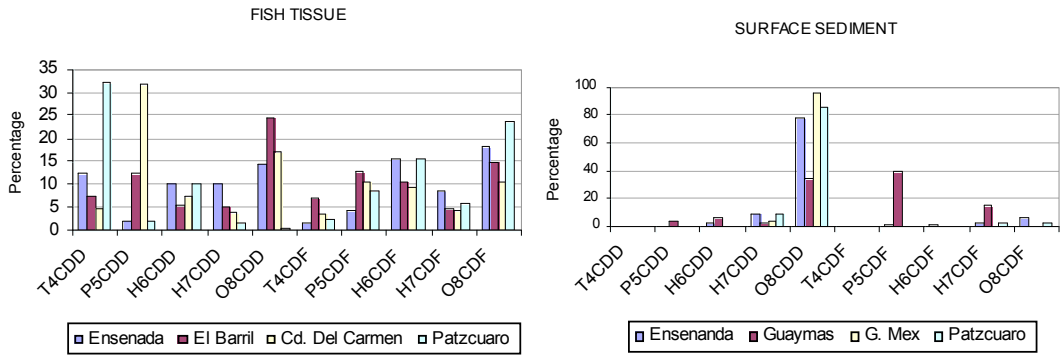


Figure 2. Homologue comparison (in percentage) of dioxins and furans between fish tissue and surface sediment.

The homologue composition of fish was more complex and diverse. The homologue distribution for surface sediments at each core site was mainly dominated by the OCDD abundance, which has been reported also for other sites (Ferrario *et al*., 2000; Gaus *et al*., 2001; Green *et al*. 2004). The only exception was that of Guaymas basin surface site that showed a larger abundance of penta-homologues. We did not find a relationship between the homologues found at the sediment site and the samples of the fish tissue obtained in the

vicinity of those sites. This is not unexpected as it has also been reported previously for other sites (Bonn, 1998).

With respect to the possible similarities between our sites and those reported elsewhere, first, we made a principal component analysis to see if there were any similarities between our sites. The results are shown in Figure 3.

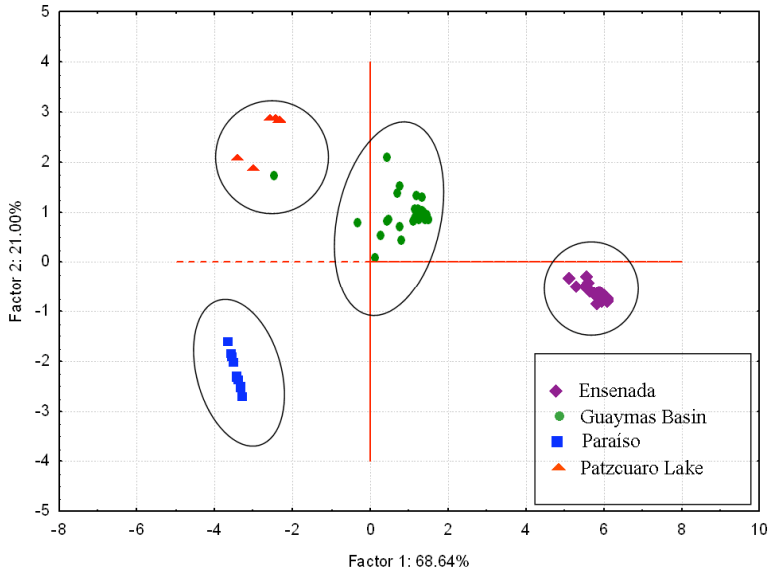
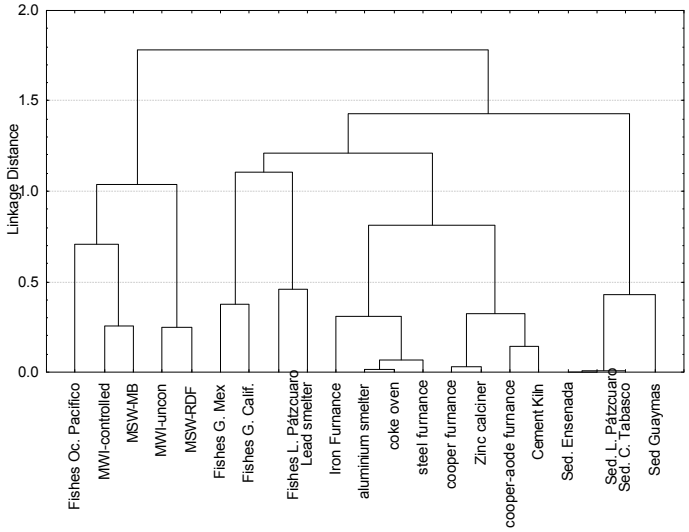


Figure 3. Principal component analysis (PCA) for all sediment data concentration of PCDDs/Fs transformed (Log (x+1)) and standardized, for all four sediment core data.

The formation of four groups of data suggests that there are not many similarities between sites and that the sources are thus unrelated. Again, with the exception of one superficial data from Guaymas basin, all other data suggest differences in the sources for each site.

To further investigate the possibility of similarities with typical sources, we made a cluster analysis to find out which of those potential sources have patterns that may indicate source similarities with known homologue patterns, we present those results in Figure 4 below.

Figure 4. Cluster analysis for reported sources from other localities compared to Mexican sites.



We had determined that TEQs are similar and below those considered dangerous for human consumption. We also observed that the sediment profiles were dominated by octa-*p*-dibenzo dioxin. Finally, on a wet weight basis, the concentrations of PCCDs/Fs and their toxic equivalents were lower or within the range as other reported around the world (Jacobs *et al*., 2002; Bordajandi *et al.*, 2003).

Conclusions.

The homologue profile for fish tissues was unrelated to those of surface sediments collected at nearby sites. This suggests that other factors such as fish mobility and feeding habits preclude the similarities between fish and sediment for PCDDs/Fs. All sediments group together in the cluster analysis suggesting that they are different from those sources considered here. It is noteworthy that the Ensenada sediment site showed similarity with a cement kiln fingerprint source reported elsewhere. In Ensenada, there's been one in operation for many years.

We did not find clear similarities of homologue patterns from our sediment sites to those sources reported in the literature. This may indicate that either a mixture of sources has occurred or local and atypical sources are responsible for the patterns shown at each site.

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